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Nickel catalyzed olefin oligomerization and dimerization

H. Olivier-Bourbigou*, P.A. R. Breuil, L. Magna, T. Michel, M. Fernandez Espada Pastor*, D. Delcroix*

ABSTRACT: Brought to life more than half a century ago and successfully applied for high-value petrochemical intermediates production, nickel-catalyzed olefin oligomerization is still a very dynamic topic, with many fundamental questions to address and industrial challenges to overcome. The unique and versatile reactivity of nickel enables the oligomerization of ethylene, propylene and butenes into a wide range of oligomers that are highly sought-after in numerous fields to be controlled. Interestingly, both homogeneous and heterogeneous nickel catalysts have been scrutinized and employed to do this. This rare specificity encouraged us to interlink them in this review so as to open up opportunities for further catalyst development and innovation. An in-depth understanding of the reaction mechanisms in play is essential to being able to fine-tune the selectivity and achieve efficiency in the rational design of novel catalytic systems. This review thus provides a complete overview of the subject, compiling the main fundamental/industrial milestones and remaining challenges facing homogeneous/heterogeneous approaches as well as emerging catalytic concepts, with a focus on the last 10 years.

CONTENTS

Author Information

Corresponding authors

Authors

Notes

Biographies

Acknowledgments

Abbreviations used

References

1 Introduction and scope

1.1 Context

The oligomerization of light olefins is an attractive method for the production of a wide range of key intermediates for fuel, petro- and fine chemistry. The rich and unique reactivity of nickel with unsaturated compounds has made this metal tremendously successful in olefin oligomerization, for both homogeneous and heterogeneous catalysis, and from academic and industrial points of view. [1–14] Contrary to other well-known metals in oligomerization such as titanium and chromium, nickel is able to oligomerize not only ethylene, but also propylene and butenes, two classically elusive alkenes as regards metal-catalyzed oligomerization. This versatility allows nickel-based catalytic systems to transform light olefins into specific high-value products. The biggest challenge in the nickel-catalyzed oligomerization of short olefins is selectivity: the distribution profile of longer olefins, the linearity and the position of the double bond are important as regards the properties and use of the products. The flip side of the high reactivity of nickel with propylene and butenes is poorer control of the selectivity when ethylene is to be oligomerized. Over the years, an impressive research effort has been conducted in order to rationally design ligands and solid supports, for homogeneous and heterogeneous catalysis respectively, in order to better control the oligomerization mechanisms, and the corresponding selectivities, especially with ethylene. However, investigating these structure/reactivity/selectivity relationships and identifying and designing nickel active sites and mechanisms with the final goal being to choose the most appropriate nickel environment and operating conditions for optimal implementation has proved to be extremely challenging and long drawn-out. While selective propylene oligomerization was the main goal in the 70s for fuel production, the market changes have given rise to new challenges for nickel in the forthcoming years with the growing demand of essential petrochemical intermediates such as short linear alpha-olefins, 1-butene, 1-hexene and 1-octene. Their selective and on-purpose production from ethylene thus constitutes an exciting research area for the next decade. Furthermore, nickel-catalyzed olefin oligomerization represents a rare opportunity to draw parallels between homogeneous and heterogeneous catalysis: active sites and mechanism comparisons, highlighting similarities and differences, can eventually help to design the most active, selective and stable catalysts for future conceivable industrial developments.

1.2 History

The first registered evidence for nickel as part of a catalytic system was reported in a patent by Phillips in 1942. Ethylene polymerization was carried out at 150°C on a heterogeneous nickel oxide-based system. However, although it was already known that olefins could be oligomerized or polymerized in the absence of promoting catalysts, temperatures as high as 500 °C were needed.[15] As a consequence, although the results were not interpreted by the authors at that time, their work brought out the presence of an as-yet unidentified catalytic species. This breakthrough was closely followed by a serendipitous discovery by Ziegler and his team: while studying ethylene polymerization with trialkylaluminum ($AlEt_3$) as the catalyst, they showed that traces of nickel, in contrast to other metals, could prevent polymerization, leading instead to butenes, *via* dimerization. This phenomenon, although poorly understood, was called the “nickel effect”.[16,17] This pioneering work of Karl Ziegler paved the way for the ulterior development of Ziegler-Natta catalysts, which represented a pivotal discovery and a stimulus towards the race for comprehension of the “Ni story”. Further investigations by Wilke[18] and his team demonstrated, into the bargain, that a nickel species, (π-allyl)Ni(II)halide, was capable of catalyzing the dimerization of monoolefins in the absence of an aluminum-based co-catalyst, while Lewis acids were found to be strong activators, thanks to the generation of cationic nickel species, which are much more active in catalysis. In this succession of events, the concept of a ligand was introduced in 1966, with phosphines as the most characteristic example. Modulation of the phosphine ligands would allow the electronic and steric properties around the nickel center to be fine-tuned, gaining control over the selectivity of the process.[19] Thus, the basis for a successful nickel-based oligomerization catalytic system was set: in the late 70's, IFPEN implemented the first industrial oligomerization process, Dimersol®, for dimerizing propylene into hexenes, running with a Ziegler-type homogeneous catalyst. This first industrial breakthrough was rapidly followed by another important milestone in Ni oligomerization: the discovery of a new family of bidentate P-O ligands by Keim in the 80's resulted in the industrialization of the Shell Higher Olefins Process (SHOP) for ethylene oligomerization.

In parallel to these studies, heterogeneous nickel-based olefin oligomerization catalytic systems were also extensively studied. In most cases, when compared with homogeneous systems, the properties of the oxide supports (alumina, aluminosilicates) induce co-oligomerization of the primary products and double bond isomerization. Selective production of linear olefins containing high proportions of α-olefins, as obtained in homogeneous systems, is thus hampered. As a result, the industrial applications of Ni-based heterogeneous catalysts were less successful, and only achieved for butene dimerization by Hüls AG, industrialized during the 80's by UOP and BASF.

Thus, homogeneous and heterogeneous catalysis have been progressing in parallel over the years, with research being complementary in some respects. This is illustrated well in the case of butene dimerization, for which both technologies were licensed and industrially implemented. However, although both approaches share a common metal, often expressing analogous reactivities, mutual enrichment was scarce until very recently. As a matter of fact, homogeneous and heterogeneous nickel-catalyzed oligomerization have a common objective: selectivity.

1.3 Feeds and target for selective transformations

Ethylene, propylene and butenes are readily available from Steam Cracking or Fluid Catalytic Cracking. These olefins constitute very attractive feeds for the production of high-value intermediates, after their catalytic transformation promoted by specifically designed nickel-based systems. These feeds, the corresponding intermediate products and their final applications are schematized in Figure 1. The most representative examples will be further detailed in the industrial developments, in the next chapter.

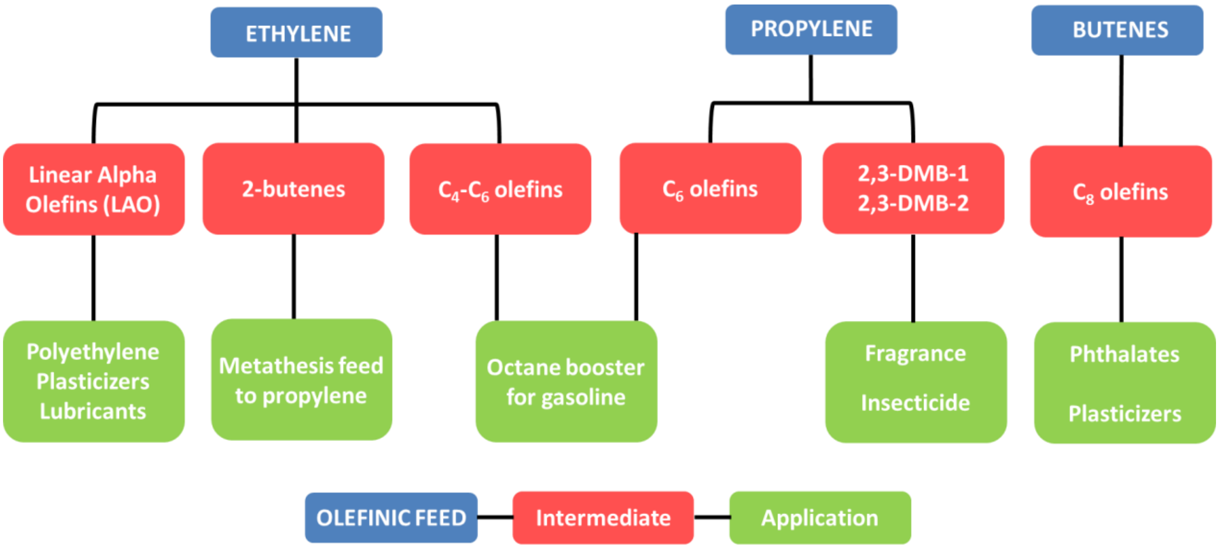


Figure 1. Oligomerization of light olefins to fuels and petrochemical intermediates and their applications

However, despite the broad spectrum of high-value intermediates available from light olefin oligomerization detailed in Figure 1, demand is currently highly focussed on Linear Alpha Olefins (LAO). These intermediates, obtained selectively from the oligomerization of ethylene, are of utmost importance. Their increasing demand on the global market is illustrated by an estimated growth from 7 million metric tons per year (Mtpy) in 2016 to more than 8.5 Mtpy in 2021. This growth is in to a large extent driven by the demand of short chain LAOs within the C_4–C_8 range (1-butene, 1-hexene and 1-octene), following the market appetite for Linear Low Density Polyethylene (LLDPE) and HDPE (High Density polyethylene). Those three LAOs constitute the comonomers of ethylene for obtaining specialty polyethylene. Consequently, obtaining their selective production from ethylene outside the classical Schulz-Flory distribution obtained from SHOP-type systems represents one of the main challenges for nickel-catalyzed ethylene oligomerization.

As mentioned above, there are two main approaches facing these challenges: homogeneous and heterogeneous catalytic systems. Thanks to the versatility endowed by the ligand environment, the homogeneous approach has enjoyed rapid success for ethylene, propylene and butene oligomerization. On the contrary, nickel-based heterogeneous catalytic systems are only implemented for butene dimerization, to form octenes. Thus, from the heterogeneous perspective, an important challenge resides in the development of selective and stable heterogeneous systems for the catalytic oligomerization of the shortest olefins, especially ethylene.

The history of nickel in olefin oligomerization is obviously an excellent illustration of the importance of the synergy between the knowledge provided in the scientific literature and the advances published in the form of patents, mainly followed by the corresponding industrial developments. It is also evident that although Ni-catalyzed olefin oligomerization is a research field born more than half a century ago, it is still alive, with many questions and challenges to overcome. Consequently, in this review we will endeavor to provide readers with a critical up-to-date survey of the main advances in homogeneous and heterogeneous nickel-catalyzed olefin oligomerization. Moreover, in contrast to most reviews in the field, we will highlight the most relevant results published in patents, together with the corresponding actual and potential industrial developments. Relevant academic and industrial challenges regarding nickel use for oligomerization will be presented and discussed.

Globally, this review offers an overview of the subject including the industrial perspective, from both homogeneous and heterogeneous viewpoints. Therefore, we aim to compile the main milestones of both approaches, and face up to the tough task of building bridges between them, looking for mutual enrichment of the subject. In order to narrow the vast scope of the topic, we will focus on the short-chain olefins that have been the most studied, *i.e.* ethylene, propylene and butenes. Functional olefins, alkynes and dienes are excluded.

Although we will keep an industrial perspective of the subject throughout the document, **Chapter 2** is entirely devoted to an overview of the major industrial breakthroughs involving nickel-based catalytic systems, mainly constituted by homogeneous systems. This industrial angle of attack helps to identify the remaining challenges to be faced that will be addressed in the following chapter. As detailed above, control of reactivity in homogeneous nickel-catalyzed ethylene oligomerization systems, with the final aim of orienting the selectivity, mainly towards short linear alpha olefins, is an arduous task. Therefore, **Chapter 3** is dedicated to summarizing the latest efforts in ligand design in order to gain selectivity or, more rarely, activity. The subsequent chapter is directed towards catalyst recycling. It is well known that one of the main drawbacks of homogeneous catalysis is the need for recycling of the metal catalyst, nickel in our particular case, as well as the potential ligand, activator and solvent. Thus, **Chapter 4** is dedicated to the segregation of molecular oligomerization catalysts either by multiphasic implementation or by immobilization on solid supports such as metal organic frameworks. Following this immobilization approach to inorganic solids, **Chapter 5** deals with the quest for active, selective, stable and scalable nickel promoted oxide supports, including the question of the non-existence of fully industrialized heterogeneous ethylene oligomerization systems. Combining the homogeneous and heterogeneous approaches, the number of nickel-based catalytic systems that have been evaluated for olefin oligomerization is huge, and often based on a trial/error methodology. In this regard **Chapter 6** is of particular interest, as it deals with the identification and characterization of nickel active species in both homogeneous and heterogeneous catalysis, as well as the resulting mechanisms. A deep understanding of these reaction mechanisms is essential in order to obtain fine control of the selectivity: this knowledge allows us to gain efficiency in the rational design of new active catalytic systems and leads to potential industrial products, which are desirable high-value petrochemical intermediates.

2 Industrial developments of nickel-catalyzed olefin oligomerization

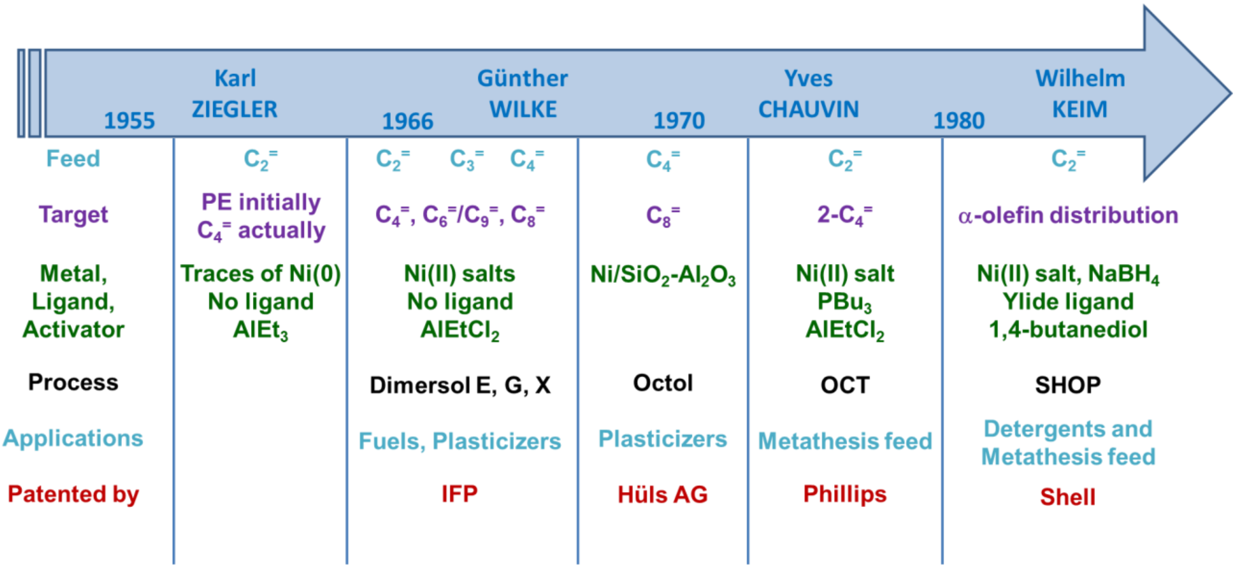
A quick overview of the literature on nickel-catalyzed olefin oligomerization is enough to realize that there is a vast amount of knowledge on this topic which has been gathered by the scientific community. Surprisingly, only a few processes have been successfully commercialized and industrialized, especially during the 70-80's, evidencing the complex process behind successful industrialization. Indeed, in order to obtain an oligomerization process, a large number of parameters, often not limited to purely scientific reasons, must be taken into consideration. It is more than just the economics of the process; other variables such as plant capacity, geographical location or feed availability have to be carefully taken into account. This section aims to give an overview of the most marked developments and breakthroughs present in often-forgotten patent literature.

2.1 Technologies operated on an industrial scale

It is crucial to bear in mind that the workflow for the development and subsequent industrialization of a new oligomerization catalytic system and the corresponding technology is an arduous process. Simple, realistic and cheap catalytic precursors that can easily be handled and stored must be chosen. In the first stages, the research focuses on the definition and optimization of the catalytic formulation (ligand, promotors, additives, solvent). Preliminary adjustment of operating set points for the reaction technological design and scale-up are carried out, including catalyst neutralization and disposal.

These questions are of course relevant for all oligomerization catalysts, but they must be taken into particular consideration with nickel. Nickel is indeed well-known for catalyzing side reactions such as α-olefin double bond isomerization or co-oligomerization. These undesirable reactions depend not only on the chemical nature of the nickel catalyst, but also on the way it is implemented on a large scale: solvent, residence time (feed conversion), temperature and reactor design. All those parameters can have detrimental effects on selectivity in an actual industrial plant, compared to a batch reactor on a laboratory scale.

The full development of the process must encompass the optimization of the operating conditions, with kinetic and thermodynamic data. Separation and purification steps, heat integration, economics and environmental assessments have to be set up in parallel. Furthermore, the technical feasibility of these new processing steps must be validated along with pilot or demonstration plants. This evaluation is carried out under representative conditions, in a continuous mode, with good control of the operating conditions and without transfer limitations. Temperature, pressure, olefin and catalyst concentration in the liquid phase and residence time are key parameters which will help in defining variables such as catalyst productivity, selectivity and build-up of by-products. These investigations would also allow critical parameters such as the impact of potential feed impurities, catalyst deactivation/lifetime and, in some cases, corrosion issues, to be detected. Moreover, representative samples might be needed at all points of the process in order to validate their quality in further uses and for marketing purposes. Despite the complexity of scaling-up of such processes, successful industrial implementation were carried out by some companies for nickel-based catalytic systems for the oligomerization of ethylene, propylene and butenes into important hydrocarbons intermediates. The milestones along the pathway towards industrialization in the story of using nickel for oligomerization are schematized in Figure 2.



1955	Karl ZIEGLER	1966 Günther WILKE	1970	Yves CHAUVIN	1980 Wilhelm KEIM
Feed	$C_2^=$	$C_2^=$ $C_3^=$ $C_4^=$	$C_4^=$	$C_2^=$	$C_2^=$
Target	PE initially $C_4^=$ actually	$C_4^=$, $C_6^=/C_9^=$, $C_8^=$	$C_8^=$	2-$C_4^=$	α-olefin distribution
Metal, Ligand, Activator	Traces of Ni(0) No ligand $AlEt_3$	Ni(II) salts No ligand $AlEtCl_2$	Ni/SiO_2-Al_2O_3	Ni(II) salt PBu_3 $AlEtCl_2$	Ni(II) salt, $NaBH_4$ Ylide ligand 1,4-butanediol
Process		Dimersol E, G, X	Octol	OCT	SHOP
Applications		Fuels, Plasticizers	Plasticizers	Metathesis feed	Detergents and Metathesis feed
Patented by		IFP	Hüls AG	Phillips	Shell

Figure 2. Milestones in the industrial development of light olefin oligomerization by nickel

The first industrial formulations were composed of a neutral nickel(II) salt promoted with an alkyl aluminum halide to form a Ziegler-type catalyst exploited by CPChem and IFPEN (Dimersol® G, dimerization of propylene[8]) in the late 70's. The industrialization of this Ziegler-type catalyst, with an alkylaluminum halide co-catalyst, was not a straightforward decision. A careful comparison with heterogeneous catalysts like $NiSO_4/Al_2O_3$ was carried out, as no alkylaluminum is needed to activate this system, which is furthermore regenerable and easily disposable.[20] However, when operated at high propylene conversion, the superior hexenes selectivity induced by the homogeneous nickel systems compared with its heterogeneous counterpart was decisive in turning towards the implementation of the homogeneous system.

Over the years, Dimersol® technology has employed propylene (Dimersol® G, 1977), then butenes (Dimersol® X, 1980) and ethylene (Dimersol® E, 1989). The dimers produced (Dimates™) found numerous applications as gasoline additives and for the production of phthalates with a low branching index.[21,22] On an industrial scale, the reaction typically takes place through consecutive Continuous Stirred Tank Reactors (CSTR) in a solvent-free liquid phase without any additional ligand, under mild reaction conditions. The catalyst is deactivated after the reaction section by ammonia and aqueous caustic soda treatment. In total, Axens has licensed 37 of these units worldwide.

Shortly after, Phillips launched a new industrial process[23] involving a Ziegler-type catalyst as well for the dimerization of ethylene to 2-butenes (Lummus technology now licensed by McDermott). In this formulation, the catalytic precursor, bis(tri-*n*-butylphosphine)dichloronickel ($NiCl_2(PBu_3)_2$),[24] is associated with dichloroethylaluminum as an activator. In this case, the Bu_3P ligand orientates the selectivity towards 2-butenes, which reveals its dramatic influence on the selectivity compared to the IFPEN ligand-free composition. 2-butenes find many applications as starting materials in a number of reactions such as isobutene alkylation to trimethylpentanes, dehydrogenation to butadiene and cross-metathesis with ethylene to form propylene.[25] Based on a patent survey, the industrial reaction of ethylene dimerization to 2-butenes is preferably carried out in a circulating loop reactor under mild conditions (T = 35-45 °C, P = 10-15 bar).[26]

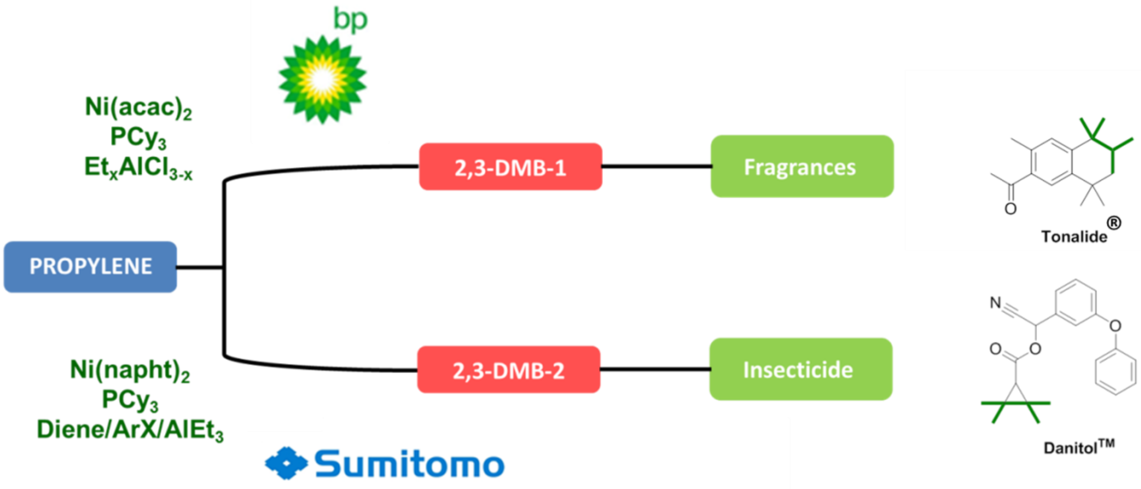


Figure 3. Selective dimerization of propylene to 2,3-DMB-1 and 2,3-DMB-2

The power of nickel reactivity in respect of oligomerization processes reaches a whole new dimension in the quest for selective propylene dimerization, an unknown process with other ethylene oligomerization metals such as titanium, zirconium or chromium. While the Dimersol G® process produces linear hexenes, methylpentenes and dimethylbutenes indiscriminately, a specific need for 2,3-dimethylbutenes was expressed by BP[27] and Sumitomo[28] in the 80's (Figure 3). The selective production of 2,3-dimethyl-1-butene (2,3-DMB-1) and 2,3-dimethyl-2-butene (2,3-DMB-2), for fragrance and agrochemistry respectively, requires a catalytic system that is reactive towards propene and that induces not only regioselectivity with tail-to-tail dimerization, but also double bond selectivity thanks to fine control of the olefin isomerization, often occurring with nickel catalytic systems. The first catalysts envisaged by BP were prepared *in situ* by the reaction of $Ni(acac)_2$ with PCy_3 (tricyclohexylphosphine) and ethylaluminumchloride derivatives. The bulk of the phosphine appeared to be a key parameter in the high 2,3-DMBs selectivity. However, separation of high purity 2,3-DMB-1 from the other isomers was a main issue of the process. BP provided a process for the production of 2,3-DMB-1 that minimized the problem of separation. A first industrial unit was put on stream in Grangemouth, UK in 1991. 2,3-DMB-1 was, for instance, used for the production of fragrances like Tonalide®. In parallel, Sumitomo[29] disclosed an improved catalytic formulation consisting of nickel$(naphthenate)_2/PCy_3$/diene/chlorinated phenol/$AlEt_3$/water, carried out in toluene. This formulation displays a remarkable enhancement of activity, ascribed to water addition. Moreover, the control of 2,3-DMB-1 to 2,3-DMB-2 could only be obtained by changing the ratio of chlorinated phenol to $AlEt_3$. Over 86 % 2,3-DMB-2 selectivity was obtained and in 1983, Sumitomo started its commercial production for the synthesis of high performance conventional insecticide such as Danitol™.[30]

In parallel to the industrialization of these dimerizations, a third major actor in the field was about to appear. Shell was eager to produce linear C_{12}-C_{20} olefins for its posterior hydroformylation section, finding application in the detergent industry. Thus, parallel research by Keim et al. allowed him to report a new family of bidentate P,O-ligands, particularly those containing a tertiary organophosphorus moiety, described as influencing the formation of linear olefins.[31] Thus, in 1968, ylides were introduced as organic precursors in the formation of P,O-ligands generated *in situ*. Furthermore, the nickel precursor employed initially, *i.e.* the low-stability $Ni(COD)_2$ complex, was rapidly replaced by a simple combination of a divalent nickel salt and a borohydride reducing agent. Furthermore, the solvent played a major role. Changing toluene for a polar protic solvent, such as 1,4-butanediol, generates biphasic systems allowing the the catalysts.[32,33,34] to be recycled.Thus, the SHOP process was born. The first large production plant was put into operation in Geismar, USA in 1977 and capacity increase over the years led the total alpha olefins production to 1.3 Mtpy with the fourth line in 2018. Stanlow, UK, is the other location of LAO production operated by Essar Oil with the Shell Higher Olefin Process. The typical linear olefin distribution of this process after oligomerization is 54 % C_4-C_{10}, 18 % C_{12}-C_{14}, 28 % C_{16}-C_{20}, with a margin of flexibility to enhance the formation of longer olefins.

Homogeneous nickel catalytic systems offer a broad range of possibilities for adapting the reactivity of the nickel complex to the olefinic feed and the particular selectivity needed for the industrial production of specific high-value intermediates. In parallel, some companies developed the isolation or immobilization of the active sites to increase the ease of recycling of the catalyst. Heterogeneous catalysts promoted by nickel were thus successfully industrialized, but only on butene feedstocks. Homogeneous catalysts were preferred on ethylene or propylene feeds due to the finer control of the selectivity that these catalysts offered in comparison with the heterogeneous catalysts available at that time. In the 80's, the German-American companies Hüls and UOP developed a nickel-heterogeneous catalytic system, industrialized in 1983 in Marl, Germany.[35] This process entered the literature as the OCTOL process,[36] designed to produce low branching octenes from butenes for their subsequent use in hydroformylation (phthalate plasticizers manufacture). It is reported that a second unit was licensed in Japan in 1986 using butenes as a feed from FCC (GSK General Sekiyu Refineries, 45 ktpy of octenes). Two options are proposed, both of them using Montmorillonite supports promoted with nickel. The branching indices in both OCTOL options are lower than those obtained within a typical gasoline dimerization process. OCTOL A leads to higher branching index, which is preferred for gasoline application,[37]; octenes produced with OCTOL B have a lower branching index (Table 1) and are used for hydroformylation. The company Evonik is now offering the technology for licensing. In 1999, BASF developed a catalyst formulation prepared by the impregnation of a mixture of $Ni(NO_3)_2$ and H_2SO_4 onto aluminum oxide (S/Ni molar ratio comprised between 0.25 and 0.38). This technology has been industrialized in Germany.[38]

Table 1. Branching of C_8 olefins produced via different oligomerization process

Source of C_8 olefins (C_4 dimerization)	Iso-Index
Shell SHOP	0
Hüls Octol B	1.1
Dimersol® X	1.3
Hüls Octol A	1.9
Benchmark gasoline dimer fraction	2.1

ISO-index : mean number of methylbranched in the C_8 olefins . methylheptenes = 1, dimethyl-hexenes = 2, n-octenes = 0.

The 1960-1995 period enjoyed a profusion of industrial successes for many homogeneous and a few heterogeneous catalytic systems based on nickel for the oligomerization of short olefins to longer hydrocarbons (Table 2).

Table 2. Key patent literature on industrial Ni catalysts & process for olefin oligomerization

Company	Priority data	Catalytic system	Feed	Application	Reference
BP	1987	$Ni(II)/Et_{3-x}AlCl_x/PCy_3$	C_3	2,3-DMB-1	27
Sumitomo	1986-91	$Ni(naphthenate)_2/PCy_3$/diene/ chlorinated phenol/$AlEt_3$ and water	C_3	2,3-DMB-2	28, 29, 39
IFPEN (Dimersol® G)	1968	$Ni(II)/AlEtCl_2$	C_2 or C_3	Fuels	21
IFPEN (Dimersol® X)			C_4	Isooctenes	22
Phillips	1969	$Ni(II)/PBu_3$	C_2	2-butenes	23
Phillips	1977	$NiCl_2,2PR_3$ (catalyst preparation)	C_2	2-butenes	24
Phillips	1978	$NiCl_2,2PR_3/AlRCl_2$	C_2	2-butenes	26
Shell (SHOP)	1971	$Ni(II)/NaBH_4$/(P-O) ligand	C_2	LAO	31, 32, 33, 34
Hüls (Octol)	~ 1980	Heterogeneous Ni on Montmorillonite	C_4	Isooctenes	35
BASF	~ 1999	Heterogeneous Ni on Alumina	C_4	Isooctenes	38

These first-in-class processes have then galvanized academic and industrial research groups to continuously optimize the existing catalytic systems and understand the relationships between structure and selectivity. New formulations and new implementations were thus sought in order to extend the limits of productivity and process economics. Based on patent literature, examples of such improvements are given in the next paragraph.

2.2 Examples of technologies improvements and related challenges

Because the majority of the industrial processes deal with homogeneous catalytic systems, recycling nickel complexes became a major challenge, all the more so because no particular breakthroughs have been made since then for heterogeneous catalysts. As an example, in the homogeneous Dimersol® process, although the technology requires a low capital cost, the nickel catalyst is not recycled, which hampers the global economics by enhancing the operational costs. A biphasic technology using acidic chloroalkylaluminate ionic liquids as a solvent for the nickel catalyst was provided by IFPEN in the late 80's.[40] The resulting Difasol™ biphasic process offers higher octenes selectivity (90-95%) for butene dimerization, by segregation of the octenes produced and the nickel catalyst, avoiding unwanted consecutive reactions. This makes the Difasol™ technology more interesting and differentiates it from the original Dimersol®, particularly regarding the conversion of poorly concentrated olefin feedstocks.[41]

In the late 1990s, BP proposed buffering the acidic chloroaluminate ionic liquids with an organic nitrogen base, while maintaining a latent acidity of the solvent for Ni activation.[42] The aim of this strategy, first developed by Keim, was to avoid side reactions which could be caused by the presence of an acidic aluminic compound. Interesting performances are described with N-methylpyrrole or 2,6-lutidine additives, applied to the dimerization of 1-butene to highly linear octenes with an acetylacetonate-derived nickel complex. The use of acidic chloroaluminate ionic liquids buffers was developed further by another company (Table 3).

Until the late 90's, it was believed that olefin oligomerization was restricted to phosphorous type ligands. This taboo was broken with the introduction of imine ligands and aryl-substituted N,N-bidentate (α-diimine)nickel-based systems, developed by DuPont in 1995, initially for polymerization.[43] One of the main breakthroughs was the activation of a series of (α-diimine)nickel(II) precatalysts by Modified MethylAluminOxane (MMAO). Depending on the bulk of the substituents on the imine, these systems can switch from polymerization to highly active catalysts for the oligomerization of ethylene or propylene. Many companies then started investigations in this field.[44,45,46,47] However, bis(imino)pyridine iron complexes were preferred instead of nickel complexes, probably due to the exaggerated propensity of nickel to isomerize α-olefins into internal olefins (technology developed under the Versipol® process trade name by DuPont).

Following this breakthrough, tremendous efforts have been made into the search for different nickel ligands. The main breakthrough was the catalytic systems described by R. Grubbs et al. and patented by Grace, with a series of sophisticated salicylaldiimine ligands.[48] These systems were initially described for olefin polymerization, however, fine-tuning of the substituents on the aryl group of the imines switched the selectivity towards oligomerization.

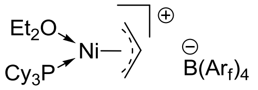
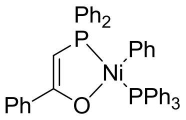
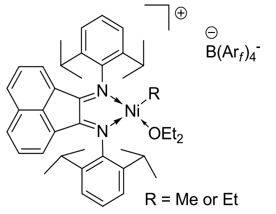
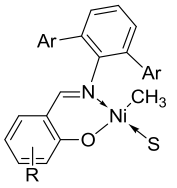
Table 3. Technology improvements based on patent literature

Company	Priority data	Catalytic system	Feed	Application	Reference
IFPEN (Difasol^{TM})	1987	Ni(II)/chloroaluminate ionic liquids	C_4	Isooctenes	40,41
BP	1998	Ni(II)/buffered chloroaluminate ionic liquids	C_4	Octenes	42
Conoco	2010	Ni(II)/buffered chloroaluminate ionic liquids	C_4	Isooctenes	49
Evonik	2015	Ni(II)/buffered chloroaluminate ionic liquids	C_4	Isooctenes	50
DuPont	1995	NiX_2/α-diimine/MAO	C_2	LAO	51, 44
Exxon	2002	NiX_2/α-diimine/MAO	C_2	LAO	46
BP	2003	NiX_2/α-diimine/MAO	C_2	LAO	47
Grace	1997	NiX_2/Salicylaldimine/MAO	C_2	polymers	48

2.3 Towards fundamental understanding of industrial catalytic systems

Despite their ~40 year history of industrial developments, the need for improved fundamental understanding is still great, in order to trigger further rationally driven improvements and satisfy economic and environmental considerations. The understanding of catalytic systems encompasses the synthesis, the isolation and the characterization of models of active species, and the study of their reactivity with olefins. Some typical organometallic complexes have been isolated, most of the time thanks to the addition of stabilizing coordinating Lewis bases (phosphine ligand, ether solvent, Table 4). Their activities are much lower than those showed by the industrial formulation, but they proved to be active without the addition of organometallic activators. Allyl cationic nickel species were representative models of the Ziegler-Natta type system used in Dimersol® and CPChem technologies. A deeper understanding of these active species is given in Chapter 6. Organometallic neutral nickel complexes were also isolated and representative of SHOP type formulations. Diimine and phenoxyimine based complexes could be isolated and stabilized only with bulky isopropyl substituents on the aryl group of the imine, leading to polymerization catalysts. Nevertheless, they were key models in discerning the relationships between nickel structure and their reactivity.

Table 4. Examples of isolated catalyst models of industrial or "in development" formulations.

Cationic complexes	Neutral complexes	Bimetallic complexes
 **Dimersol®/Phillips-like**	 **SHOP-like**	[Ni(η^3-allyl)(PCy_3)(μ-Cl)Al(Me)Cl_2] **Dimersol®/ Phillips-like**
 **Versipol®-like**	 **Grace-like**	

As can be seen in Table 4, homogeneous nickel complexes for olefin oligomerization can address a huge number of ligand families, stabilization modes and electronic states. The research methodology based on ligand modulation is definitely promising to address the new challenges found in olefin oligomerization catalyzed by nickel in homogeneous catalysis. The possibilities that can be explored by research groups for improving existing catalysts and for discovering new stalwarts are practically endless. Unfortunately, the rational design of ligands leading to clear structure/reactivity/selectivity relationships has not yet lived up to its promise. A trial/error strategy implying numerous ligand families is still mainly used in this research area. Those ligands and the corresponding nickel complexes for ethylene oligomerization are listed and commented in the following chapter.

3 Ligand design approach for homogeneous ethylene oligomerization with nickel complexes

Although the first examples of Ni-catalyzed olefin oligomerization lacked a defined ligand in the coordination sphere of the nickel center, the concept of the ligand, introduced in 1966, was rapidly embraced. The first examples of ligands studied for this transformation included monophosphines, and showed significant positive effects on the selectivity of olefin oligomerization, even leading to industrial successes (see Chapter 2).[52,53] In fact, new families of ligands did not take long to appear: in the early 1970s, Keim et al.[54] developed a new type of (P,O)-neutral nickel(II) complexes (models of SHOP catalysts) for the production of linear α-olefins from ethylene, reaffirming the enormous potential of the use of ligands to tune the catalytic properties of the nickel centers. From these seminal breakthroughs, research around the concept of a ligand as a modulating agent for the reactivity of the catalyst exploded, and a vast amount of ligands of very varied natures started to appear. Nonetheless, it is worth noting the contribution of Brookhart et al.[55] in 1995, who developed a highly electrophilic cationic nickel complex bearing α-diimine ligands. This discovery led to numerous further developments in the oligomerization of ethylene, since by tuning the structure of the ligand, the selectivity of these cationic nickel(II) complexes could impressively be switched from polymerization to oligomerization. Another prominent example published in 1998 by Grubbs et al.[56] used the knowledge acquired on the relationship between reactivity and structure of (P,O)-neutral- and α-diimine cationic nickel(II) complexes to develop neutral phenoxy-imine nickel(II), leading to active polymerization catalysts.

Thus, although nickel complexes have been partly summarized in the literature,[4,5,7,11,12,57–65] this chapter aims to give an overview of the main advances made since 2010 in ligand design with a focus on selective ethylene oligomerization. It is necessary to mention that this task turns out to be arduous and complex and reflects the main challenges of the last decades in nickel-catalyzed olefin oligomerization. The large amount of accumulated knowledge and research that is often based on trial and error means that the results are usually difficult to rationalize and compare, due to the great diversity of the reaction conditions used. Nevertheless, we have classified the ligands into two big main groups: the neutral and the anionic ligands. These ligands form, in the presence of nickel, two different kind of complexes: cationic and neutral nickel(II) complexes, respectively, which possess different catalytic behavior. Cationic nickel complexes are usually selective for short chain olefins, but produce large amounts of internal olefins by isomerization of the double bond, while neutral nickel complexes produce large distributions of α-olefins. Consequently, the main challenge of the oligomerization of ethylene employing nickel-based catalysts remains to produce one α-olefin selectively.

The catalytic performance (activity and selectivity) of selected neutral and cationic nickel(II) complexes are listed in Table 5 and Table 6 respectively, at the end of each paragraph. Even though a comparison of the activity of different catalytic systems was not possible due to the different conditions used (P, T, catalyst concentration…), the activities given in the table were converted into g/(gNi.h) for each catalytic system.

3.1 Neutral ligands

In the presence of nickel precursors, neutral ligands form cationic nickel (II) complexes, described as highly active for ethylene oligomerization after activation with a co-catalyst. Early catalytic systems for the dimerization of lower olefins such as ethylene and propylene, reported by Wilke[52] and Phillips,[53] are based on monodentate ligands like phosphines. After the development of cationic α-diimine nickel(II) complexes by Brookhart et al., a great deal of research effort has been expended on neutral bidentate ligands, leading to a large number of catalysts that oligomerize ethylene to a mixture of butenes, hexenes, and octenes. Nickel(II) complexes with different ligand backbones were synthesized, consisting of metal complexes with bidentate neutral (N,N)-, (P,P)- or (P,N)-based ligands and tridentate neutral (N,N,N)-ligands.[11]

3.1.1 *Monodentate neutral ligands L*

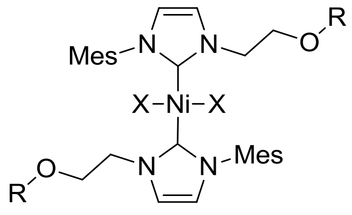
3.1.1.1 Neutral monophosphine ligands

Neutral monophosphine ligands were the first ligands developed for the nickel-catalyzed oligomerization of olefins. The electronic properties and steric hindrance of the monophosphine play an important role in the catalytic system performance. Wilke et al.[52] reported nickel complexes modified by monophosphine ligands (PR_3, R=alkyl or phenyl) for selective propylene dimerization, while the Phillips company patented $(Bu_3P)_2Ni(II)$ complexes which are highly selective for the dimerization of ethylene to 2-butenes.[26] Recently, Schmidt et al.[66] described the reactivity of nickel (0) and nickel (I) pre-catalysts carrying monophosphine ligands (PPh_3) in the presence of a Brønsted acid or Lewis acid for the oligomerization of ethylene. The nickel (0) complex $Ni(PPh_3)_2(C_2H_4)$ as a single component catalyst is slightly active in the dimerization of ethylene, whereas nickel(I) complexes $Ni(PPh_3)_2Cl$ and $Ni(PPh_3)_3Cl$ are inactive. The activation of Ni(0) and Ni(I) complexes by $BF_3.OEt_2$ induces higher activity of the Ni(0) complex $Ni(PPh_3)_2(C_2H_4)$ compared to the Ni(I) complex $Ni(PPh_3)_2Cl$. Butenes are the main products reported. Moreover, the Schmidt's group[67] showed that the activation of several Ni(0) and Ni(I) complexes ($Ni(PPh_3)_2Cl$ or $Ni(PPh_3)_2(C_2H_4)$) with $AlEtCl_2$ induced similar catalytic activity and product distribution. This observation suggests that the same active species may form for all pre-catalysts.

3.1.1.2 N-Heterocyclic Carbenes (NHC) ligands

N-Heterocyclic carbenes (NHCs) usually form highly stable bonds with late transition metals due to their strong σ-electron-donating properties. Nickel(II) complexes bearing non-functionalized NHC ligands display good selectivity but only moderate activity towards ethylene dimerization.[68–71] The main issue concerns the catalyst desactivation coming from the formation of imidazolium salt by reductive elimination. This drawback can be overcome by the use of ionic liquid as a solvent [69]or the addition of a second donor group.

Braunstein et al.[72–74] followed the second strategy and described the synthesis and characterization of alcoholate- and ether-functionalized NHC complexes and their reactivity towards ethylene oligomerization (Figure 4).



1a R = Me, X = Cl
1b R = Me, X = Br
1c R = Ph, X = Cl

Figure 4. Ether functionalized NHC complexes

The catalytic activities of complexes **1a-c** were investigated in the presence of $AlEtCl_2$ as co-catalyst. Increasing the size of the ether group from **1b** (OMe) to **1c** (OPh) results in a drastic decrease of the activity of the catalytic system. Moreover, the dibromide complex **1b** displays higher activity than its dichloro analogue **1a**. In all cases, the catalytic systems form mainly butenes, hexenes and traces of octene (Table 5, example for **1b**).[74]

3.1.1.3 Others monodentate neutral ligands

Although a tridentate coordination mode could be expected for ether-iminofurfural ligands, developed by Casagrande et al.,[75] these ligands coordinate in a surprising monodentate fashion, to form the corresponding nickel(II) complexes (**Figure 5**). However, XPS (X-Ray Photoelectron Spectrometry) and DFT studies confirmed the formation of nickel dimeric species bearing a monodentate ether-imino-furfural ligand.

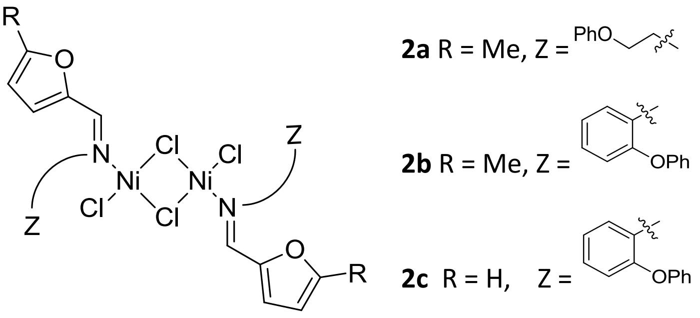


Figure 5. Ether-functionalized imino-furfural complexes

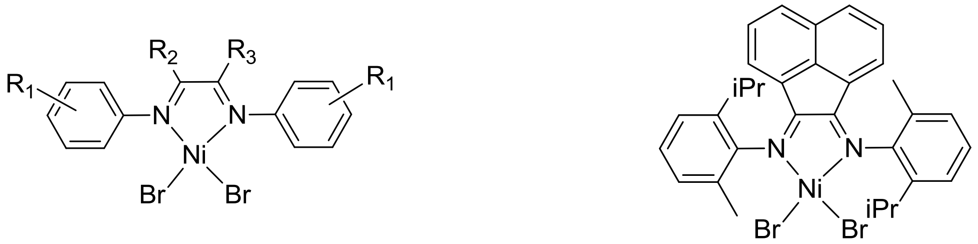
Complexes **2** are paramagnetic and, upon activation with PMAO-IP (polymethylaluminoxane-improved performance), show low to moderate activities toward ethylene oligomerization and high selectivity for the formation of butenes with small amounts of hexenes formed. Moderate selectivities towards 1-butene are also observed. A rigid spacer Z (**2b**, phenyl) leads to higher activity, compared to a flexible spacer (**2a**, ethyl). On the other hand, lower steric hindrance on the furfural moiety from **2c** (H) to **2b** (Me) induces a decrease of activity (one example for **2b** is given in Table 5).

3.1.2 *Bidentate neutral ligand LL*

Bidentate chelating ligands play a central role in the development of late transition metal catalysts for the oligomerization of ethylene.[5,61,62] The active coordination sites of tetracoordinated Ni(II) complexes are set in a cis-arrangement, favoring the migratory insertion and thus chain growth.[76] The investigation of catalytic ethylene oligomerization led numerous research groups to prepare various nickel complexes with neutral bidentate ligands such as (N,N)- or (P,P)-ligands. Moreover, the association within functional ligands of donor sets of different hard-soft properties as in (P,N)-neutral bidentate ligands led to hybrid ligands. These ligands brought stereoelectronic differentiation within the metal coordination sphere and their metal complexes can exhibit a hemilabile behavior resulting from the reversible coordination of the weaker donor. This feature allows stabilization of the active species and facilitates substrate coordination.

3.1.2.1 Neutral N,N-ligands

The most famous bidentate neutral (N,N)-ligands are the α-diimine ligands developed by Brookhart et al.[55] in the mid-1990s (Figure 6). These ligands produce highly electrophilic nickel(II) complexes upon activation with a co-catalyst, favoring olefin insertion over β-H elimination.[58] Brookhart's catalysts **3** bear bis(aryl)-α-diimine ligand-chelating nickel(II) metal centers and generate high molecular weight polymers with high activity. Moreover, the α-diimine based nickel(II) complexes **4** are able to undergo co-oligomerization of ethylene in presence of polar olefins.[61,62] The steric hindrance of the aryl groups attached to the imino nitrogens (**3**, R_1) plays a crucial role in the switch between polymerization and oligomerization. When its bulk is reduced, the selectivity can be shifted towards linear oligomers.[77]



3 **4**

Figure 6. Brookhart type α-diimine nickel(II) complexes

Following this breakthrough, late transition metal catalysts and especially nickel complexes attracted a great deal of attention in respect of ethylene oligomerization. Modification of the α-diimine ligands in order to tune the catalytic performance of the nickel pre-catalyst was investigated by Tuskaev et al (Figure 7).[78,79] They have recently studied the impact of electron-withdrawing groups on the performance of these catalytic systems.

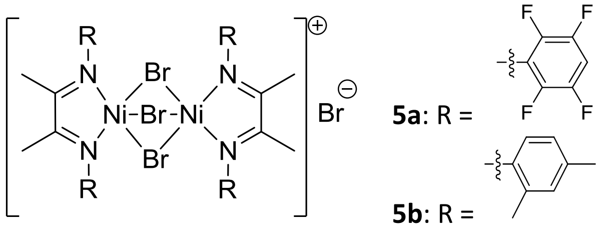
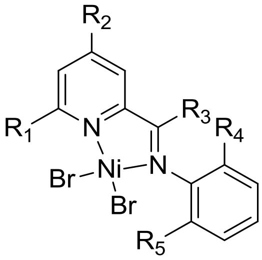


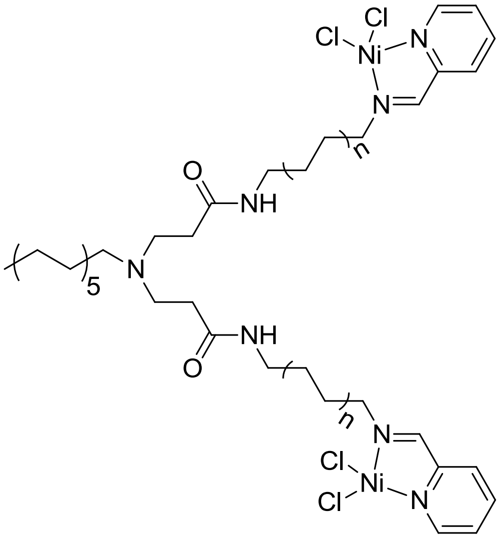
Figure 7. Modified α-diimine nickel(II) complexes

Complexes **5** crystallize as ionic dimers[79] and are active upon activation by $AlEt_2Cl$ as co-catalysts in the oligomerization of ethylene. Depending on the ligand structure at the R position, low molecular weight oligomers (mainly butenes and hexenes) **5a** or a broad molecular weight (M_w) distribution of oligomers **5b** can be formed.[78]



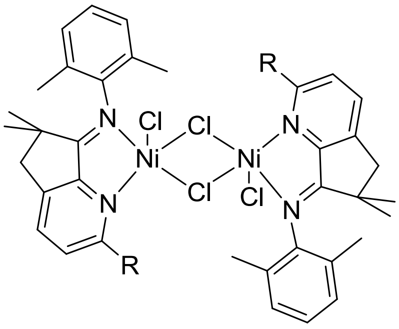
6a R_1 = Ph, R_3 = H
6b R_1 = Ph, R_3 = Ph
6c R_1 = Br, R_3 = F

Kim et al. et Bryliakov et al.



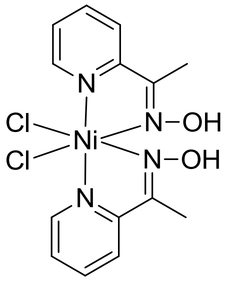
7a n=0
7b n = 4

Wang et al.

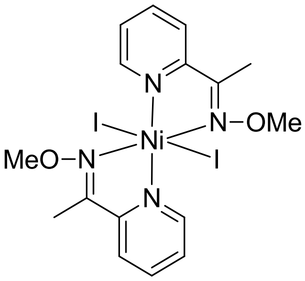


8a R = Cl
8b R = Ph

Sun et al.



9a



9b

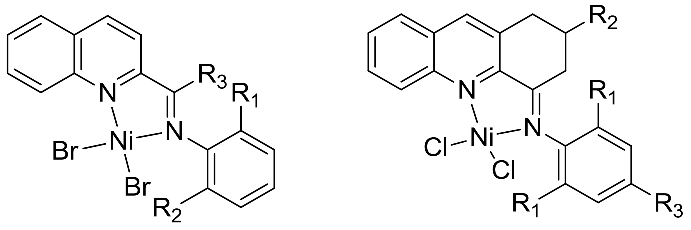
Mukherjee et al.

Figure 8. Iminopyridine and oxime nickel(II) complexes

Nickel(II) complexes bearing bidentate iminopyridine ligands were first described by Leskelae et al.[77,80] They intended to mimic the structure of bipyridine type alkene oligomerization catalysts and α - diimine based polymerization systems in order to study the impact of steric and electronic effects on the "interface/line" between oligomerization and polymerization. They mainly observed low molecular weight and highly branched polyethylene, but tuning the nature of the substituents, especially by adding bulky substituents to the pyridine moeity, can turn these polymerization catalytic systems to oligomerization systems. Kim et al[81,82] studied several iminopyridine ligands **6a-b** in which the pyridine moiety is substituted by a phenyl group at the R1 position (Figure 8). The complex **6** carried out ethylene oligomerization in the presence of $Al_2Et_3Cl_3$ co-catalyst. They are highly active and produce 1-butene as a major product together with small amounts of 1-hexene. A bulky phenyl substituent at R3 position **6b** induces higher activity than complex **6a** bearing methylenic hydrogen (example given in Table 5 for **6b**).[81] Bryliakov et al.[83] showed that introducing electron-withdrawing groups at the R1 and R3 positions **6c** reduces the activity of the iminopyridine nickel(II) complexes when activated by MAO. Paramagnetic bimetallic hyperbranched iminopyridyl nickel(II) complexes **7** were developed by Wang et al. (Figure 8).[84] These complexes are active, in the presence of MAO, and produce broad Schulz-Flory distributions (C_4-C_{23}). Increasing the alkyl chain from 2 carbons **7a** to 4 carbons **7b** decreases the catalytic activity due to lower solubility of the complex in the reaction media (Table 5, example given for complex **7a**). On the other hand, a constrained environment on the iminopyridyl ligand and the impact of chloro and phenyl substituents on the pyridyl moiety was studied by Sun et al.[85] Complexes **8a-b** (Figure 8) display good activities towards ethylene oligomerization in the presence of MAO. The R substituent on the pyridyl moiety has a strong impact on the selectivity of the catalytic species: nickel precursor **8a** bearing the 2-chloro ligands produced oligomers in a Schulz-Flory distribution from C_4 to C_{12}, while the nickel precursor **8b** containing the 2-phenyl group produced mainly oligomers limited to butenes and hexenes (Table 5).

The wide variety of pyridine based ligands active in the oligomerization of ethylene encouraged Mukherjee et al.[86,87] to develop ligands that are easily synthesized or readily available, such as oximes. Complexes **9a-b** (Figure 8) have good to high activities in the presence of $AlEt_2Cl$, forming mainly butenes and hexenes. Much higher activities are obtained when X is a chloride (**9a**) instead of an iodide atom (**9b**) (See Table 5).

Iminoquinoline nickel(II) complexes (Figure 9) have been studied for the oligomerization of ethylene in the presence of an aluminum based co-catalyst.[11,12] They usually display lower activities and higher short chain olefins selectivities compared with iminopyridyl nickel(II) complexes. This property could be explained by the higher electron density at the nickel center. Several groups further investigated the influence of substituents on the catalytic performance of quinoline arylimino-based nickel(II) complexes (Figure 9).

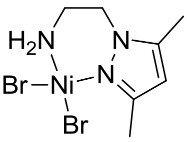


10a $R_1 = R_2 = Me$, $R_3 = nBu$
10b $R_1 = CF_3$, $R_2 = H$, $R_3 = H$

11a $R_1 = iPr$, $R_2 = H$
11b $R_1 = Me$, $R_2 = H$
11c $R_1 = iPr$, $R_2 = nBu$

Figure 9. Iminoquinoline based nickel(II) complexes

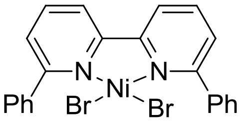
Sun et al.[88] studied the impact of alkyl-substituted iminoaryl moieties **10a-b** on the performance of nickel(II) complexes (Figure 9). The complex **10a** displays moderate activity for ethylene oligomerization in the presence of $Al_2Et_3Cl_3$, producing a large distribution of oligomers. Interestingly, when MMAO is used as a co-catalyst, the activity decreases and the selectivity switches towards hexenes (Table 5). Introducing an electron-withdrawing R_1 group onto the iminoaryl moiety (**10b**) drastically changed the selectivity of the catalytic system, as shown by Bryliakov et al.[83] Indeed, in the presence of MAO, the complex **10b** produced mainly butenes with moderate selectivity towards 1-butene and minor amount of hexenes (Table 5). Sun et al.[89,90] further investigated the impact of introducing a constrained environment on the (N,N)-ligand. In the presence of $AlMe_3$, complexes **11** achieved low to moderate activity for ethylene oligomerization and products ranging from C_4 to C_{16} in a Schulz-Flory distribution are formed. The complex **11c** substituted at the R_3 position displayed lower activities than its unsubstituted **11a** analogue.[90] Regarding complexes **10**, greater hindrance at the aryl moiety (**11b** vs **11a**) induced higher activity of the catalytic system (Table 5, **11b**).[90]



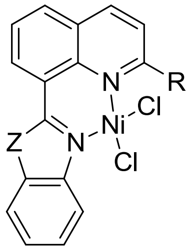
12

Figure 10. Pyrazole based N,N-heterocycle based nickel(II) complexes

N,N-pyrazoyl based nickel(II) complex **12** was studied by Darkwa et al (Figure 10).[91] The complex **12** displays a distorted octahedral environment at the nickel center and is active in the presence of $AlEtCl_2$, forming an almost equimolar amount of butenes and hexenes as the main products; higher olefins are also detected.



13



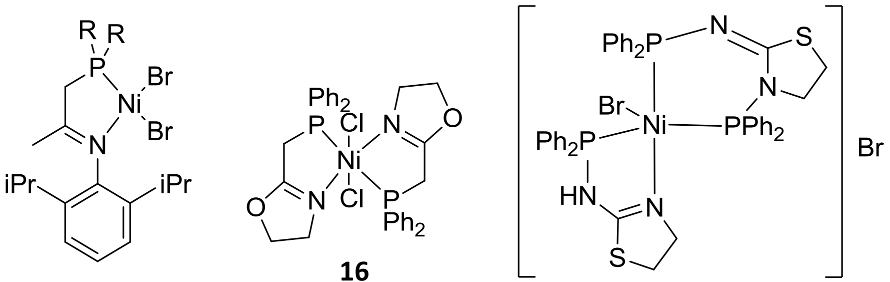
14a R = Me, Z = O
14b R = Pr, Z = O
14c R = Me, Z = S

Figure 11. Imino-bis-heterocyclic-based nickel(II) complexes

Kim et al.[82] synthesized and investigated the reactivity of several bipyridine ligands (Figure 11). Complex **13** exists as monomeric unit and catalyzes ethylene dimerization, yielding 1-butene as the major product with low activity (Table 5). Quinoline benzothiazole/benzoxazolyl nickel(II) complexes **14** (Figure 11) were synthesized by Sun et al.[92] Upon activation with $Al_2Et_3Cl_3$, these complexes display good activity for ethylene dimerization. Comparing complexes **14a** and **14b**, it appears that the less bulky the R substituent, the higher the activity of the corresponding nickel pre-catalyst. The authors suggest that bulk around the nickel center hinders the coordination of ethylene. Moreover, the ligand with a benzothiazolyl group (**14c**, Z = S) (Table 5) enhanced the catalytic activities of the corresponding nickel complexes compared with the benzoxazolyl group (**14b**, Z = O).

3.1.2.2 (P,N)-Neutral ligands

Nickel catalysts bearing (P,N)-ligands possess potential hemilability, allowing an efficient molecular activation procedure under mild conditions, and therefore have received much attention. The phosphorous donor moiety usually stabilizes the complex and the imine moiety improves the activity and selectivity of the catalyst.[61,93] A strategy to enhance the thermal and chemical stability of those catalysts has been investigated and reviewed, consisting in using non-enolizable imine donors such as phosphino-pyridine and phosphino-oxazoline ligands.[5] These ligands proved to enhance selectivity towards α-olefins. In addition, the molecular weight of the products may be tuned by varying the bulk of the N-alkyl substituents on the imino moiety.[93] Most nickel(II) bearing (P,N)-ligands are selective towards short-chain oligomers such as butenes and hexenes in the presence of ethylene and a co-catalyst.[86]



15a R = tBu
15b R = iPr

16

17

Figure 12. (P,N)-based nickel(II) complexes

Phosphinito-imine ligands were investigated by Campora et al.[93] Upon activation with $AlEt_2Cl$, nickel complexes **15** are active. Mainly butenes, minor amounts of hexenes and traces of octenes are produced. The activity and selectivity of these catalytic systems depend on the substituents on the PR_2 group. A bulky group on the phosphorous atom **15a** (R = tBu) induces lower activity and higher selectivity towards butenes than **15b** (R = iPr) (see Table 5, example for **15b**). Among the diverse N-functions encountered in (P,N)-ligands, the oxazoline heterocycle and its derivatives have been widely studied.[5] Braunstein et al.[94] speculated that non-enolizable imine donors should be beneficial for both chemical and thermic stability of the catalyst. Therefore, they developed phosphino-oxazoline ligands. In the presence of $AlEtCl_2$, phosphino-oxazoline complexes **16** (Figure 10) exhibit moderate activity, yielding mostly dimers and trimers. Small amount of tetramers are observed and very low selectivity towards 1-butene are obtained (Table 5).[94] The authors further investigated the replacement of the oxygen atom in the oxazoline moiety by a sulphur atom. Complex **17** (Figure 10) shows moderate activity for ethylene oligomerization in the presence of $AlEtCl_2$ and produces mainly butenes and hexenes with low selectivity towards butene-1 (Table 5). [95]

3.1.2.3 (P,P)-Neutral ligands

Research on (P,P)-based catalytic systems mainly focused on the impact of bite angles and electronic properties of several symmetrical diphosphine ligands. Short bite angle ligands such as bis(phenylphosphino)methane type (DPPM) ligands behaves as four-electron donors upon coordination to a nickel center through both phosphines. Symmetrical carbon-bridged diphosphines ligands have shown activity leading to the formation of oligomeric/polymeric products.[11] Furthermore, various N-substituents can be introduced into DPPM type ligands, such as bis(phenylphosphino)amine (DPPA). The four-membered-ring nickel(II) complexes bearing DPPA ligand have been applied to ethylene oligomerization. However, the high selectivity of the corresponding Cr complexes was not achieved.[96] Several diphosphine nickel (II) complexes displaying good catalytic activities have been developed by Wass et al.[97] for the polymerization and oligomerization of ethylene (Figure 13).

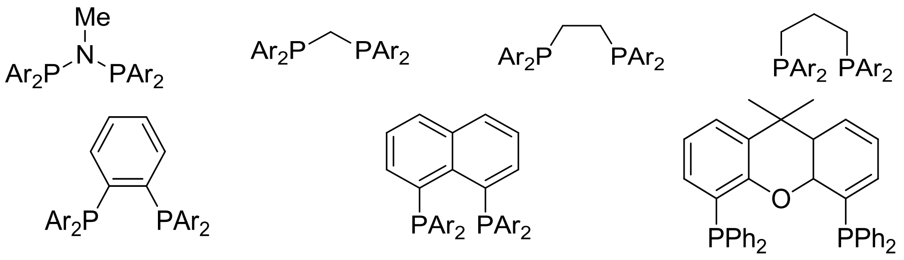
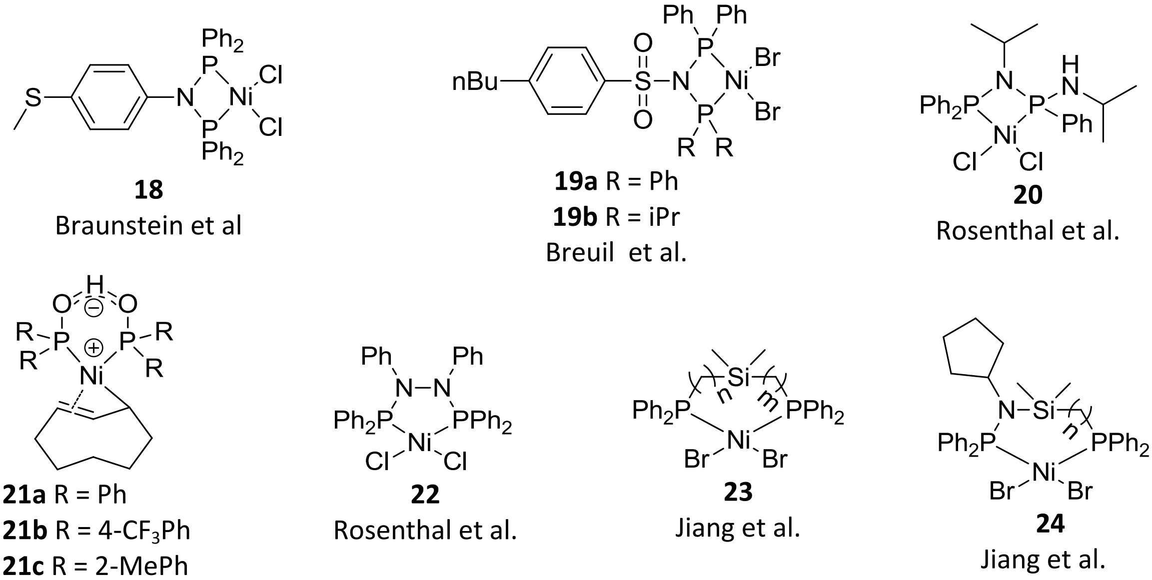


Figure 13. Different (P,P)-bidentate ligands developed by Wass et al.[11]



18
Braunstein et al

19a R = Ph
19b R = iPr
Breuil et al.

20
Rosenthal et al.

21a R = Ph
21b R = 4-CF_3Ph
21c R = 2-MePh
Breuil et al.

22
Rosenthal et al.

23
Jiang et al.

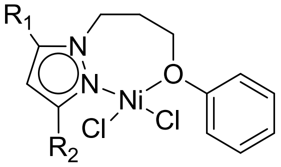
24
Jiang et al.

Figure 14. Diphosphine based nickel(II) complexes

The catalytic behavior of bis(phosphanyl)amine nickel(II) complexes (PNP) in ethylene oligomerization was studied by Wu et al.[98] These complexes showed high activity for ethylene oligomerization in the presence of MAO or $AlEt_2Cl$, producing mainly dimers with high selectivity towards α-olefins.[11] Several groups studied the impact of the substituents in PNP–based nickel (II) complexes on the oligomerization of ethylene. All pre-catalysts **18, 19** and **20** are active in the oligomerization of ethylene in the presence of an aluminum-based co-catalyst, favoring the formation of butenes, hexenes and higher olefins; no polyethylene is observed. Braunstein et al.[96] demonstrated that, in complex **18**, employing N-aryl substituents instead of N-alkyl improves the activity of the catalytic system (Table 5). Breuil et al.[99] showed that in complexes **19**, basic phosphorus moieties in **19b** are beneficial to the activity of the catalytic system, but the best selectivity to butenes is obtained with phenyl groups **19a** (Table 5, examples for **19a** and **19b**). Finally, complex **20** developed by Rosenthal et al.[100] displays very low activities (Table 5). Secondary phosphine oxide (SPO) ligands were previously reported for the nickel-catalyzed hydrophosphinylation of terminal alkynes.[101] Breuil et al.[102] speculated that a cationic nickel(II) species bearing metal-hydride or metal-carbon bonds could be favorable for ethylene oligo- or polymerization (Figure 14. **21**). The addition of a Lewis acid such as $B(C_6F_5)_3$ activates the complexes **21**, which then catalyze the transformation of ethylene into linear short chain oligomers (C_4 to C_8) with very high selectivity towards 1-butene in the butenes fraction, although deactivation is noticed after 1 h of reaction. Compared with **21a,** introducing an electron-withdrawing group R in the phosphorous substituents of **21b** produces higher activity, while steric hindrance in complex **21c** induces a broader product distribution (Table 5, example for **21b**). The catalytic potential of bis(phosphine)hydrazine-based ligands has been discussed by Bollmann, Wasserscheid et al.,[103] who described the use of $Ph_2PN(Me)N(Me)PPh_2$ with chromium pre-catalysts in ethylene tetramerization. Rosenthal et al.[104] reported the coordination properties of bis(diphenylphosphino)-1,2-diphenylhydrazine ($Ph_2PN(Ph)N(Ph)PPh_2$) and the catalytic reactivity of the corresponding nickel(II) complex. Complex **22** (Figure 14) showed low catalytic activity in the presence of MAO. The oligomers were formed in a Schulz-Flory distribution centered on short chain olefins and traces of polyethylene were also observed (Table 5). The development of varieties of pincer ligands with non-symmetrical backbones and the potential impact of the electronic property of silyl groups on the ligand backbone prompted Jiang et al.[105–107] to study several silane-bridged diphosphine complexes **23-24.** Complex **23**, activated by MAO, catalyzed the oligomerization of ethylene to butenes and hexenes with low selectivities towards 1-butene. The impact on the activity of the catalytic system of the carbon bridge length in **23** is not clear and may be due to ligand rigidity and electronic effects (Table 5, example for n=1 and m=0).[105] Introducing a nitrogen group into the ligand backbone **24** induces greater activities towards the oligomerization of ethylene. The selectivity follows a Schulz-Flory distribution with high butenes content and higher selectivities towards 1-butene in the C4 fraction.[106] The activity of the catalytic system decreases with the augmentation of the carbon bridge length from n = 0 to 1.[107] However, the selectivity towards butenes fraction stays stable, while 1-butene selectivity increases (Table 5, example for n=0).

3.1.2.4 Neutral N,O ligands

Most of the (N,O)-type ligands developed in the oligomerization of ethylene are monoanionic ligands and form neutral nickel complexes (for more detail see § 3.2.1.2). On the other hand, some examples of Ni(II) complexes based on neutral (N,O)-type ligands have been reported in the literature.



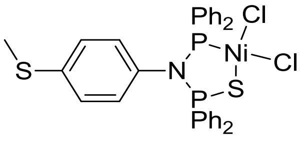
25a R_1 = Me, R_2 = Me
25b R_1 = H, R_2 = *t*Bu

Figure 15. Neutral (N,O)-based nickel(II) complexes

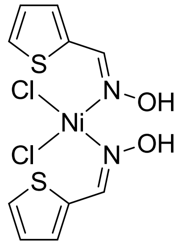
Phenyl ether-pyrazole nickel(II) complexes **25** (Figure 15) are paramagnetic and were developed by Casagrande Jr et al.[108] They present low to moderate activities and produce short-chain olefins with butenes as the major product and hexenes as side products with moderate to good 1-butene selectivities. The authors suggest that the bulky substituent at R_2 in **25b** hinders the coordination of the monomers to the metal center and therefore induces a decrease of the activity compared with **25a** (Table 5).

3.1.2.5 Neutral (P,S)- and (N,S) ligands

Although transition metal complexes containing sulfur ligands are reported to catalyze several homogeneous reactions, only few have been applied to olefin oligomerization reactions.[109] Nickel phosphine complexes bearing 2,4-pentanedithionate ligands constituted some of the few sulfur containing catalytic systems active in ethylene oligomerization.[110]



26



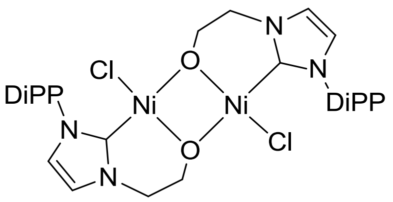
27

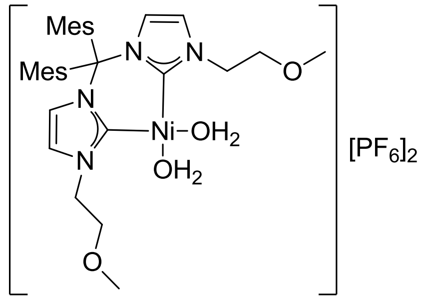
Figure 16. (P,S)- and (N,S)-based nickel(II) complexes

The catalytic behavior of the bis(phenylphosphino)(N-thioether) amine nickel(II) complex **26** (Figure 16) was studied by Braunstein et al.[96] Complex **26** was evaluated in the oligomerization of ethylene with $AlEtCl_2$. Butenes are formed as the main product with hexenes and traces of octenes and higher olefins, with good activities (Table 5). Tembe, Mucherjeee et al.[87] demonstrated that in the presence of $AlEt_2Cl$, the complex **27** produces mainly butenes and hexenes with very high selectivity towards 1-butene in the butenes fraction (Table 5).

3.1.2.6 Other bidentate neutral ligands

Braunstein et al.[72–74] studied bis-NHC nickel(II) complexes and mono-NHC bearing a second chelate donor group in order to fix the metal in the surroundings of the NHC donor site (Figure 17).

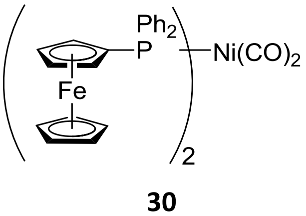


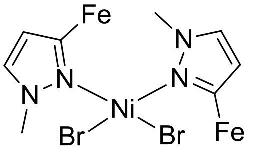


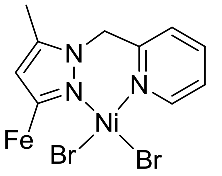
28 **29**

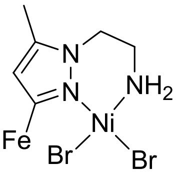
Figure 17. N-Heterocyclic carbene-based nickel(II) complexes

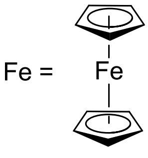
The catalytic activity of complexes **28** and **29** was investigated in presence of $AlEtCl_2$. Complex **28** displays moderate selectivity for butenes and low selectivity for 1-butene[73], while complex **29** forms mainly butenes and hexenes with traces of octenes but with very low selectivity for alpha olefins (Table 5).[74]











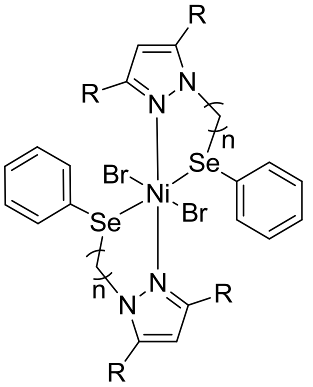
30 **31** **32** **33**

Figure 18. Iron containing nickel complexes

In the presence of MAO, the ferrocenyl phosphane nickel(0) complex **30** described by Lang et al.[111] displays low activity and forms hexenes as the main product followed by butenes and higher oligomers (Table 5). Darkwa et al.[112] suggest that the use of bulky ferrocenyl groups in pyrazolyl ligands may enhance catalyst stability and thus favor the activity of the catalytic system. Complexes

31-33 (Figure 18) are active in presence of $AlEtCl_2$ and form butenes and higher oligomers from C_{16}^+ without C_6-C_{14} oligomers. The authors compared the catalytic activity between monodentate ligands **31**, bidentate pyrazolyl-pyridine **32** and bidentate pyrazolyl-amine ligands **33**. The bidentate nickel complexes bearing pyridine groups **32** dislayed higher activity than pre-catalysts with amine groups **33** and the most active catalyst was **31**. The σ-donor capabilities of the nitrogen donor atoms in the ligands and thus the electrophility of the nickel center increase in the order: pyrazolyl < amine < pyridyl and may explain the higher activity of pre-catalyst **31** compared with **33** and **32** (Table 5) respectively.

Selenium based ligands applied to homogeneous reactions are scarce; several examples have been synthesized and used in coupling reactions, but none of them have been employed in ethylene oligomerization.[113] Casagrande Jr et al.[113–115] previously reported that in tridentate pyrazole ligands, replacing the nitrogen or oxygen donor by a sulfur atom induces higher activity and suggested that the presence of a softer donor atom stabilizes the active species. In this context, they developed nickel(II) complexes containing selenium-based bidentate ligands for the purposes of generating highly active oligomerization systems (Figure 19).[113]



34a R_1 = Me, n = 2
34b R_1 = Me, n = 1
34c R_1 = H, n = 1

Figure 19. Selenium-functionalized pyrazole complexes

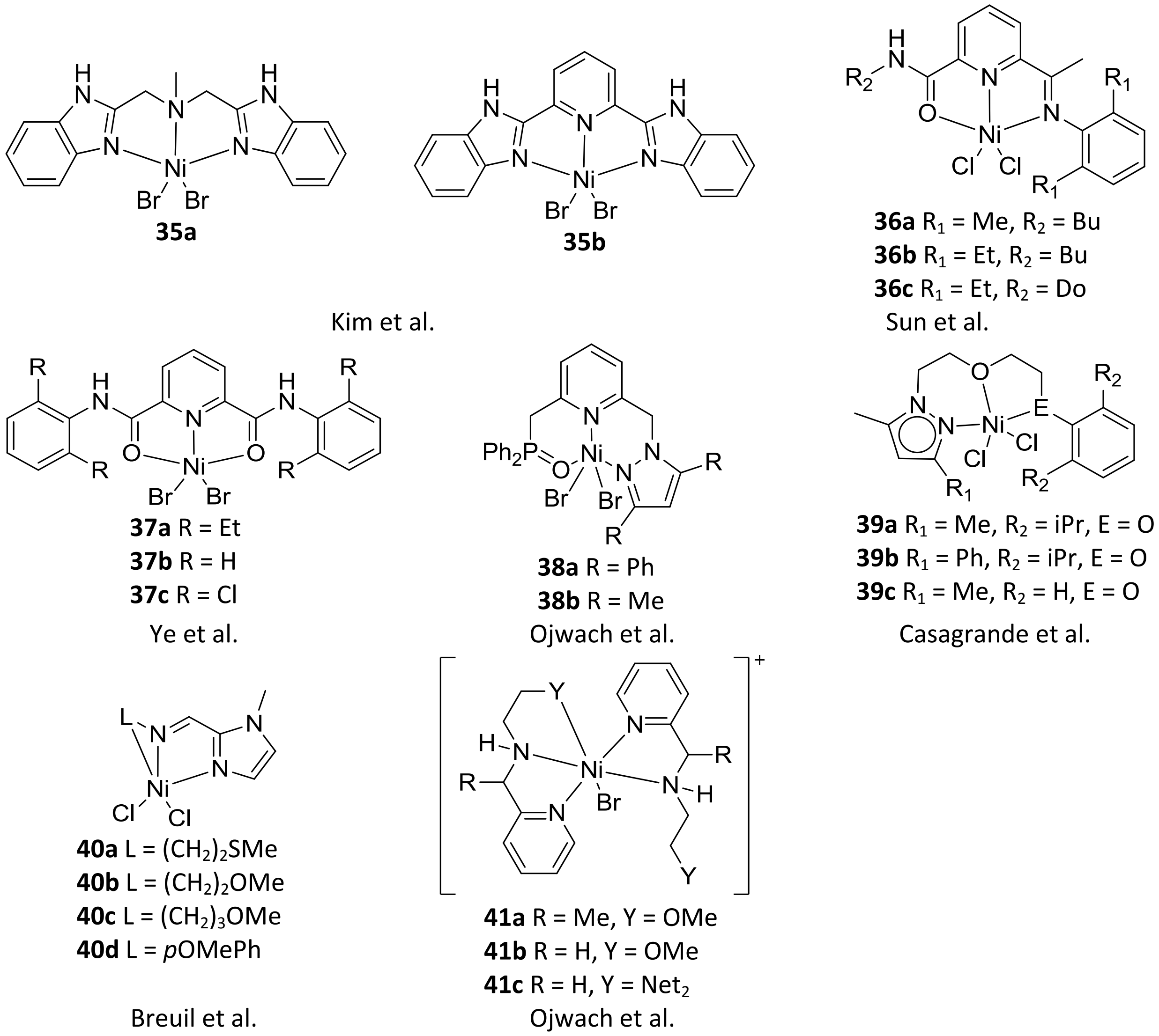
In the presence of MAO, the complexes **34** are active, affording mainly butenes and minor amounts of hexenes. Good to high selectivities towards 1-butene in the butenes fraction are obtained. The presence of methyl groups at the 3 and 5 positions of the pyrazolyl ring (R_1) (**34b** vs **34c**) and the formation of five-membered nickel complexes (**34a** vs **34b**) afforded more active systems (Table 5, example for **34b**).

3.1.3 *Tridentate neutral ligands LLL*

Tridentate neutral ligands offer a wide diversity of structure and, even though they generally display lower activities than bidentate ligands,[11,61] they present good selectivities towards the production of α-olefins. Several strategies have been employed in the development of these ligands:

- Mimicing ligands used with other metals and studying their impact on the nickel-based oligomerization of ethylene
- Introducing an additional donor group into bidentate ligands

Several reviews discuss progress regarding the oligomerization of ethylene employing tridentate ligands such as (P,N,P)[59] and (N,N,N)[11], among others.



35a

35b

Kim et al.

36a R_1 = Me, R_2 = Bu
36b R_1 = Et, R_2 = Bu
36c R_1 = Et, R_2 = Do
Sun et al.

37a R = Et
37b R = H
37c R = Cl
Ye et al.

38a R = Ph
38b R = Me
Ojwach et al.

39a R_1 = Me, R_2 = iPr, E = O
39b R_1 = Ph, R_2 = iPr, E = O
39c R_1 = Me, R_2 = H, E = O
Casagrande et al.

40a L = $(CH_2)_2SMe$
40b L = $(CH_2)_2OMe$
40c L = $(CH_2)_3OMe$
40d L = *p*OMePh

Breuil et al.

41a R = Me, Y = OMe
41b R = H, Y = OMe
41c R = H, Y = Net_2
Ojwach et al.

Figure 20. Tridentate nickel complexes

The first strategy was applied to the bis(iminopyridine) ligand originally developed by Brookhart[116] and Gibson[117] with Co and Fe complexes. Fan et al.[118] applied these ligands to nickel and further work has been carried out in order to develop alternative variations of the bis(imino)pyridine ligand. In this context, Kim et al.[119] postulated that bis(benzimidazolyl)amine/pyridine, having a wide open coordination site, should facilitate β-H transfer and the oligomerization of ethylene. This family of ligands also has the advantage of possessing a backbone that is easy to derivatize. Complexes **35a-b** activated by $Al_2Et_3Cl_3$ display moderate-to-good activities for ethylene oligomerization and produce mainly butenes and hexenes. The pyridyl complexe **35b** displays higher activities and selectivities for 1-butene in the butene fraction than their amine counterpart **35a** (Table 5). The authors suggest that this difference in activity is due to the resonance effect in the pyridyl ring increasing the electrophility of the nickel center compared with the methyl group. Moreover, the planar nature of the pyridine complexes may facilitate incoming monomer accessibility. The alkylcarboxamide-based nickel complexes **36** were studied by Sun et al.[120] (Figure 20) and displayed moderate-to-high activities for the dimerization of ethylene in the presence of $AlEt_2Cl$. The activity of the catalytic system decreases significantly when the benzene substituent (R1) in **36a** (Me) is replaced by an ethyl group in **36b**. This property may be explained by the proximity of the R1 position to the metal center and may hinder the coordination of ethylene to the active species. On the other hand, the authors suggest that the longer alkyl chains at R2 position in **36c** are able to protect the active species and thereby lead to higher activities compared with **36b**. Consequently, small chains R1 and long alkyl chains R2 lead to higher activity of the catalytic system (Table 5, example for **36a**).[120] The reactivity of nickel(II) complexes bearing 2,6-pyridinecarboxamide ligands **37** was discussed by Ye et al.[121] (Figure 20). Activated by $AlEt_2Cl$, these complexes produce high selectivity for butenes and good selectivity towards 1-butene in the butene fraction. The R substituent on the phenyl moiety has an impact on the activity of the catalytic system. A bulky alkyl substituent R (**37a** vs **37b**) increases the activity, whereas introducing an electron-withdrawing group (**37c**) decreases the activity. A compromise is found for R = Et: **37a** (Table 5).

The characterization and ethylene oligomerization behavior of unsymmetrical (pyrazolyl)-phosphinoyl pyridine nickel(II) complexes **38** were described by Ojwach et al.[122] High butene selectivities are obtained with these complexes in the presence of $AlEtCl_2$, along with moderate to good selectivities towards 1-butene. Employing pyrazolyl-phosphinoyl pyridine pre-catalysts exhibits lower activity compared to previously reported catalysts such as pyrazolylmethyl pyridine.[123,124] The substituent (R) on the pyrazole ring has an impact on the catalyst activity without influencing the olefin distribution. Bulky aryl groups R **38a** may hinder the coordination of ethylene to the metallic center and therefore decrease the activity of the catalytic system compared to alkyl groups R **38b** (Table 5). Ether pyrazolyl ligands with O- and S-donor groups were further developed by Casagrande et al.[125] for the oligomerization of ethylene (Figure 20). In the presence of MAO, complexes **39** display high selectivity towards butenes and good selectivities towards 1-butene; the best performances are obtained for E = O (Table 5). Regarding complex **39**, greater steric hindrance on the pyrazolyl ring (R1, **39b** vs **39a**) decreases the activity of the catalytic system. Similarly, decreasing the bulk at the R2 position from the isopropyl group in **39a** to hydrogen in **39c** induces higher activity. These observations are consistent with the effect of bulkier substituents, which hinder the insertion of a monomer into the active metal center. The nature of E has an impact on the activity of the catalytic system in the order O > Se > S.[125,126]

Another strategy employed in the development of tridentate ligands consists of introducing an additional donor group into bidentate ligands. To this end, Breuil et al.[127] studied the behavior of nickel complexes bearing imino-imidazole ligands with pendant donor groups (SR, OR, NR_2, PR_2) on the oligomerization of ethylene. Complexes **40** (Figure 20), activated by $AlEtCl_2$, produce mainly butenes followed by hexenes and higher olefins, with low selectivity towards 1-butene. Replacing the sulfur pendant group in **40a** with an ether **40b** induced to a slight increase in the activity without modification of the olefin distribution, suggesting a limited role of pendant donor groups. Increasing the linker to three carbon **40c** decreases drastically the activity. The best activity is obtained when a non-flexible linker (phenyl) is introduced between the imine and the functional group **40d** (Table 5). The complexes **41** were developed by Ojwach et al.[128] and present moderate activity and selectivity towards butenes in the presence of $AlEtCl_2$. The authors suggested that an electron donating R group **41a** may decrease the electrophilicity of the nickel atom, and therefore reduce the activity of the catalytic system compared with **41b**. The strength of the coordination ability of the pendant group Y influences the activity of the catalytic system. Therefore, replacing the ether function **41b** with an amine **41c** slightly increases the activity of the catalytic system but decreases the selectivity towards butenes (Table 5, **41b**).

Table 5. Catalytic performances in the oligomerization of ethylene for selected cationic nickel(II)complexes (1/2)

Ligand	Pre-catalyst	Co-catalyst (ratio / Ni)	Solvent	T(°C)	P (bar)	Time (h)	Activity (g/(g_{Ni}.h))	Selectivity (wt%)				Ref
								C_4	C_6	C_8	1-C_4	
P	$Ni(PPh_3)_2(C_2H_4)$	None	nd	12	1	32	0.11	83.4	14.6	-	7.1	66
P	$Ni(PPh_3)_2(C_2H_4)$	$BF_3.OEt_2$ (2)	nd	12	1	0.13	544.9	96.8	3.1	-	41.6	
P	$Ni(PPh_3)_2Cl$						229.4	98.8	1.2	-	49.3	
P	$Ni(PPh_3)_2(C_2H_4)$	$AlEtCl_2$ (10)	nd	12	1	0.4	4015	71	20.8	8.2	-	67
P	$Ni(PPh_3)_2Cl$					0.5	3441	69.4	25.7	4.9	-	
NHC	**1b**	$AlEtCl_2$ (10)	Toluene	25	10	0.6	11700	77	21	2	12	74
N	**2b**	PMAO-IP (500)	Toluene	30	20	0.25	27384	91.4	8.6	-	69.2	75
(N,N)	**5a**	$AlEt_2Cl$ (150)	Toluene	30	3	0.5	5512	64	31	5	31	78,79
(N,N)	**5b**						14055	Low and high M_w oligomers				
(N,N)	**6b**	$Al_2Et_3Cl_3$ (150)	chlorobenzene	30	1.3	0.5	790630	88	12	-	92.0	81,82
(N,N)	**7a**	MAO (500)	Toluene	25	5	0.5	10273	Schulz-Flory distribution (C_4-C_{23})				84
(N,N)	**8a**	MAO (2000)	Toluene	30	10	0.5	81942	65.5	24.1	10.4	76	85
(N,N)	**8b**		Toluene				38160	96.6	3.4	-	87.5	
(N,N)	**9a**	$AlEt_2Cl$ (100)	Toluene	45	20	1	208518	81	19	-	99.5	86,87
(N,N)	**9b**		Toluene			0.5	68143	90	10	-	>99.5	
(N,N)	**10a**	$Al_2Et_3Cl_3$ (500)	Toluene	40	5	0.5	56900	15.7	22.9	61.4	-	88
(N,N)		MMAO (2500)	Toluene				29813	7.8	88.4	3.8	-	
(N,N)	**10b**	MAO (500)	Toluene	35	2	0.25	258988	90.4	9.6	-	56.2	83
(N,N)	**11b**	$AlMe_3$ (300)	Toluene	30	10	0.5	14242	Schulz-Flory C_4- C_{16}				89
(N,N)	**12**	$AlEtCl_2$ (540)	Toluene	30	10	0.75	128586	57	43	-	-	91
(N,N)	**13**	$Al_2Et_3Cl_3$ (150)	Toluene	-	1.3	0.5	3408	95	4	-	85.3	82
(N,N)	**14c**	Al_2 Et_3Cl_3 (600)	Toluene	40	10	0.3	61670	94.7	5.3	-	52.3	92
(P,N)	**15b**	$AlEt_2Cl$ (200)	Toluene	30	5	1	73647	88	12	-	40	93
(P,N)	**16**	$AlEtCl_2$ (6)	Chlorobenzene	30	10	0.6	29000	58	36	5	6	94
(P,N)	**17**	$AlEtCl_2$ (6)	Chlorobenzene	30	10	0.6	15150	85	13	1	14	95
(P,P)	**18**	$AlEtCl_2$ (10)	Chlorobenzene	30	10	1	32800	68	26	5	1	96

Table 5. Catalytic performances in the oligomerization of ethylene for selected cationic nickel(II) complexes (2/2)

Ligand	Pre-catalyst	Co-catalyst (ratio / Ni)	Solvent	T (°C)	P (bar)	Time (h)	Activity (g/(gNi.h))	Selectivity (wt%)				Ref
								C_4	C_6	C_8	1-C_4	
(P,P)	**19a**	MAO (300)	Toluene	45	30	1	14000	92.4	6.6	1	57.7	[99]
(P,P)	**19b**						81000	71.7	17.9	10.4	20.9	
(P,P)	**20**	Et_3Al (100)	Toluene	65	30	2	75	72	11.9	16.1	-	[100]
(P,P)	**21b**	$B(C_6F_5)_3$ (2)	Toluene	40	30	1.5	6467	67.4	22.8	9.8	91.9	[102]
(P,P)	**22**	MAO (300)	Toluene	100	30	1.5	5215	69.6	23.8	4.7	-	[104]
(P,P)	**23** n=1, m=0	MAO (700)	Toluene	45	10	0.5	53152	94.7	5.3	-	14.0	[105]
(P,P)	**24**	$EtAlCl_2$ (500)	methylcyclohexane	45	10	0.5	1601362	83.8	16.2	-	34.4	[106]
(N,O)	**25a**	MAO (250)	Toluene	30	20	0.3	21841	90.8	9.2	-	69	[108]
(P,S)	**26**	$AlEtCl_2$ (40)	Chlorobenzene	28 – 30	10	0.6	32200	73	23	4	-	[96]
(N,S)	**27**	$AlEt_2Cl$ (250)	Toluene	45	20	1	16000	76	24	-	>99.5	[87]
(NHC,O)	**28**	$AlEtCl_2$ (10)	Chlorobenzene	20	10	0.6	19000	56	-	-	6	[73]
(NHC,O)	**29**						16600	75	22	3	7	[74]
(P,P)	**30**	MAO (2500)	n-pentane	60	10	1	4941	28	68	4	-	[111]
(N,N)	**31**	$AlEtCl_2$ (400)	Chlorobenzene	25	10	1	33884	Butenes + olefins (C_{16}^+) No C_6-C_{14} observed				[112]
(N,N)	**32**						17428					
(N,N)	**33**						9847					
(N,Se)	**34b**	MAO (400)	Toluene	30	20	0.3	10992	96.5	3.5	-	87.2	[113]
(N,N,N)	**35a**	$Al_2Et_3Cl_3$ (200)	Toluene	30	1.3	0.5	24051	84.1	15.9	-	15.9	[119]
(N,N,N)	**35b**		Toluene				37893	86.3	13.7	-	36.1	
(N,N,O)	**36a**	$AlEt_2Cl$ (500)	Toluene	20	10	0.3	142078	-	-	-	92.1	[120]
(O,N,O)	**37a**	$AlEt_2Cl$ (200)	Toluene	20	10	0.5	119762	98.9	1.1	-	72	[121]
(N,N,O)	**38b**	$AlEtCl_2$ (250)	Toluene	30	10	1	6133	94	6	-	65	[122]
(N,O,O)	**39c**	MAO (250)	Toluene	30	20	0.3	17109	93.6	6.4	-	75	[125]
(N,N,O)	**40d**	$AlEtCl_2$ (15)	Toluene	45	10	0.25	204940	83	16	-	18	[127]
(N,N,O)	**41b**	$AlEtCl_2$ (200)	Toluene	30	10	1	40545	61	35	4	72	[128]

nd = not described

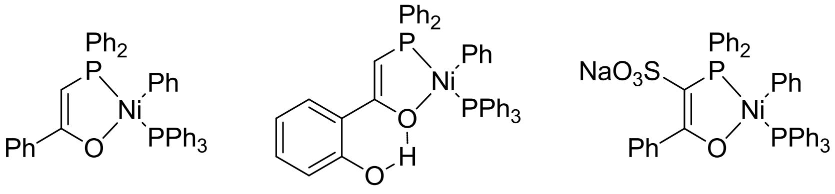
3.2 Monoanionic ligands

Monoanionic ligands form neutral nickel (II) complexes in the presence of nickel precursors, which have been described as active for ethylene oligomerization as single component catalyst or activated by a co-catalyst. The discoveries of monoanionic (P,O)-based nickel(II) complexes (SHOP catalysts, **42**) by Keim et al.[54] and phenoxyimine nickel(II) complexes ((N,O)-based ligand) by Grubbs et al.[56], respectively producing α-olefins in a broad Schulz-Flory distribution and high molecular weight polyethylene, demonstrate that the catalytic properties of nickel(II) complexes can readily be modified with suitable ligands. In this context, neutral nickel complexes have attracted much attention. Different ligand backbones were developed consisting, among others, of metal complexes with bidentate monoanionic (P,OH)- or (N,OH)- and tridentate monoanionique ligands.[57,58,62,64,129] Catalytic results are summarized in Table 6.

3.2.1 *Bidentate monoanionic ligands LX*

3.2.1.1 P,O-Monoanionic ligands

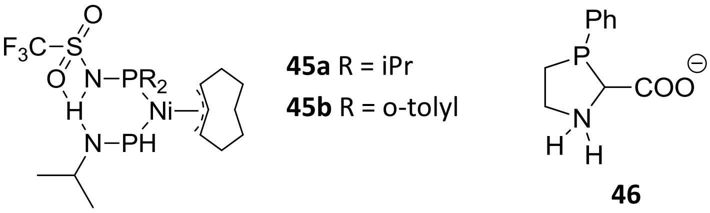
The major breakthrough with monoanionic (P,O)-based ligands are the SHOP catalysts developed by Keim et al.[54] This catalyst generates a wide range of low molecular weight α-olefins in a Schulz-Flory distribution. A key factor regarding their design is the facile β-hydride elimination promoted by late transition metals. Industrial oligomerization process based on SHOP catalysts leads to the manufacture of surfactants, lubricants, and fine chemicals.[62,129]



42 **43** **44**

Figure 21. Reviewed (P,O)-bidentate monoanionic nickel complexes

Matt et al.[57] has extensively reviewed these systems and rationalized the relationship between structure and reactivity. The monodentate tertiary phosphine (for example in complex **42**: PPh_3) has a great impact on the product distribution: its coordination strength to the nickel center increases with its basicity and consequently favors chain termination by β-H elimination. On the other hand, the structure of the bidentate (P,O)-chelate part is also crucial for activity and selectivity control. The basicity of the (P,O)-phosphorous substituents usually favors the formation of higher molecular weight olefins. Decreasing the basicity of the oxygen chelate favors chain termination over chain propagation. This property can be achieved with a hydrogen bond formed between (P,O)-chelate and the phenolic OH group **43**. These catalysts display good activity and are able to produce high lower α-olefin contents. Adding a sulfonyl group to the C=C backbone **44** increases the solubility of the complex and helps to separate the catalyst from the oligomers in the industrial process.[130] These nickel(II) catalysts possess good tolerance towards functional groups and allow 1,4-butanediol to be used as a polar catalyst phase.[58,61,62] Following this breakthrough, numerous studies have been carried out on screening SHOP-type catalysts and optimizing their catalytic systems in the oligomerization of ethylene (Figure 22).



45a R = iPr
45b R = o-tolyl

46

Figure 22. (P,O)-bidentate monoanionic based ligands and nickel complexes

Breuil et al.[131] investigated self-assembled sulfonamidophosphine and aminophosphine ligands for the selective dimerization of ethylene to 1-butene. These ligands display several key properties, such as adaptative coordination behavior and the ability to construct supramolecular bidentate or tridentate complexes through hydrogen bonding. The authors anticipated that the hemilability of the supramolecular bonds in the nickel complex could protect the vacant site during the ethylene dimerization process and therefore stabilize the catalytic active species. *In situ* NMR experiments of complexes **45** under ethylene pressure suggested the chelation of the nickel center by a monoanionic (P,O)-ligand (Figure 23), which may explain its specific properties.

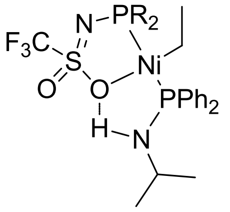


Figure 23. Suggested in situ-formed catalytic species for **45** (**a.** R = o-tol, **b** = iPr)

Complexes **45a-b** are active in the oligomerization of ethylene and present great differences in terms of selectivity. Complex **45a** produces a large linear α-olefin distribution, while complex **45b** is selective towards butenes. In both cases, the selectivity for 1-butene is very high (See Table 6).

The particularity of heterocyclic α-phosphanyl amino acid-based ligand **46**, combining the acido-basic property of amino acids with the ability of the phosphine donors to chelate a transition metal complex, prompted Heinicke et al.[132] to investigate their reactivity in the oligomerization of ethylene. However, in the presence of $Ni(COD)_2$, the activity of the catalytic system decreases compared with linear α-phosphanyl amino acids. The choice of cyclic α-phosphanyl amino acid-based ligands instead of linear ligands was justified by a better air and moisture stability. The selectivity is oriented towards oligomers with a higher content of inner olefins compared with SHOP-type catalysts (Table 6). The active species formation, stabilized by a (P,O)-chelate backbone (Figure 24) as in SHOP like catalysts, is still suggested due to the high selectivity observed towards linear olefins.

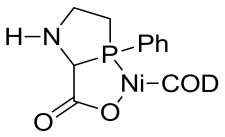
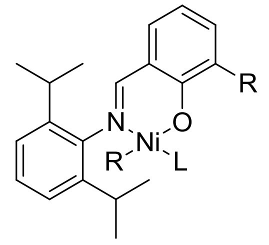


Figure 24. Suggested *in situ*-formed catalytic species for **46**

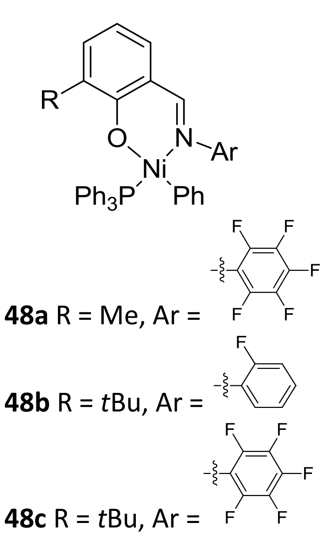
3.2.1.2 Monoanionic N,O ligands

In 1998, Grubbs et al.[56] used the knowledge acquired on the relationship between reactivity and structure of (P,O)-neutral- and α-diimine cationic- nickel(II) complexes to develop neutral phenoxy-imine nickel(II) complexes **47** leading to active polymerization catalysts. (Figure 25) Thanks to the presence of a bulky substituent on the nitrogen imine (2,6-diisopropylphenyl, **47**) and on the ortho position of the phenol (R, **47**), phenoxy-imine nickel(II) complexes display a steric environment that effectively block the axial face of the nickel center. This bulk prevents the chain transfer reaction via β-H elimination and favors the formation of high molecular weight polyethylene. These ligands form with nickel neutral active species which are even more tolerant to polar groups than cationic α-diimine nickel(II)complexes. Regarding the latter, decreasing the bulk of the substituants, mentioned above, favors the switch between polymerization and oligomerization active species. Following this major breakthrough, bidentate monoanionic (N,O)-nickel complexes were extensively studied and reviewed for ethylene polymerization and oligomerization.[62,64,129]



47

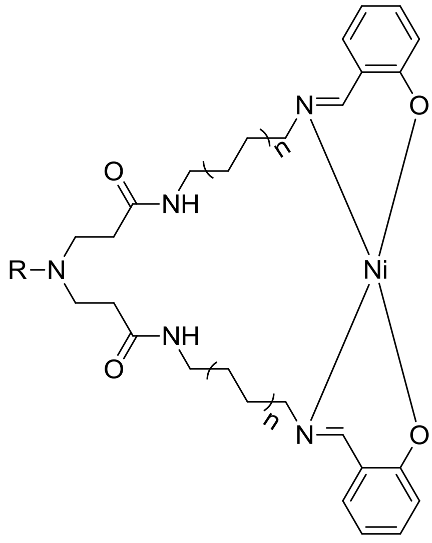
Figure 25. Reviewed (N,O)-phenoxyimine based nickel complexes



48a R = Me, Ar =

48b R = *t*Bu, Ar =

48c R = *t*Bu, Ar =



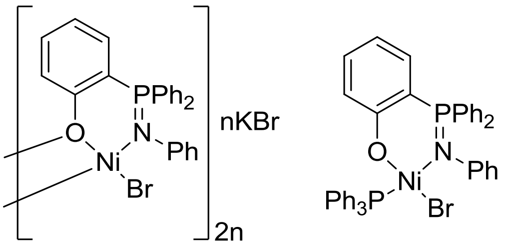
49a R = dodecyl, n = 1
49b R = dodecyl, n = 0
49c R = ethyl, n = 0
49d R = cyclohexyl, n = 0

Figure 26. Salicylaldimine-based nickel(II) complexes

The impact of the electronic density of the iminoaryl moiety on the activity of the catalytic system was demonstrated for oligomerization-active species as well as for polymerization species. Highly electron withdrawing substituted ligands lead to greater activity of the catalytic system.[64] In this context, Song et al.[133] studied the impact of electron-withdrawing groups on the iminoaryl moiety of salicylaldiminato nickel(II) complexes. The catalyst precursors **48** (Figure 26) display moderate catalytic activities and high selectivities for ethylene oligomerization forming hexenes as the main products, butenes are observed but no polyethylene. The rate of ethylene oligomerization is directly correlated to the electrophilicity of the nickel center (**48b** vs **48c**). In fact, chain propagation is favored by the introduction of electron-withdrawing groups which enhances the electrophilic nature of the nickel atom. The presence of a bulky group in the *ortho*-position of the phenol moiety (R) increases the activity of the catalytic system but has little effect on the oligomer distribution (**48c**, Table 6).

Wang et al.[134–137] developed hyperbranched salicylaldimine nickel complex **49** (Figure 25) with the intention of combining the best properties of homogeneous and heterogeneous catalyst. The choice of the co-catalyst has a great impact on the selectivity of the catalytic system. In the presence of MAO, the complexes **49** exhibit good activity and a Schulz-Flory distribution with low selectivity for butenes, whereas in the presence of Et_3Al, high selectivities for butenes are observed. Increasing the carbon chain length in both positions (n and R) leads to less soluble pre-catalysts, and thus decreases the rate of oligomerization (**49a-c**).[134–136] Replacing the linear alkyl R **49c** with a cyclic alkyl **49d** induces higher activity of the catalytic system without changing the selectivity (Table 6, example for **49d**).[137]

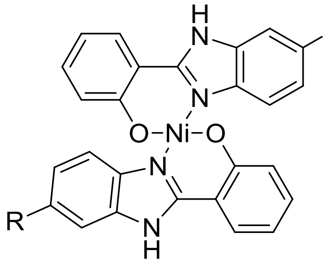
Bidentate phenoxide-iminophosphorane nickel(II) complexes **50** and **51** (Figure 27) were described by Cheisson et al.[138]



50 **51**

Figure 27. Iminophosphorane (N,O)-bidentate nickel(II) complexes

The complexes **50** and **51** were evaluated and compared for the catalytic oligomerization of ethylene in the presence of $AlEt_2Cl$. They are active and selective for butenes with no mention of polyethylene formation. The selectivity towards 1-butene in the butenes fraction is moderate-to-good. The activity of the catalytic system is reduced with strong coordinating ligands such as PPh_3 (**51**) in the vicinity of the nickel center compared with **50** (Table 6).



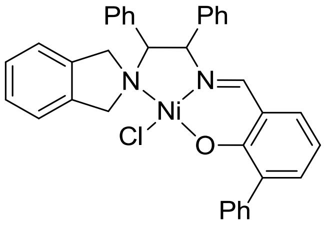
52a R = Cl
52b R = Me

Figure 28. Other (N,O)-bidendate nickel(II)complexes

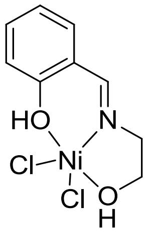
Benzimidazoyl-phenol based nickel II complexes were studied by Tadjarodi et al.[139] for the oligomerization of ethylene. The authors confirmed the coordination of the oxygen atom of the phenol to the metal, since no OH bond was observed. The complexes **52a-b** display high activities for the selective dimerization of ethylene to butene-1. The reactivity of **52a** containing an electron-withdrawing halide is much more active than **52b** containing an alkyl substituent. The role of the electron-withdrawing group is assumed to decrease the electron density at the metal center, favoring the coordination of ethylene.

3.2.2 *Tridentate monoanionic ligands LLX*

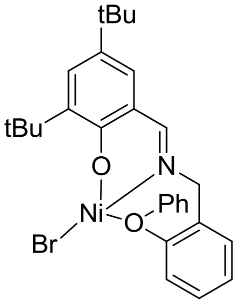
Research into new nickel-based complexes capable of selectively oligomerizing ethylene to alpha-oligomers led to the development of ligands offering a wide diversity of structures, such as tridentate ligands. One of the strategies employed with monoanionic tridentate ligands is to introduce an additional donor group into bidentate monoanionic ligands known to possess interesting properties as regards the oligomerization of ethylene.[140]



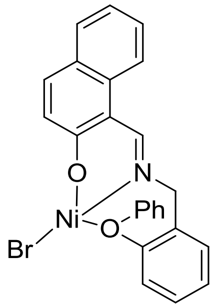
53
Wang et al.



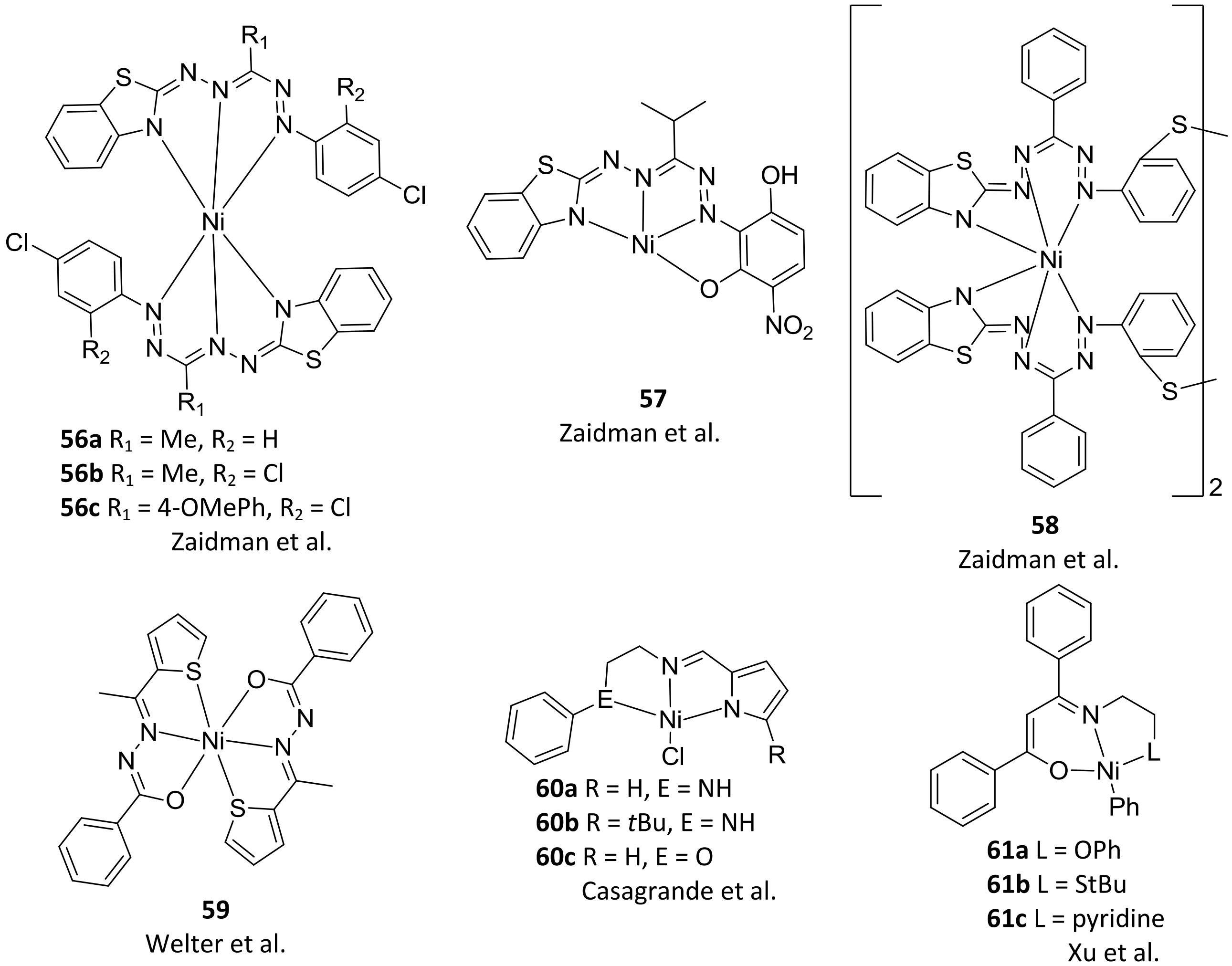
54
Ngcobo et al.



55a
Casagrande et al.



55b
Casagrande et al.



56a R_1 = Me, R_2 = H
56b R_1 = Me, R_2 = Cl
56c R_1 = 4-OMePh, R_2 = Cl
Zaidman et al.

57
Zaidman et al.

58
Zaidman et al.

59
Welter et al.

60a R = H, E = NH
60b R = *t*Bu, E = NH
60c R = H, E = O
Casagrande et al.

61a L = OPh
61b L = StBu
61c L = pyridine
Xu et al.

Figure 29. Tridentate nickel complexes

Wang et al.[141] reported tridentate phenoxy-imine based nickel complexes **53** (Figure 29). The complex **53** transforms ethylene into butenes as the main product in the presence of MAO. Butene is formed with very high selectivity and small amounts of hexenes. A good selectivity towards 1-butene in the butene fraction is also observed (Table 6). Ngcobo et al.[142] described the synthesis, characterization and catalytic performance of a tridente anionic phenoxyimine (O,N,O)-nickel(II) complex **54** (Figure 29). In presence of ethylene, the nickel(II) complexes **54** activated by $AlEtCl_2$ predominantly produce butenes and hexenes as the main products with good activity (Table 6). Casagrande et al.[140] studied the impact of replacing the phenoxy moiety with a naphthoxy moiety in a phenoxy-imine based nickel catalyst bearing a pendant oxygen group on the oligomerization of ethylene **55a-b** (Figure 29). All complexes are active in the oligomerization of ethylene when activated by MAO. They produce mainly butenes and hexenes with a high α-olefins content. The complex **55a** containing a phenoxy moiety displays much higher activity than the naphthoxy moiety **55b** (Table 6). The authors suggest that the presence of a bulky *t*-butyl group in the ortho position of the phenoxy moiety may stabilize the active species and therefore explain the higher activity observed.

The formazan ligand family possesses a wide diversity of easily accessible substituents. Thus, Zaidman et al. [143,144] studied new nickel(II) tridentate formazanate complexes (Figure 29, **56**-**58**) and the impact of the ligand structure on their performance in ethylene oligomerization. Two ligands bind to the nickel center in the form L_2Ni in **56**. The presence of a hydroxyl group in the *ortho*-position of the phenyl moiety (R_2) leads to the formation of mononuclear LNi complexes **57** with tetradentate (N,N,N,O)-coordination. Complexes **58** present tridentate bimetallic L_2Ni_2 structures. All complexes were tested in the oligomerization of ethylene activated by $AlEtCl_2$ and produced a mixture of higher olefins following the Schulz-Flory distribution with a low content of α-olefins such as 1-butene and 1-hexene. In L_2Ni **56** complexes, adding an electron-withdrawing group to the aryl moiety (R_2) increases the electrophilicity of the nickel(II), and therefore the catalytic performance of the pre-catalyst, with a switch in selectivity from butenes (**56a**) to hexenes (**56b**). The use of an electron donating group in the R_1 position drastically decreases the activity of the catalytic system (**56c**). The LNi tetradentate complexes **57** and the L_2Ni_2 **58** complexes exhibited lower activity in ethylene oligomerization compared with L_2Ni complexes **56** (Table 6). Welter et al.[145] reported the coordination and catalytic behavior of nickel(II) complexes bearing tridentate benzohydrazide based ligands **59** (Figure 29). The complex activated by $AlEtCl_2$ is moderately active in the oligomerization of ethylene and produces a Schulz-Flory distribution of olefins with low selectivity towards 1-butene (Table 6).

As seen previously in paragraph 3.1.2.4, Casagrande et al.[108] explored the impact of tridentate based ligands for the selective oligomerization of ethylene. They reported, for instance, the use of tridentate ether pyrazolyl ligands with O- or S-donor pendant groups. Following this investigation, the authors decided to study the reactivity towards ethylene oligomerization of (pyrrolide)-based nickel(II) complexes **60** (Figure 29).[146] These complexes are active in the dimerization of ethylene when activated by MAO. High selectivity towards butenes and good selectivity towards 1-butene were obtained, while minor amounts of hexenes were also observed. The activity of the catalytic system is favored with the steric hindrance on the pyrrolide unit (R), as can be observed from **60a** (H) to **60b** (tBu), suggesting that a bulky alkyl group behaves as a protective group for the active species. The use of an amine **60a** induces higher activity compared with an ether group **60c** (Table 6, example for **60c**).

Xu et al.[147] reported the synthesis, characterization and catalytic performances of (O,N,X)-nickel(II) complexes **61** (Figure 29). In the presence of MAO, these complexes are active in the dimerization of ethylene, with good selectivity for butenes. The nature of the pendant group has a great impact on the performance of the catalytic system. The best activity is achieved when the functional group is a bulky ether **61a,** as compared to alkylsulfur **61b** or pyridine **61c**. The coordination of the pendant group to the nickel center induces good selectivity towards butene-1 and lower activities (Table 6, examples for **61a** and **61b**).

Table 6. Catalytic performances in the oligomerization of ethylene for selected cationic nickel(II)complexes

Ligand	Pre-catalyst	Co-catalyst (ratio / Ni)	Solvent	T(°C)	P (bar)	Time (h)	Activity (g/(g_{Ni}.h))	Selectivity (wt%)				Ref
								C_4	C_6	C_8	1-C_4	
(P,O^-)	**45a**	none	Toluene	40	30	1.5	24000	85	13	2	99.0	131
(P,O^-)	**45b**						12000	35	28	37	99.7	
(P,O^-)	**46** + Ni(COD)$_2$ (1)	none	THF/Toluene	100	50	14	102	Linear inner olefins (major products)				132
(N,O^-)	**48c**	MAO (2000)	Toluene	30	12	0.5	16968	7.3	92.7	-	-	133
(N,O^-)	**49d**	Et_3Al (1000)	Toluene	25	5	0.5	14140	95.6	3.1	1.3	67.8	137
(N,O^-)	**50**	$AlEt_2Cl$ (22.5)	Toluene	25	30	1	32546	98.2	1.8	-	59.8	138
(N,O^-)	**51**						7551	99	1	-	55.6	
(N,O^-)	**52a**	Et_2AlCl (200)	Toluene	30	20	0.5	112400	100	-	-	100	139
(N,N,O^-)	**53**	MAO (250)	Toluene	30	20	0.5	5622	97	3	-	83	141
(O,N,O^-)	**54**	$AlEtCl_2$ (250)	Chlorobenzene	25	10	1	32368	31	69	-	87	142
(O^-,N,O)	**55a**	MAO (300)	Toluene	30	20	0.3	11600	97.7	2.3	-	83.4	140
(N^-,N,N)	**56a**	$AlEtCl_2$ (100)	*n*-heptane	80	4	1	21100	73	11	16	41	143,144
(N^-,N,N)	**56b**						26500	40	58	2	36	
(N^-,N,N)	**57**						11100	12	16	72	35	
(N^-,N,N)	**58**						8200	25	31	46	24	
(O^-,N,S)	**59**	$AlEtCl_2$ (10)	Toluene	-	10	0.6	14913	65	31	5	10	145
(O^-,N,N)	**60c**	MAO (250)	Toluene	30	20	0.3	20789	97	3	-	85	146
(N,N^-,O)	**61a**	MAO (1000)	Dichloromethane	0	10	0.08	1592845	91	-	-	13	147
(N,N^-,S)	**61b**						534923	99	-	-	82	

Despite a large number of studies reported on the oligomerization of ethylene catalyzed by nickel, a large majority of the catalytic precursors described in the literature in the oligomerization of ethylene still produces either a wide range of α-olefins (Schulz-Flory distribution) or short chain oligomers such as butenes with inadequate 1-butene content. Moreover, most of the catalytic systems described as highly selective for 1-butene need improvement before considering industrial application (low conversion, difficulty in scaling up the synthesis of organometallic complexes). Catalytic systems displaying good selectivity towards higher α-olefins (1-hexene, or 1-octene) are scarce. Only a few catalytic systems present unusual selectivity for hexenes, which depends greatly on the co-catalyst used. The selectivity towards 1-hexene and the mechanisms involved are unfortunately not discussed by the authors. Consequently, the development of highly selective processes for the formation of α-olefin employing nickel-based catalysts remains a major challenge academically and industrially.

4 Approaches for supporting Ni molecular oligomerization catalysts

As exemplified earlier, the design of well-defined coordination complexes inherent to homogeneous catalysis remains one of the best ways of controlling productivities and selectivities for this reaction. While the heterogenization of homogeneous catalysts has been used to facilitate catalyst recyclability, it can also be envisaged for tuning the activity and the selectivity by modification of the nickel environment, for example through the introduction of a support or another liquid phase. The literature is full of original approaches in this regard, with nickel complexes immobilized on solid supports (polymers, metal–organic framework, inorganic porous materials…), liquid supports (fluorous solvent, non-aqueous ionic liquids…), or a combination of both (supported ionic liquid phase catalysis). These approaches are described in the following paragraphs.

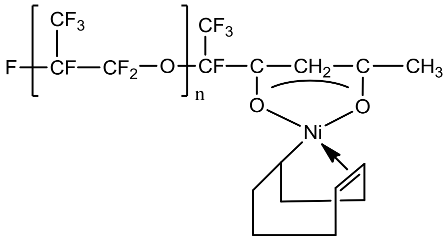
4.1 Liquid-liquid biphasic catalysis in unconventional media

The immobilization of a homogeneous catalyst in a liquid support is one of the most successful approaches described in the literature, the best example with a nickel catalyst being the industrial SHOP process for ethylene oligomerization. In such systems, the Ni-catalyst is immobilized in a polar liquid phase (butanediol) in which the organic products are poorly miscible; this renders recycling of the catalyst possible. In that field, the selection of the catalyst-containing phase and the design of the catalyst itself are often key elements for success.

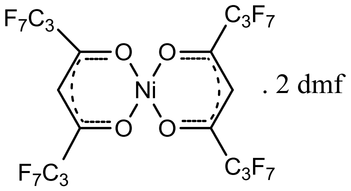
4.1.1 *Perfluorinated solvents*

Despite its extensive application, only few examples reported the use of perfluorinated solvents for Ni-catalyst immobilization. Fluorocarbons are characterized by their non-polar nature and their low miscibility with most common organic solvents and hydrocarbons. In 1999, Keim et al. reported the immobilization of neutral Ni-complexes in a perfluorinated ether solvent (Hostinert 216®) for the biphasic oligomerization of ethylene.[148] In order to optimize the immobilization of the Ni-complex in the perfluorinated solvent, a specific Ni-complex **62** has been developed. This complex appeared to be active for ethylene oligomerization with rather low productivity and no complete separation of the catalyst phase and product. Carlini et al. later tried to develop Fluorinated Biphasic Systems (FBS) using Ziegler–Natta-type catalysts based on bis(fluorinated-β-diketonate)nickel(II) precursors (complexes **63** and **64** in Figure 30).[149] In this work, the nature of the fluorinated phase (*n*-

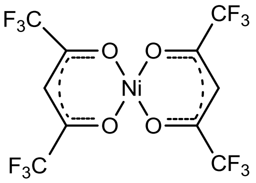
perfluorohexane, perfluorodecaline, perfluorobenzene, galden perfluoroether) and the use of additional fluorinated phosphine ($P^{i}Pr_2(C_6F_5)$, $P(C_6F_5)_3$) were considered for a better immobilization of the catalyst in the fluorous phase. Once activated with MAO, MAO/$Al_2Et_3Cl_3$ or $AlEt_3$/$B(C_6F_5)_3$, these systems appeared to be active for the selective dimerization of propylene to 2,3-dimethylbutenes (TOF up to 25 000 h^{-1}). The authors pointed out that for all the catalytic experiments, a progressive migration of the catalyst towards the hydrocarbon phase, generated by the formation of the oligomeric products, was observed, thus evidencing the difficulty of carrying out a catalytic FBS olefin oligomerization process.



62



63



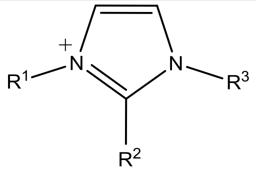
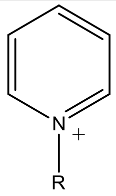
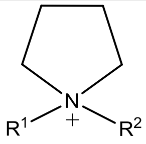
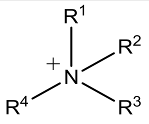
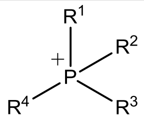
64

Figure 30. Perfluorinated Ni-complexes for FBS olefins oligomerization

4.1.2 *Ionic liquids*

Because the olefin oligomerization reaction involves the formation of reactive metal-carbon bonds that are considered to be prone to hydrolysis, non-protic weakly coordinating solvents should be preferred. In this regard, ionic liquids (ILs) provide good alternative solvents for olefins oligomerization in a liquid-liquid biphasic mode.[150–153] ILs generally appeared to be good solvents for organometallic nickel catalysts, while being immiscible with long chain olefins produced during oligomerization. They are formally based on combinations of organic cations and inorganic or organic anions. Over the years, different generations of ILs for olefin oligomerization have been developed, from water-sensitive chloroaluminates and organochloroaluminates to neutral ILs (Table 7).

Table 7. Selected examples of organic cations and anions in ILs

Cations				
				
imidazolium	pyridinium	pyrrolidinium	Ammonium	Phosphonium

Anions	
Cl^-, Br^-, I^-	$[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$
$[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$,	$[NTf_2]^-$, $[OTf\ ]^-$, $[OTs]^-$

$[AlEt_xCl_{3-x}]^-$	$[ZnCl_3]^-$, $[CuCl_2]^-$, $[SnCl_3]^-$ $[NO_3]^-$, $[PO_4]^{3-}$, $[HSO_4]^-$, $[SO_4]^{2-}$
halides, chloroaluminates and organochloroaluminates	Neutral and others

The use of ILs for the Ni-based oligomerization of propylene was initially reported by Chauvin et al. at the beginning of the 1990s.[154,155] In this work, several Ni complexes (η^3-methallylnickel bromide, $[Ni(acac)_2]$, $[NiCl_2(P^iPr_3)_2]$) were first dissolved in chloroaluminate ILs prepared by mixing $AlCl_3$ with imidazolium, pyridinium or phosphonium chloride. The Lewis acidity of the IL varies within a wide range, depending on the mole fraction of $AlCl_3$ in the melt (N). With acidic IL ($N > 0.5$), uncontrolled cationic oligomerization of propylene occurred, while no activity could be observed for basic ILs ($N < 0.5$). To overcome the drawback of cationic side reactions, the authors developed new salts based on ethylaluminum dichloride ($AlEtCl_2$) and conventional quaternary salts (pyridinium and imidazolium). For ILs with a $AlEtCl_2$ mole fraction higher than 0.5, cationic side reactions were suppressed and selective dimerization of propylene occurred. Interestingly, the selectivity for 2,3-dimethylbutenes when using $[NiCl_2(P^iPr_3)_2]$ increases, thus demonstrating the effectiveness of the “phosphine effect” in these ILs. Ternary mixtures of “$[BMI][Cl]/AlCl_3/AlEtCl_2$” (BMI = butylmethylimidazolium) were later developed for the same reaction.[156] Anionic species formed in the melt were characterized by NMR and Raman spectroscopy.[157,158] When the $AlCl_3$ molar fraction (N) is lower than 0.5 (typical mixture $[BMI][Cl]/AlCl_3/AlEtCl_2$ 1:0.82:0.26), the IL phase mainly contains $[AlCl_4]^-$, $[AlEtCl_3]^-$ and $[Al_2Et_2Cl_5]^-$ anions. For $N > 0.5$ (typical mixture $[BMI][Cl]/AlCl_3/AlEtCl_2$ 1:1.2:0.1), the IL phase mainly contains $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_2EtCl_6]^-$, and $[Al_2Et_2Cl_5]^-$ anions. Used in combination with $NiCl_2.2L$ precursors (L = triisopropylphosphine, tri-*n*-butylphosphine, tribenzylphosphine or tricyclohexylphosphine), catalyst deactivation occurred with ternary mixtures with $N < 0.5$. By using ternary mixtures with $N > 0.5$, catalyst activities were enhanced. However, the high initial selectivity for 2,3-dimethylbutenes (84% after 1h with PCy_3) decreased rapidly with reaction time (10% after 8 h), which was assumed to be a consequence of coordinating competition, for the phosphine, between "soft" nickel active species and "hard" aluminum chloride. The authors demonstrated that aromatic hydrocarbons could be considered as buffers in this mixture, thus stabilizing the “phosphine effect”.

Following these first reports, biphasic olefin oligomerization by Ni complexes using ILs has undergone incredible development. In 1996, de Souza et al. extended the scope of acidic organochloroaluminates ILs to the dimerization of ethylene to *n*-butenes.[159] Neutral (NiF_2, $NiCl_2(PCy_3)_2$) or cationic ($[Ni(MeCN)_6][BF_4]_2$) Ni(II)-precursors were used in combination with $[BMI][Cl]/AlCl_3/AlEtCl_2$ (1:1.2:0.1 molar ratio → N = 0.57). The best selectivity for 1-butene was obtained with $[Ni(MeCN)_6][BF_4]_2$ (83% 1-$C_4^=$) with turnover frequencies of up to 1 731 h^{-1}, but only at very low temperatures (-10°C). Following the observations of Chauvin et al. on the role of aromatics in ILs,[156] the authors also noticed that the use of toluene as a co-solvent appeared essential to the modulation of the ethylene dimerization activity and selectivity. In addition, Chauvin *et al*. showed that butenes could also be oligomerized by nickel complexes immobilized in organochloroaluminate ionic liquids ($[BMI][Cl]/AlCl_3/AlEtCl_2$ (1:1.2:0.1 molar ratio → N = 0.57).[158,160]. Both batch and semi-continuous experiments were conducted using $[Ni(MeCN)_6][BF_4]_2$ as catalyst precursors and phosphines (PPh_3, PBu_3, PCy_3 or $PCy_3.CS_2$) in some cases. Selectivity for octenes appeared very high, from 92% up to 98% depending on the phosphine. The best activities were observed with $[Ni(MeCN)_6][BF_4]_2$ combined with a $PCy_3.CS_2$ adduct. Contrary to what was observed in propene dimers, the structure of the butene dimers (typically 39±1% dimethylhexenes, 56±2%

monomethylheptenes and 6±1% *n*-octenes) does not depend on the phosphine ligands and feedstock, with both 1-butene and 2-butene yielding the same dimers distribution. The unusual promoting effect of the $PCy_3.CS_2$ adduct was later found to be dependent on the nature of the anionic aluminum species present on the IL, making it observable only in acid ILs.[161] By means of ^{31}P NMR measurements, the authors demonstrated that the $PCy_3.CS_2$ adduct reacts with aluminum species of the IL, generating different species depending on the IL acidity. The impact of counteranions in the $[Ni(MeCN)_6][X]_2$ precursor was later described.[162] Results obtained showed that TOF is strongly dependent upon the anions with a reactivity order $[Ni(MeCN)_6][BF_4]_2)$ < $([Ni(MeCN)_6][AlCl_4]_2)\approx$ $([Ni(MeCN)_6][ZnCl_4]$, assumed to be a consequence of the highly reactive behavior of the BF_4 anion towards alkyl aluminum compounds. Systematic investigations of $[BMIC/AlCl_3/AlEtCl_2]$ ratios were later conducted for the dimerization of 1-butene catalyzed by $[Ni(CH_3CN)_6][BF_4]_2$ pre-catalyst.[163] It has been observed that the optimal $[BMIC]/AlCl_3$ ratio is 0.5, while a minimal $AlEtCl_2$ content avoids a drop in catalyst activity and selectivity after the recycle of the catalytic system.

Biphasic Ni-catalyzed butene dimerization using acidic chlorolaluminates as the catalyst solvent was then improved and developed by IFPEN in a continuous pilot plant providing the basis for the industrial Difasol^{TM} process.[158] In this process, the active Ni cationic catalyst is generated *in situ* in the ionic liquid by the reaction of a Ni(II) precursor with an alkylaluminum derivative. The cationic nickel catalyst that is formed *in situ* is immobilized in the acidic chloroaluminate ionic liquid. The products are easily separated as a second layer and the catalyst phase can be recycled to the reactor and reused. Compared with the homogeneous industrial technology (Dimersol® process), the biphasic system (Difasol^{TM} process) provides an increased dimer selectivity and a lower catalyst consumption (by a factor 10 for Ni). The smaller size of the biphasic reactor (by a factor up to 40) and the long lifetime of the catalytic system are additional advantages that lead to the production of octenes at a lower cost (Figure 31).

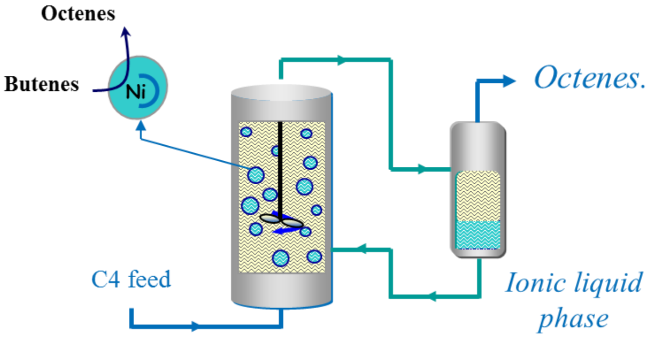
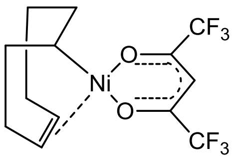


Figure 31. Difasol process

The acidity of organochloraluminate ILs has a huge impact on both the productivity and selectivity of Ni-based oligomerization reactions. As previously mentioned, the selectivity for linear octenes does not exceed 6%.[160] In order to improve the selectivity for linear octenes, Wasserscheid et al. then introduced alkali metal chloride (LiCl) or weak organic bases (pyrrole or pyridine derivatives) to control the acidity of chloroaluminate ILs.[164] The ILs were prepared by mixing 1-butyl-4-methylpyridiniumchloride [4-MBP][Cl] with a slight excess of $AlCl_3$ (typical molar ratio of 0.43:0.53). The well-known Ni-catalyst **65** was dissolved in this binary mixture.[165] Additional alkalimetal chloride or organic bases were added afterwards to adjust the desired melt composition (Figure 32). With these buffered compositions, the authors demonstrated that octenes selectivity can reach 98% with linear octenes higher than 50%. In contrast to the previous systems, no additional alkylaluminum is involved, preventing decomposition of the catalyst **65.** To investigate further, a continuous reactor was designed to demonstrate the general technical applicability of this approach using a loop reactor concept.[166]



65

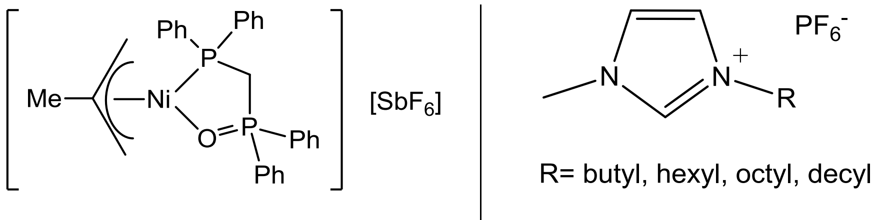
[4-MBP][Cl]/AlCl$_3$ (0.33/0.66)
buffered with excess LiCl

[4-MBP][Cl]/AlCl$_3$/base
(0.43/0.53/0.04);

Figure 32. Buffered chloroaluminates

This work was extended to propylene dimerization using complex **65 (**Figure 32**).** In buffered chloroaluminate ILs ([RMIM]Cl)/AlCl$_3$ 0.45/0.55 molar ratio with 3.7 wt% of N-methylpyrrole),[167] very high productivity as well as unprecedented selectivity for C$_6$ dimers was reported (97%). Detailed kinetic studies and propene solubility measurements indicated strong mass transport limitation of the overall reaction rate. Interestingly, the solubility of 1-hexene in the IL was up to 22 times lower than the solubility of the propene substrate, preventing consecutive reactions of the hexenes formed with propene to produce C$_9$ alkenes.

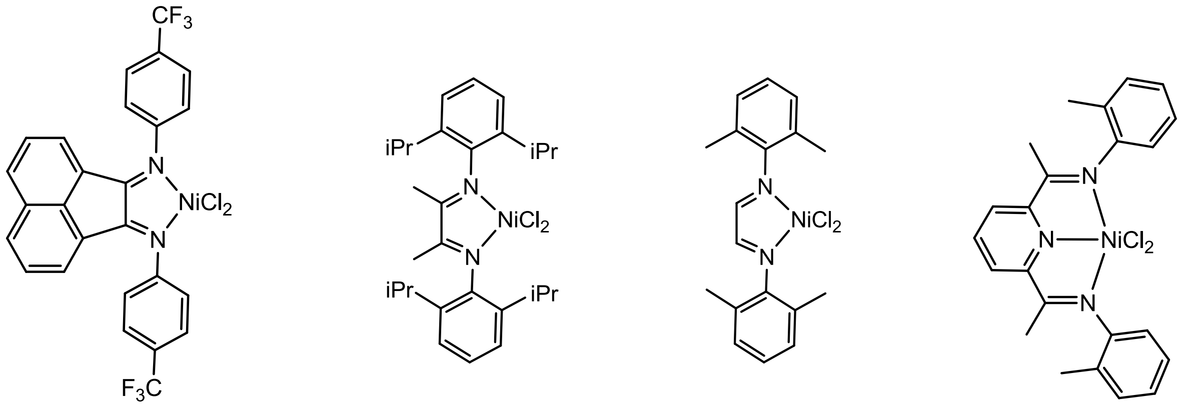
The same group later introduced cationic Ni-catalysts into neutral ionic liquids.[168,169] They reported the use of complex **66** in several [RMI][SbF$_6$] ionic liquids for the biphasic ethylene oligomerization to higher α-olefins (Figure 33). Catalyst **66** was found to be highly active and selective for α-olefins in [BMI][SbF$_6$]. The oligomer distribution appeared to be significantly shorter than in conventional solvents such as CH$_2$Cl$_2$. Interestingly, with increasing alkyl chain length at the ionic liquid cation, the oligomer distribution becomes gradually broader; this was explained as a consequence of both higher ethylene and product solubility in the IL phase. A significant impact on the catalytic activity of the R group on the imidazolium ring was also observed that surprisingly decreases with increasing alkyl chain of the ionic liquid cation (despite better ethylene solubility in this later case). This result was explained by the higher solubility of oligomerization and isomerization products that are described as potential catalyst poisons. The ionic catalyst solution was recyclable with little change in selectivity, although with somewhat lower activity; this was attributed to the practical problem of quantitative transfer back into the autoclave under completely inert conditions (catalyst leaching < 0.1%, detection limit).



66

Figure 33. Weakly-coordinating ILs for the biphasic ethylene oligomerization using cationic Ni-complexes

The use of neutral ILs for ethylene oligomerization was also reported with α-diimine or bis-iminopyridine Ni(II) precursors (**67**-**70**, Figure 34).[170] Complex **67** was first evaluated in neutral ILs presenting different anions (PF_6^-, BF_4^-, SbF_6^-, NTf_2^-, OTf^-) and cations (imidazolium or pyrrolidinium). Upon activation with MAO, low productivity was observed with most ILs employed. The formation of black particles suggested that nickel was reduced to colloidal Ni(0). Adding small amounts of organic bases (THF, 20 eq/Ni) prevents the formation of black Ni(0) particles while increasing catalyst productivity and selectivity for butenes (95%). The authors also reported that MAO reacts with [BMIM][PF_6] to produce a white precipitate that prevents its use with most alkylaluminum activators. In [BMIM][NTf_2], stoichiometric catalyst deactivation occurred, demonstrating the poisoning effect of the NTf_2 anion on the Ni catalyst. Screening of the Ni(II) precursors demonstrated that active and stable catalysts can be generated. The best results were obtained with complex **70** (Prod.: 2 600 g/gNi/h; Sel. C_4: 93%; Sel. 1-C_4: 47%). Active nickel catalysts were also generated from Ni(0) and $HB[3,5\text{-}(CF_3)_2C_6H_3]_4.OEt_2$ ($HBAr_F$) in ILs such as [BMI][NTf_2] or [BMI][SbF_6] without the addition of alkylaluminum activators. Adding α-diimine ligands completely changed the product distribution from high C_4 selectivity to polyethylene formation following the steric hindrance of the ligand. Good results were also obtained using chloroaluminate ionic liquids.



67 **68** **69** **70**

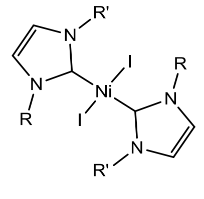
Figure 34. α-diimine and bis-iminopyridine Ni(II) precursors

Specially designed ligands for applications in chloroaluminate ILs were also developed (**Figure 35**). In 2002, N-heterocyclic carbene (NHC) derived from 1,3-dialkylimidazolium salts were described.[69] Several NHC-Ni(II) precursors (**71-74** in Figure 35) were evaluated for propene and 1-butene dimerization. While the complexes are quite inactive in toluene after activation with alkylaluminum co-catalyst (MAO, $AlEt_2Cl$), highly active catalysts are produced in buffered ILs composed of a mixture of 1-butyl-3-methylimidazolium chloride, $AlCl_3$, and N-methylpyrrole (0.45:0.55:0.1 molar ratio). The results were interpreted in terms of catalyst stabilization by the imidazolium-based IL that prevents catalyst decomposition through reductive elimination of an imidazolium salt.

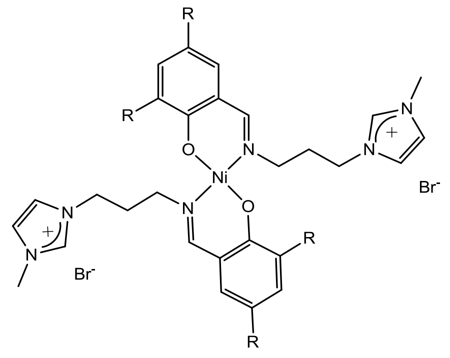
Bis-(salicylaldimine)Ni(II) complexes were also evaluated for ethylene oligomerization in organochloraluminate ILs ([BMI][Cl]/$AlCl_3$, 1/1 ratio with variable amounts of $AlEt_2Cl$).[171] Imidazolium tags were attached to the bis-(salicylaldimine) scaffold for better solubility of the nickel complex in ILs (complexes **75-76**, Figure 35). While these complexes appeared inactive in common organic solvents (toluene or heptane), they exhibited very high productivity in IL/toluene or IL/heptane biphasic mixtures with marked selectivity for C_4-C_8 oligomers. The ionic liquid phase containing the catalyst can be recycled and reused at least three times without much change in the activity and the composition of the products.

Réau and de Souza later evaluated Ni(II) precursors bearing 1,2-diiminophosphorane ligands (**77**) immobilized in 1-butyl-3-methylimidazolium organochloroaluminate ([BMI][Cl]/$AlCl_3$/ $AlEt_2Cl$: N=0.57) for ethylene oligomerization.[172] Upon repeated catalytic runs in ionic liquids, the authors observed an increase in the reaction rate with a dramatic change of oligomer distribution. It was proposed that anionic species present in the IL (almost $AlCl_{4-x}Et_x$) progressively displace the diiminophosphorane ligands, leading to new active catalytic species. This hypothesis was recently considered by Hieringer et al. who conducted DFT study on possible active species in nickel(II)/PPh_3-catalyzed 1-butene dimerization in $[BMIM]^+[AlCl_4]^-$ ionic liquid solution.[173] The calculated relative energies of various possible active catalyst complexes suggest that anion coordination to the nickel center may be thermodynamically favorable.

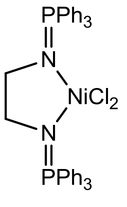
Very recently, Bernardo-Gusmão et al. described the potential of β-diimine nickel complexes **78-80** **(**Figure 35) as oligomerization catalysts in chloroaluminate ILs ([BMI][Cl]/$AlCl_3$, 0.45/0.55 mol fraction)[174] Once activated with ethylaluminum sesquichloride (EASC) as a co-catalyst (Al/Ni $\approx$ 200), these complexes exhibited moderate activity for propylene dimerization, however with high selectivity for C_6 dimers (98.3% with complex **80**). Interestingly, the use of ionic liquids leads to a decrease in isomerization reactions of the products compared with homogeneous conditions.



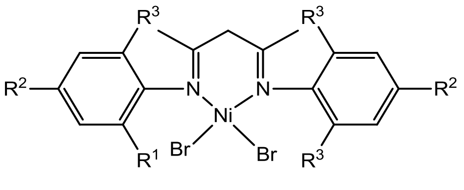
71: R=Me, R'=^{n}Pr
72: R=Me, R'=^{n}Bu
73: R=Me, R'=^{i}Pr
74: R=^{i}Pr, R'=^{i}Pr



75 : R=H
76 : R=$C(CH_3)_3$



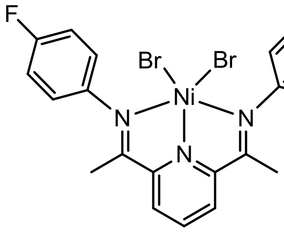
77



78 : $R^1=R^2=R^3=H$
79 : $R^1=R^3=CH_3$; $R^2=H$
80 : $R^1=R^2=R^3=CH_3$

Figure 35. Examples Ni(II)-complexes applied in chloroaluminate ILs

The most promising development in the field of Ni-based olefins oligomerization in ILs certainly resides in the use of buffered acidic ILs. Since the first statements by Wasserscheid et al.,[164] several groups have attempted to optimize this approach. Following the concept of Lewis base buffered systems, Dotterl and Alt found that triarylamine, triarylphosphine, and triarylbismuth compounds efficiently buffer ionic liquids derived from $AlCl_3$.[175] The bis(imino)pyridine-Ni(II) complex **81** dissolved readily in the buffered ionic liquid [BMI][Cl]/$AlCl_3$/Ph_3Bi (1/1.2/0.3), yielding ionic liquid catalysts that dimerize propene with high productivities and selectivities (up to 96%). An optimized system consisting of [N-methylpyrrolidinium][Al_2Cl_7]/Ph_3Bi (1/0.15-0.3) also dimerized ethylene, propylene, 1-butene and 1-hexene with high selectivities. The authors demonstrated that amines and buffers used for these compositions can be recycled using acid-base extraction of the spent ionic liquid catalyst systems. Through ^{27}Al NMR studies, the authors later demonstrated donor–acceptor interactions of aluminum chloride and triphenylbismuth or N-methylpyrrole.[176] A sharp ^{27}Al NMR signal was assigned to weak donor–acceptor interaction and thus a high Lewis acidity. Both activities and selectivities of homogeneous $(PCy_3)_2NiCl_2$-catalyzed propylene dimerization reactions with buffered $AlCl_3$ co-catalysts (Al/Ni=850, seem to correlate with this analysis.



81

Figure 36. Catalyst precursor used for propylene dimerization in triphenylbismuth buffered Lewis acidic chloroaluminate ionic liquids

The oligomerization of 1-butene in N-methylpyrrole-buffered ionic liquid ([BMI][Cl]/$AlCl_3$/NMP) was later studied in more details.[177,178] Systematic investigations of IL/NMP/$Ni(PMe_3)_2Cl_2$ ratios demonstrated that NMP and IL concentrations are critical parameters. The molar ratio of the IL to N-methylpyrrole needs to be balanced at 1:10, since a high buffer concentration leads to catalyst blockage, whereas a low buffer concentration promotes the formation of higher oligomers. The highest yield of dimer (91%) was obtained at an n(IL)/n(buffer)/n(cat.) ratio of 50:5:1. Additionally, the structure of the pyrrole derivatives also has an impact on reactivity. Pyrroles with low steric hindrance improve dimer selectivity. The impact of other Lewis acids ($GaCl_3$, $InCl_3$, $FeCl_3$, $SnCl_2$ → 1.2 eq. / [BMI][Cl]) was also investigated. Active systems were only observed when $AlCl_3$ was used as a Lewis acid. The recyclability of such systems has been recently optimized.[178]

4.2 Supported Ionic liquids

In analogy to the well-established Supported Aqueous-Phase Catalysis (SAPC), immobilization of the ionic liquids on solid supports has recently emerged as a promising alternative to the more classical liquid-liquid biphasic catalysis.[179,180] In this strategy, called Supported Ionic Liquid Phase (SILP), the catalyst is immobilized in an ionic liquid film coated on the porous solid (e.g., silica). With the SILP approach, smaller amounts of sometimes expensive ILs are required. Furthermore, the catalysts behave as homogeneous catalysts, while implementation of the process in fixed or fluidized bed reactor becomes feasible. Initially developed for olefin hydroformylation and hydrogenation, SILP was only recently described for Ni-based olefin oligomerization reactions.

In line with their previous work on triphenylbismuth-buffered Lewis acidic chloroaluminate ionic liquids,[175,176] Alt and Dötterl tried to coat this material onto silica to yield a SILP system.[181] Mixtures of [BMIM][Cl]/$AlCl_3$/$BiPh_3$ (typical ratio 1/1.5/0.6) were first dissolved in CH_2Cl_2 prior to impregnation onto a silica support. The best results for propylene dimerization using complex **81** as Ni-precursor were obtained using dehydrated silica modified with $AlEtCl_2$. In that case, the selectivity for hexenes was initially 94.2%. It gradually decreased to 80.4% after 7 recycles. The nature of the Ni-precatalyst **81** did not affect the C_6 isomers distribution that correlates to the typical product distribution obtained from ligand free nickel salts. Productivity was reported to be very low due to the absence of mixing during catalysis in order to prevent silica structure alteration, highlighting the preferred applicability of this approach for gas phase application.

Recently, Wasserscheid et al. reported the continuous gas phase dimerization and isomerization of ethylene to 2-butenes using SILP-type cationic nickel catalysts[182]. The SILP system was prepared by dissolving the relevant amount of IL and Ni-precursor in CH_2Cl_2 prior to adding the calcined silica. The slurry medium was subsequently evaporated, yielding a free flowing powder. In this work, cationic nickel complexes **82**-**84** already described to be active and selective for ethylene dimerization were chosen. Because of its low coordination strength toward the nickel center, [EMIM][FAP] was chosen for dissolving these complexes. Under mild reaction conditions (0.1 MPa, 40°C) a SILP system prepared with catalyst **82** initially achieved full conversion of ethylene during the first 10 h with 94% selectivity for butenes presenting 95% selectivity for 2-butenes. Afterwards, rapid deactivation occurred that was ascribed to the formation of a hot spot that migrates from the top to the bottom of the catalyst bed. Optimization of IL and Ni loadings as well as reaction temperature (40°C→15°C) yielded an improved catalyst lifetime (up to 130 h), however with lower selectivity for the desired butenes. Best results in terms of both catalyst life time and selectivity for butenes were obtained by using a more sterically demanding ligand in complex **84** that prevents simultaneous coordination of ethylene and butenes, leading to longer-chain olefins.

82: R=Me
83: R=$C_{10}H_{21}$
84: R= 2,6-diMe(C_6H_3)

Figure 37. Composition of the SILP catalyst system used for ethylene dimerization

In order to improve heat removal from the SILP catalyst, this work was later extended to fluidized bed reactor technology.[183] The better heat removal in the fluidized bed improved catalyst stability and allowed for a more detailed investigation of the deactivation mechanism. Based on kinetic studies, a second order deactivation mechanism was proposed, in which two nickel complexes dimerized if the supply of ethylene was insufficient.

In 2012, Wasserscheid et al. described functional nickel complexes of N-heterocyclic carbene ligands in pre-organized and supported thin film materials.[184] The initial idea was to influence the selectivity of dimerization processes by manipulating the nickel catalyst in a highly ordered solvent environment. To realize the concept, the authors used pre-organized Ionic Liquid Crystals (ILCs), based on $[C_{12}C_{12}Im][BF_4]$ in combination with Ni-catalyst complexes presenting NHC ligands with C_{12} alkyl chains (Figure 38). Extended characterization of the mixture revealed that this system retains an ionic liquid crystalline phase, even after immobilization onto a silica support. The application of this material to olefin oligomerization was announced but as yet has not been reported.

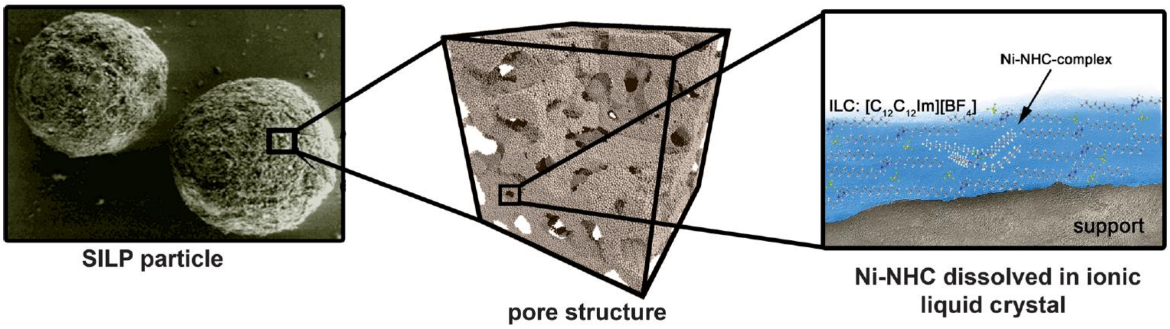


Figure 38. Schematic representation of a SILP material composed of ionic liquid crystal $[C_{12}C_{12}IM][BF_4]$ with a Ni–NHC complex dissolved therein (reproduced with permission from ref 184. Copyright 2012 The Royal Society of Chemistry).

4.3 Metal Organic Frameworks (MOF)

Metal–organic frameworks are a relatively new class of porous materials consisting of crystalline arrays of metal cations connected in three dimensions by multitopic organic linkers. Due to their well-defined solid-state structures, MOFs have recently emerged as promising heterogeneous supports for incorporating transition metal catalysts.[185–187] Since 2010, Ni-based MOFs for olefin oligomerization have been noted, with most reports focusing on the selective dimerization of ethylene to 1-butene. In the following examples, we have focused on the different strategies used for incorporating nickel into MOFs and discuss the performances obtained for olefins oligomerization with a link, when possible, with the MOF's characteristics. Cross-comparison of performances with MOF systems described in the literature remains difficult because operating conditions (pressure, temperature, conversion…) and implementation (gas phase, liquid phase, batch or flow reactor) are not identical.

Miyake et al. have first described the use of MOFs containing a Ni-bipyridyl complex.[188] MOFs were prepared using 2,2'-bipyridine-5,5'-dicarboxylic acid (bpydc) as a linker with aluminum or nickel nitrate as nodes. The MOF compounds, [Al]-Ni-bpydc and [Ni]-Ni-bpydc (the metal in square parentheses indicates the corner cation of the MOF) present micropores with diameter less than 1 nm and BET surface areas that do not exceed 350 $m^2.g^{-1}$. Poor crystallinity of [Al]-Ni-bpydc (contains amorphous materials) compared with [Ni]-Ni-bpydc was reported. Both structures were evaluated as catalysts for ethylene oligomerization in the liquid phase, expecting shape selectivity based on the microporous structure. Once activated with $AlEt_2Cl$ (Al/Ni = 70), these materials appeared to be active for ethylene oligomerization (15 bar and 5°C), with better conversion for [Al]-Ni-bpydc (99.2%) than for [Ni]-Ni-bpydc (13.4%), in line with the larger surface area of [Al]-Ni-bpydc (350 $m^2.g^{-1}$). Selectivity for butenes exceeded 90% in both cases. In contrast, selectivity for 1-butene in the C_4 cut appeared higher for [Ni]-Ni-bpydc (≈ 71%) than [Al]-Ni-bpydc (≈ 26%), possibly related to the pore size of the material.

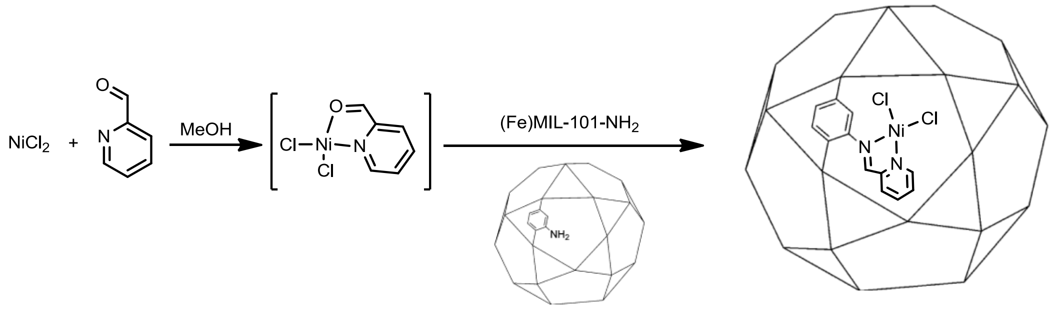
For the same application, Canivet et al. reported the first one-pot post-synthetic grafting of a nickel-based organometallic catalyst within a MOF framework whose activity and selectivity was demonstrated for selective ethylene dimerization to 1-butene.[189] Starting from the (Fe)MIL-101-NH_2 platform, an imine condensation occurs in the presence of a $[Ni(PyCHO)Cl_2]$ precursor to directly form the diimino nickel complex anchored into the MOF (Scheme 1). This strategy avoids the competitive N-coordination of the pyridyl moieties to the coordinatively unsaturated metal sites of the (Fe)MIL-101-NH_2. The amino site density of the (Fe)MIL-101-NH_2 platform, evaluated at four per square nanometer, allowed MOFs presenting complex loading of approximately 10 and 33 nickel complexes per MOF cage for 10Ni@(Fe)MIL-101 and 30Ni@(Fe)MIL-101, respectively, to be synthesized. As expected, the BET surface decreased a lot following the postmodification of the native platform and the metal loading (from 1 884 $m^2.g^{-1}$ for (Fe)MIL-101-NH_2 to 1 110 $m^2.g^{-1}$ for 10Ni@(Fe)MIL-101 and only 155 $m^2.g^{-1}$ for 30Ni@(Fe)MIL-101). Once activated with $AlEt_2Cl$ (Al/Ni = 70) at 10°C and 15 bar, turn over frequencies of up to 3 215 h^{-1} were obtained. More interestingly, selectivity for butenes exceeded 94% in both cases with almost exclusively 1-butene (> 95%, exact value not reported). These results compared well with the corresponding homogeneous Ni-based catalysts. With a similar post-synthetic approach, the scope of this strategy was later extended to a series of mixed-linker MOFs (Scheme 2).[190] These mixed MOFs platforms ($Zn_4O(ABDC)_x(BDC)_{3-x}$) were synthetized by using a similar procedure than for known IRMOF-3 (x=3) with partial substitution of 2-aminobenzene-1,4-dicarboxylate (H_2ABDC) linkers by 1,4-benzenedicarboxylate (H_2BDC). Interestingly, PXRD patterns demonstrated that structural integrity of the MixMOFs-Ni are maintained following post-modification with a Ni-complex, while the crystallinity of the IRMOF-Ni had been severely damaged. As expected, the post-modification was accompanied by a reasonable decrease in the BET surface area. Once activated with $AlEt_2Cl$ (Al/Ni ≈ 100), MixMOFs-Ni exhibited higher activity and selectivity for butenes than damaged IRMOF-Ni material.

Later, postsynthetic treatment of Zn-based MOF was also described for the same reaction.[191] In this work, an α-diimine ligand with dicarboxylic acid (**L1**, Scheme 3) was connected by Zn(II) ion nodes to construct a MOF framework. The active Ni^{2+} centers were then generated with the addition of $[NiCl_2(DME)]$ to form $[Zn_3(OH)_2(L1^{Ni})_2]$ (called Zn-MOF). The XRD pattern of the synthesized Zn-MOF did not deviate much from the simulated pattern obtained from the single-crystal structure. Interestingly, ICP measurements demonstrated the high Ni content of the material (11.39wt%). Careful optimization of ethylene oligomerization conditions demonstrated the huge impact of $Al_{(AlEt2Cl)}$/Ni ratio and temperature on both productivity and oligomers distribution. As a general trend, Zn-MOF can reach a higher selectivity for dimerization (up to 91.8% at 20°C with Al/Ni = 1500) than analogous homogeneous complexes bearing α-diimine ligands (maximum value of 72.4% at 20°C).

In many cases,the nanoscale pores of the MOFs induce some turn-over limiting factors (slow transport of reactants in and out the MOF crystals). As such, NU-1000, presenting pore channels of 31 Å, was considered as an interesting support for Ni-based ethylene oligomerization catalyst.[192] The NU-

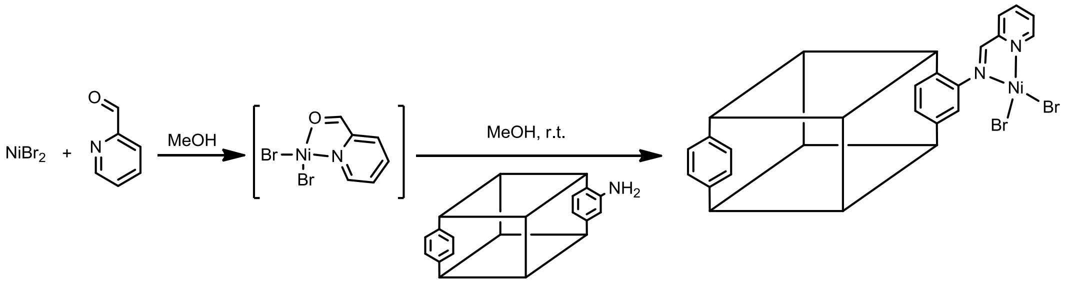
1000-bpy-$NiCl_2$ was first synthesized by postmodification of the native Nu-1000 (composed of $Zr_6(\mu^3\text{-}O)_4(\mu^3\text{-}OH)_4(H_2O)_4(OH)_4$ nodes and tetratopic 1,3,6,8-(p-benzoate)pyrene ($TBAPy^{4-}$) linkers). In this strategy, the free Zr–OH moieties of the NU-1000 are readily modified through reaction with incoming phosphonic acid derived from bipyridine (Scheme 4). Subsequent exposure of the NU-1000-bpy material to a solution of anhydrous $NiCl_2$ in methanol produced NU-1000-bpy-$NiCl_2$ with ~1.5 [Ni]/Zr_6 node and a surface area of 1 450 m^2/g. The mesoporous channels were also reduced to 28.5 Å. Liquid phase and gas phase ethylene dimerization were carried out after activation of the NU-1000-bpy-$NiCl_2$ with $AlEt_2Cl$ (Al/Ni = 70). In heptane, the NU-1000 leads to intrinsic activities approaching those observed for $(PPh_3)_2NiCl_2$ with comparable selectivity for butenes (99 *vs* 95%) but a large increase in 1-butene purity (up to 91/9, 1-$C_4^=$/2-$C_4^=$). The authors also observed the formation of a polymer layer on the surface of the MOF crystals. Most notably, when crushed to increase its external surface area, (bpy)Ni^{II}-functionalized NU-1000 appeared highly active in the gas phase under both batch and flow conditions. The activity gradually decreased over the course of 20 h, presumably due to a combination of catalyst deactivation and site blockage by polymer formation. A large loss of 1-butene purity was also observed for gas phase reactions (57/43, 1-$C_4^=$/2-$C_4^=$).

Scheme 1. One-pot synthesis of the MOF-anchored nickel complex Ni@(Fe)MIL-101

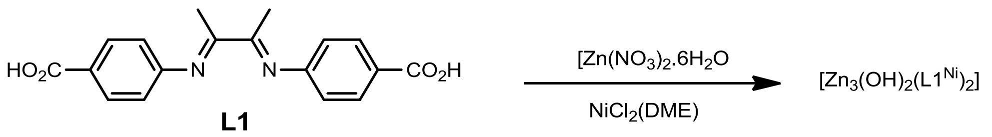


10% functionalization: 10Ni@(Fe)MIL-101
30% functionalization: 30Ni@(Fe)MIL-101

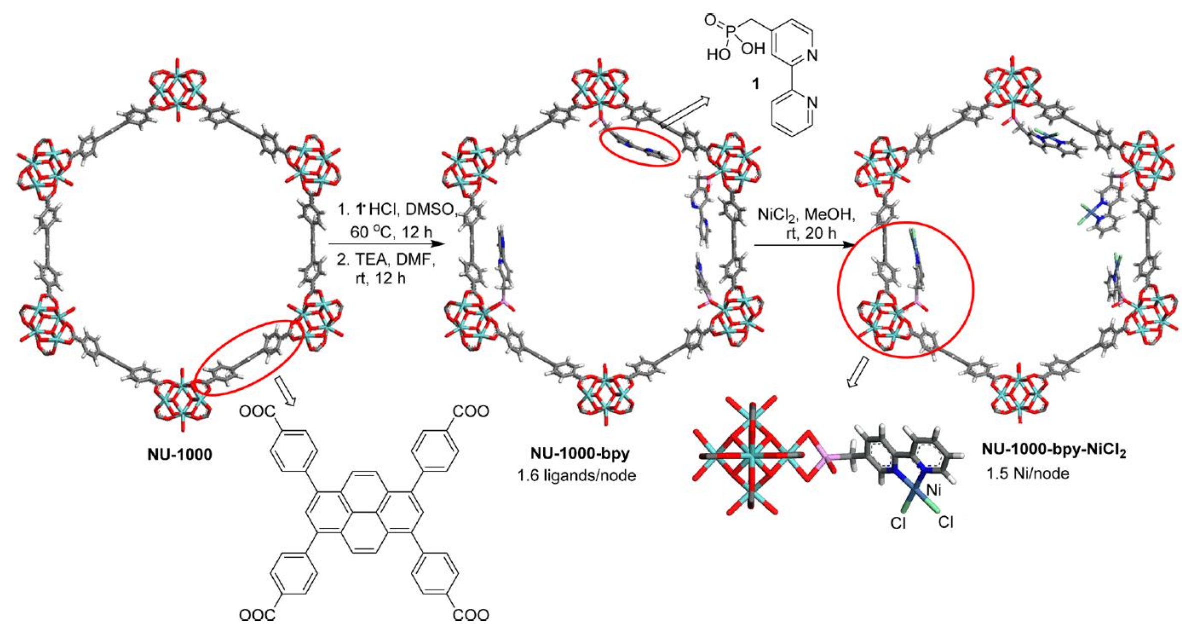
Scheme 2. Strategy for MixMOFs-Ni synthesis



Scheme 3. Strategy for Zn-MOF^{Ni} synthesis



Scheme 4. Preparation of NU-1000-bpy-$NiCl_2$ (reproduced from ref. 192 Copyright 2015 American Chemical Society)



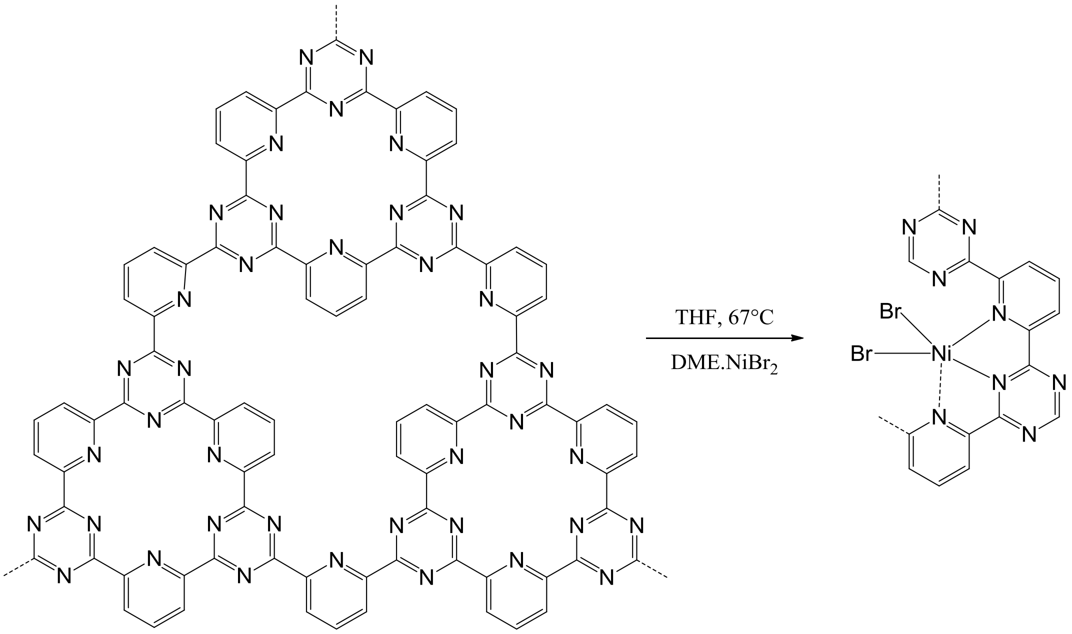
The same group of authors then extended the potential of NU-1000 frameworks by installing Ni ions directly on the node of the Zr-based MOF using atomic layer deposition (ALD).[193] Bis(N,N′-di-tert-butyl-acetamidinato)nickel(II),= was chosen as the Ni precursor due to its high thermal stability and its high volatility at relatively low temperatures. Placed in an ALD chamber, Zr_6 nodes were subjected to pulsing cycles of the nickel precursor before subjecting the MOF to H_2O pulses to ensure full metallation of the Zr_6 sites. Retention of crystallinity in Ni-AIM was confirmed by SEM and PXRD measurements. The measured surface area of the Ni-AIM material was 1 450 $m^2.g^{-1}$ with a pore-size of 27 Å. The Ni content was consistently found to be 4.1 ± 0.4 Ni atoms per Zr_6 node. Firstly evaluated for ethylene hydrogenation, the Ni-AIM material was predicted to be active for ethylene oligomerization through DFT calculations. Upon activation with $AlEt_2Cl$ at 45 °C and 2 bar pressure, TOFs of 0.3 s^{-1} were obtained. Deactivation occurred during the first 10 h on stream, which is attributed to the formation of polymeric products. Selectivity for butenes appeared to be very low (39% to 46%) compared with the previous work using a post modification approach,[192] certainly due to poorer control of the Ni-coordination sphere with ligand adapted for ethylene dimerization. Computational studies were undertaken to provide a better insight into the reactivity of these systems.[194]

In 2016, Dinca et al. introduced nickel into the secondary building units (SBUs) of MFU-4*l* ($Zn_5Cl_4(BTDD)_3$, H_2BTDD = bis(1H-1,2,3-triazolo[4,5-b],[4′,5′-i])dibenzo[1,4]dioxin) for the selective dimerization of ethylene to 1-butene.[195] Through molecular modeling, the authors reasoned that the nickel environment in the Ni-MFU-4*l* could be similar to the parent molecular nickel complexes $Tp^{Mes}NiCl$ (TpMes=HB(3-mesitylpyrazolyl)$_3$), which are known to be active and selective for butene formation. The nickel-doped MFU-4*l* was synthesized by cation exchange of the parent zinc framework. Following this approach, the structural integrity and porosity of the native MFU-4*l* were not affected. As anticipated, once activated with MAO, Ni-MFU-4*l* presented similar productivity to the $Tp^{Mes}NiCl$ analogue employed under homogeneous conditions, however with a selectivity for 1-butene that was notably superior (96.2%) to the analogue (which only reached 80.8%). It should be noted that although the selectivity for butenes is high with Ni-MFU-4*l*, the α-selectivity for the C_4 cut remains far from what is expected for its industrial use as a co-monomer for polyethylene production (> 99.7% required). Contributions from the same group demonstrated that the homogeneous organometallic chemistry toolbox can be applied to rigorously elucidate the catalytic mechanisms in MOFs.[196] By means of isotopic labeling experiments, molecular probes and DFT calculations, they conclusively showed that Ni-MFU-4l selectively dimerized ethylene via the Cossee-Arlman mechanism. This work was later extended to propylene dimerization with reduced productivity and no significant change to the C_6/C_9 distribution compared with the parent homogeneous complex.[197]

While several heterogeneous nickel aluminosilicate materials have been demonstrated to be active catalysts for propene oligomerization, with zeolite materials it remains difficult to obtain both high catalytic activity (that requires as much space as possible in the zeolite supercage) and high selectivity for linear olefins (that requires close steric and electronic control of the site). In order to combine both effects, J Long et al.[198] reported two Ni^{2+}-containing MOFs with high concentrations of coordinatively unsaturated Ni^{2+} sites, which exhibit propylene oligomerization activity comparable to Ni^{2+}-exchanged aluminosilicates while maintaining high selectivity for linear oligomers (dimer branching limited to 37% versus 47% for the evaluated zeolites).

Covalent organic frameworks (more specifically, Porous Aromatic Frameworks, PAFs) consisting of triazine- and imine-linked frameworks have recently been described (Scheme 5).[199] The high concentrations of nitrogen provided by the linker result in large amounts of $NiBr_2$ on the porous framework. This material exhibited lower activity and selectivity than the homogeneous counterpart for ethylene oligomerization (C_4 sel. up to 70% vs 90% for homogeneous catalyst), with demonstrated recyclability, however.

Scheme 5. Examples of synthesis of COFs and expected coordination of Ni^{2+} to the nitrogen species in the frameworks



4.4 Other approaches for supporting organometallic nickel complexes on (polymer, SiO_2, Al_2O_3, zeolites, etc.)

Considering the already large scope of this review, supported organometallic nickel complexes for olefin oligomerization will therefore be presented here through chosen examples without trying to be exhaustive (Table 8). We will not comment on this section, but reference may be made to the cited articles for further details.

Table 8. Selected strategies for supporting Ni-oligomerization catalysts

Date	Authors	Support	Ref.
1981 1985	Kabanov et al. Potapov et al.	Gel-immobilized catalytic system (GICS)	200 201
1984	Peukert et al.	• Supported solid-phase catalyst (SiO_2 or SiO_2-Al_2O_3) • Phosphinated polystyrene (2% divinylbenzene) • Phosphinated Merrifield resin (1% divinylbenzene)	202
1989 1991 1991	Fink et al.	• Supported solid-phase catalyst (SiO_2 or SiO_2-Al_2O_3) • Modified SiO_2 or Al_2O_3 with Ph_2P-CH_2-CH_2-$Si(OEt)_3$. • Modified SiO_2^{TMA} and Ni grafting through ligand functionalization	203 204 205
1989	Pomogailo et al.	Macromolecular metal chelates (MMC) on polyethylene surface	206,207
1995 1996	Braca et al. Sbrana et al.	Ligand modified polystryrene resins	208 209
2004	Angelescu et al.	Ni-complexes supported on molecular sieves (Y, L, mordenite, mesoporous MCM-41) and amorphous SiO_2-Al_2O_3	210
2006	De Souza et al.	Ni complex immobilized on [Al]-MCM-41	211,212

4.5 Conclusion

The heterogenization of molecular Ni-based oligomerization catalysts on supports of various natures (solid, liquid or a combination of both) has attracted enormous attention in academic and industrial circles, becoming a tremendous field of research. Thus, as illustrated in this chapter, many successful examples can be highlighted, offering very attractive and promising perspectives for this approach in selective ethylene, propylene or butenes oligomerization. Furthermore, the industrial applicability of some of the strategies compiled in this review, such as the liquid/liquid biphasic approach, has been largely demonstrated thanks to its successful application in the SHOP process. Since the beginning of the 90’s, ionic liquids have also demonstrated the scope of liquid media for liquid/liquid Ni-implementation. More recently, the use of solid supports has also become an important research area, especially with the development of MOFs. The compositional and structural versatility and diversity of these materials, far beyond conventional solid-state materials, make MOFs a tunable and a very interesting material for these applications. Therefore, although impressive developments have been achieved in this area, the challenges to overcome, such as price and recyclability of solid or liquid supports, should still be addressed for viable industrial applicability.

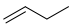
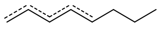
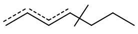
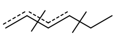
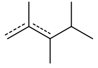
5 Nickel-promoted oxide supports for olefin oligomerization

5.1 Introduction

5.1.1 *Relationships between homogeneous and heterogeneous oligomerization catalysis*

As can be clearly discerned from the previous chapters, homogeneous catalysis has witnessed tremendous advances in the last decades and more active and selective systems for the oligomerization of olefins are constantly being developed. This research activity resulted in the industrial implementation of several catalysts for the selective production of linear and branched higher olefins, finding application for fuels and chemicals. Surprisingly, despite important research efforts and easier handling of heterogeneous catalysts in refineries and petrochemical complexes, only a few olefin oligomerization units in the world operate with heterogeneous systems. None of them concern the transformation of ethylene. Propylene and butenes, for instance, are oligomerized by solid acids through unselective cationic mechanisms[213] to form oligomers with high branching indices, mainly applied to fuels.[214,215,216] But only butenes are selectively transformed by nickel-based heterogeneous catalysts into low branched octenes for application in petrochemistry on an industrial scale, in parallel to homogeneous technologies. The promotion of oxide supports with nickel allows olefins to be oligomerized under milder conditions than raw solid acids, which orientates selectivity in a controlled fashion to more linear products with similar selectivities to their homogeneous counterpart, as exemplified in Table 9 with 1-butene oligomerization.

Table 9. Selectivities of 1-butene oligomerization : comparison of metallic (homogeneous and heterogeneous Ni-based catalysts) and solid acids[217]

			Selectivities among produced octenes			
1-butene feed 	Conversion (%wt)	C_8 selectivity (%wt)	*n*-octenes 	methyl-heptenes 	dimethyl-hexenes 	trimethyl-pentenes 
Ni-HOMOGENEOUS $Ni(acac)_2$ + EADC, 40°C, P_{atm}	70	90	5	60	35	0
Ni-PROMOTED OXIDE $Ni/SiO_2-Al_2O_3$, 70°C, P_{atm}	70	80	5	55	40	0
UNPROMOTED SOLID ACID $SiO_2-Al_2O_3$, 100°C, P_{atm}	75	45	0	5	90	5

In the case of ethylene and propylene oligomerization catalyzed by nickel species, state-of-the-art heterogeneous catalysts do not provide sufficient stabilities, selectivities, yields and atom economy towards the desired products to compete with homogeneous systems. This chapter thus reviews the development of nickel-based heterogeneous catalysts for olefin oligomerization and addresses the challenges to designing active, stable and scalable catalysts in order to broaden the scope to the two shortest olefins, especially towards ethylene oligomerization.

5.1.2 *Strategies towards providing active, selective and scalable nickel-promoted heterogeneous oligomerization catalysts*

The quest for structure/activity relationships for nickel-promoted heterogeneous oligomerization has provided numerous improvements in providing active and selective catalysts. Nevertheless, α-olefin selectivity and chain length control under productive industrial operating conditions currently provided by homogeneous catalytic systems have not yet been achieved by any heterogeneous catalysts for ethylene and propylene. This chapter thus provides some tentative insights towards further optimization in these directions.

Nickel-based solid catalysts for olefin oligomerization have attracted the interest of researchers for decades and have been reviewed on various occasions.[218–222] We are aiming to complete and detail the references and set out older and recent patent and literature results in order to analyze the evolution of the design of the catalysts towards activity, stability and selectivity. As is the case with homogeneous catalysis, temperature and pressure appear to be critical parameters in handling olefin conversion and, consequently, product selectivity. Additionally, classical factors connected to heterogeneous catalysis, such as structural and textural properties, as well as surface density of the metal and the acido-basic strength and density of the carrier, come under consideration for an overall understanding of the catalytic systems. These factors are tackled along with the description of the catalytic systems that have been developed for nickel-promoted olefin oligomerization. The story begins with poorly active silicas impregnated with high loadings of nickel, then more acidic supports were used to improve activities at lower loadings, such as amorphous or crystalline aluminosilicates or aluminas. With such supports, stability issues rapidly arose. Many new catalyst designs as well as process innovations were specifically developed in order to obtain scalability and productivity in accordance with industrial needs.

It should be noted that the preparation and performance of a representative set of catalysts is collected into tables for each section. Because catalyst activities and productivities can be expressed by different means or units depending on the research group, the performance column corresponds to the information extracted from the documents without any attempts to harmonize the expression of the results. Note also that the paragraphs below are limited to catalysts based on supported nickel species that do not require external chemical activation by co-catalysts. For a long time, this major difference with homogeneous systems has fed the debate about active site nature and genesis, nickel speciation and degree of oxidation in active heterogeneous system. Routine and cutting-edge multi-technique characterizations have been employed to sound out the seat of the activity. This exciting question is addressed in Chapter 6 within a general investigation of active sites along with homogeneous systems.

5.2 Silicas - Ni/SiO_2

Surprisingly, the first mention of nickel-supported catalyzed olefin oligomerization was made 15 years before the discovery by Ziegler of the unexpected “nickel effect” to dimerize ethylene into butenes by homogeneous catalysis.[223,224] The discovery is attributed to Morikawa in 1938 with the deposition of nickel onto Kieselguhr, a commercial silicon dioxide (SiO_2).[225] Ethylene was dimerized into butenes at ambient temperature . Ozaki et al. confirmed these results ten years later by applying a thermal treatment to fully dehydrate the catalyst under vacuum prior to reaction with ethylene.[226] The silicic support was selected from local clays and Ni loading was particularly high, around 66 wt%, expressed as nickel oxide content. The performances of all the catalysts based on siliceous supports are collected in Table 10.

As is the case for many other olefin transformations, in the early 1940s, the Phillips Petroleum Company was one of the first companies to file patents concerning the oligomerization of short olefins.[15] Many characteristic parameters of the oligomerization reaction are given in this document, so it is well worth lingering a while over this seminal work. The first catalysts were prepared by the impregnation of nickel nitrate or nickel carbonate onto Kieselguhr with a high Ni loading of around 35 wt% and contacted in a batch reactor containing pentane under ethylene pressure at a temperature around 100°C. A liquid phase process, here in the presence of pentane, is preferred to a gaseous phase in order to allow good heat transfer and avoid the deposition of high molecular weight compounds or non-volatiles on the catalyst surface, contributing to diminishing the catalyst lifetime. Despite temperature enhancement , the olefin conversions remained low with nickel oxide supported on silica. Such catalysts would later serve as benchmark catalysts for improved silica supports promoted with alumina.[227]

Examination of a series of silica gel catalyst supports by Eidus et al.[228] revealed traces of Al_2O_3 were responsible for the improved activity compared with benchmark pure silicas. The deliberate synthesis of aluminated silicas prepared by soaking $Al(NO_3)_3$ with silica gel confirmed this assumption and were active for ethylene oligomerization at 300°C and at atmospheric pressure.[229]

Precipitation-deposition of $Ni(OH)_2$ with silica and impregnation of $Ni(NO_3)_2$ onto the same silica were compared by Wendt et al.[230] The preparation method for the catalyst was shown to be of prime importance. The presence of nickel-layer-silicate present only in the precipitated catalyst is believed to be the reason for the superior activity. Inactive nickel oxide clusters are the only forms of nickel detected after impregnation of $Ni(NO_3)_2$.[231] Nickel-hydrosilicates, montmorillonite and antigorite can also be formed in the catalysts.[232] A direct activity comparison between these active 20%wtNi/SiO_2 and 15%wtNi/SiO_2-Al_2O_3 catalysts again highlights the superior activity of aluminosilicate versus silica.[233] Impregnation of an acidic precursor of nickel such as $NiSO_4$ can improve activity, but the corresponding $NiSO_4/SiO_2$-Al_2O_3 exhibited remarkably higher catalytic activity than $NiSO_4/SiO_2$ not promoted with alumina. A minimum calcining temperature of 500°C was critical to the activity in ethylene oligomerization.[234] The effect of the calcining temperatures indicates that the thermal stability of Al_2O_3-promoted catalysts was improved compared with the non-promoted catalyst $NiSO_4/SiO_2$ and allowed higher temperature treatments for activation. Correlations between acidity and activity were proposed.

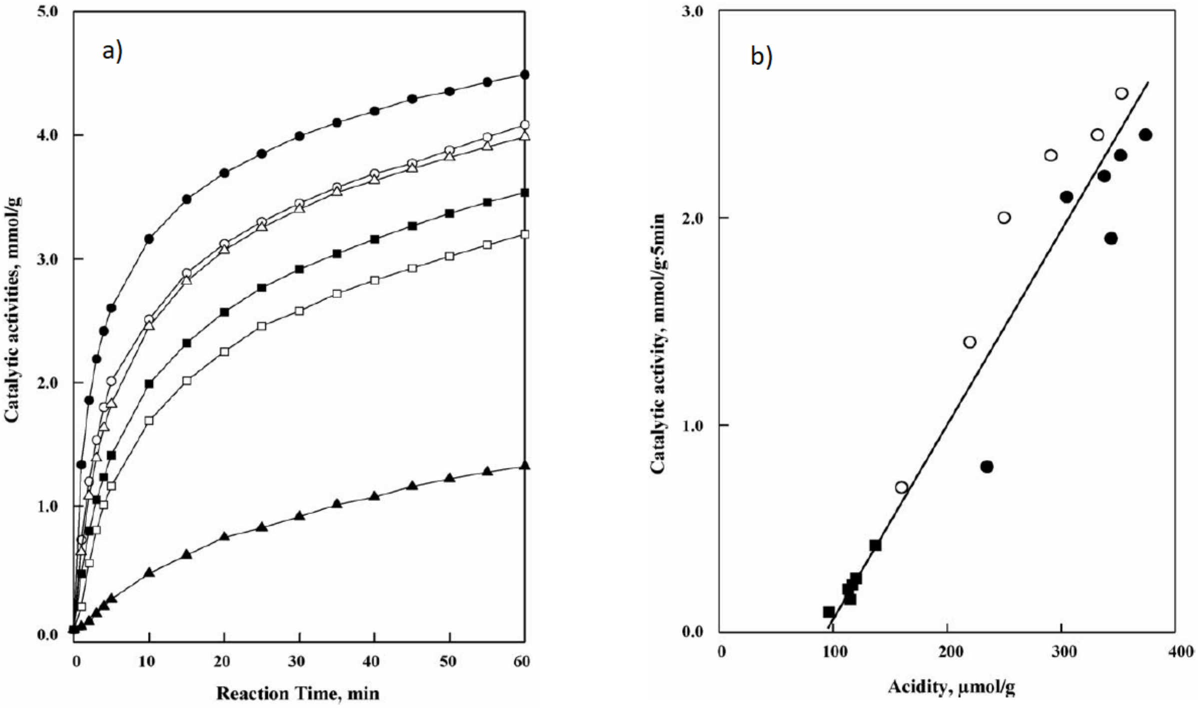


Figure 39. a) Catalytic activities of (■) 15-$NiSO_4$/82-SiO_2-Al_2O_3; (●) 15-$NiSO_4$/66-SiO_2-Al_2O_3; (▲) 20-$NiSO_4/SiO_2$ against reaction time and b) Correlationship between catalytic activity for ethylene

dimerization and acidity (■) $NiSO_4/SiO_2$; (●) 15-$NiSO_4$/66-SiO_2-Al_2O_3; (○) 20-$NiSO_4/SiO_2$ (reproduced with permission from ref. 234 Copyright 2006 Elsevier)

Because of their low activities and the need for high nickel loadings, purely siliceous materials have thus been studied very little after these fundamental results. A renewed interest for mesoporous and mesostructured solids arose in the early 1990s thanks to advances in novel material synthesis by Kuroda *et al*.[235,236] Among the most popular structures, MCM-41 and MCM-48 (MCM = Mobil Composition of Matter) belong to the M41S family and were synthesized for the first time in 1992 by Mobil researchers.[237,238] Many other families have been discovered since then by using different types of surfactants as the structure-directing agent and various syntheses such as SBA-15.[239] These solids were rapidly taken advantage of by Hartmann *et al* as a carrier for nickel oxide with application in ethylene oligomerization.[240]

More recently, at even higher temperatures above 300°C, Iwamoto et al. showed that Ni ion loaded-MCM-41 prepared by template ion exchange can efficiently convert ethylene to propylene via selective dimerization to 1-butene, isomerization of 1-butene to 2-butenes and cross-metathesis between 2-butenes and ethylene to provide propylene,[241–245] the latter metathesis step being very unusual for a Ni-based heterogeneous catalyst. Nickel phyllosilicates, a species described in great detail by Burattin et al.[246], which are formed at the surface of the catalysts, are proposed as active sites for ethylene dimerization and alkene metathesis. Other mesoporous mesostructured silica were described by Hinrichsen et al for catalyzing the same reaction under similar conditions.[247,248] and Lehmann et al.[249–251] The precise nature of the active sites has been under debate.[252,253] The metathetic activity of these catalysts has recently been robustly contested by control experiments with propylene.[254]

Once again, all of these studies show that the incorporation of aluminum into the walls of the mesostructured materials to obtain AlMCM-41, AlMCM-48 or AlSBA-15, for instance, increases the catalytic activity for ethylene oligomerization. Enhancing the acidity is suggested to be directly connected to higher conversion of olefin and a higher isomerization rate, while inducing the formation of higher molecular weight products and coke, potentially causing catalyst deactivation. The characteristics of these particular mesoporous members belonging to the whole aluminosilicate group are described further in the aluminosilicate section.

Table 10. Silica-supported nickel catalyst for ethylene oligomerization

Ni precursor	Silica nature	Deposition technique	Ni loading (%wt)	Activation	T (°C)	P (bar)	Product (%)	Performance	Ref
not disclosed	Mizusawa clay	not disclosed	52	650°C Vacuum	-	-	-	-	[225]
$Ni(NO_3)_2$ + Na_2CO_3	Kieselguhr	Precipitation of $NiCO_3$	35	600°C, 2%O_2 in N_2	105-110[a]	42	C_4 : 35 C_6 : 36 C_8 : 27 C_{10}-C_{12} : 27	-	[226]
$Ni(NO_3)_2$ + Na_2CO_3	Kieselguhr	Precipitation of $NiCO_3$	80	590°C Air	50-60	14	“polymers”	0.26 ml oligomers/g_{cata}/h	15
$Ni(NO_3)_2$	Kieselguhr	Excess impregnation	0.4	590°C Air	24	14	“polymers”	0.57 ml oligomers/g_{cata}/h	15
$Ni(NO_3)_2$	Kieselguhr	Excess impregnation	3.1	500°C Air	100	14	“polymers”	-	15
$Ni(OH)_2$ or $Ni(NO_3)_2$	Kieselguhr	Precipitation	70	500°C Argon	150-200	1	C_4 : 70-90	3 mol/m²/h	[230]

[a] *Ethylene is dissolved in pentane*

5.3 Aluminosilicates NiO/SiO_2-Al_2O_3

Aluminosilicates represent a major group within heterogeneous catalysis as catalysts themselves or as supports for mono- or polymetallic phases.[255] Depending on their cristallinity, dimensional structuration, topologies, pore size which can widely vary with preparation techniques, different families of aluminosilicates possessing variable properties like acidities can be obtained. It is generally believed that their acidities are responsible for the activity in ethylene oligomerization.[256] To draw tendencies about their behavior in olefin oligomerization, we have identified three main groups : amorphous aluminosilicates, zeolites and aluminum containing mesoporous/mesostructured silica. Their performances for olefin oligomerization are gathered in Table 11.

5.3.1 *Amorphous aluminosilicates*

Amorphous aluminosilicates were rapidly identified as the most active catalysts for olefin oligomerization. Different preparation modes afford variable structures, acidities and stabilities of supports and catalysts. Natural aluminosilicates also exist as clays, such as montmorillonite, and have been tested for olefin oligomerization after promotion with nickel.

Shortly after describing siliceous supports, in 1952, Phillips patented the promotion of the siliceous carrier by impregnating aluminum nitrate concomitantly with nickel nitrate. This promotion tripled the catalyst activity for ethylene oligomerization compared with the benchmark silicic carrier.[227] The aluminum content does not exceed 10 wt% and the Ni loading is maintained below 5 wt%. As a result, the activity of aluminum-promoted catalysts results in a drastic reduction of nickel loading compared with previous NiO/SiO_2 catalysts that contained 35 wt% Ni. This patent thus paved the way for a plethora of academic and industrial research centered around aluminosilicates – they were by far the most studied category among envisaged supports. More details have been published by the same authors about the solid and catalysis implementation.[257] As was the case with NiO/SiO_2, high temperature (500°C) treatment under air activates the catalysts before test. Catalyst regeneration is possible at 400°C under an air-nitrogen mixture, but initial activity drops after a few cycles, unless rejuvenated with nitric acid. At 40°C, ethylene conversion is almost quantitative, but deactivation is rapid. Butene selectivity is around 50%, with a high isomerization rate to 2-butenes. At 65°C, the deactivation can be strongly limited by four-fold dilution of the stream in liquid butane at 35 bar. Separation and recycling of butane automatically entails a recycle of the butenes formed, which react further. Only C_5^+ olefins are therefore produced. These results lay the foundation for subsequent research on aluminosilicates to find a compromise between acidity, activity, deactivation and stabilizing operating conditions in order to reach desired selectivities.

On-purpose preparation of aluminosilicates by the alumination of silica has been claimed by British Petroleum for propylene and butene oligomerization.[258] After the identification of the promoting effect of aluminum in silicas for ethylene oligomerization, Eidus et al. led in-depth investigations of NiO-aluminosilicate solids at high temperatures such as 275-300°C.[259] At such temperatures, skeletal isomerization and demethylation occur.[260] Contact time was thus reduced to a few seconds to reduce these phenomena.[261] A small grain size had positive effects, increasing the activity with between 1 and 10% nickel nitrate concentration in the impregnation solution.[262]

Adding minor amounts of different alkaline or metallic oxides to NiO-aluminosilicates had various influences on ethylene oligomerization activity, product selectivity and catalyst regenerability, without highlighting clear tendencies.[263] Doping with K_2CO_3 inhibits activity, while NH_4OH addition keeps the catalysts active but more unstable.[264]

Amorphous aluminosilicates promoted with heteroatoms were also described by Phillips.[265] Initial catalysts contained 2.7 wt% Ni and 13 wt% Al and were activated in air at 540°C. The use of solid Lewis acids was mentioned once by Sakaguchi et al.[266] when boron phosphate (BPO_4) was investigated to promote Ni/SiO_2-Al_2O_3 ethylene oligomerization. The combined use of Ni/SiO_2-Al_2O_3 and BPO_4 is more effective in promoting oligomerization and increased the C_6 fraction compared with a major C_4 fraction.

For ethylene oligomerization, Shell also described commercial amorphous aluminosilicates containing aluminum and nickel in similar compositions to the Phillips patents, that is to say between 10 and 30 wt% Al and between 1 and 10 wt% Ni on a metal base. Promotion by 0.3 wt% sulfur, by means of dimethyldisulfide (DMDS), slightly lowers the activity but shifts the selectivity towards 1-hexene, linear octenes and a minority of longer, even numbered olefins. Simultaneously raising the nickel loading from 3.6 to 10 wt% and sulfur from 0.3 to 2% has the same effect.[267] This is a rare example of the production of linear terminal olefins by heterogeneous catalysis with a SHOP-like distribution of olefins.

Wendt et al. prepared their nickel-based amorphous aluminosilicates by simultaneous precipitation-deposition of $Ni(OH)_2$ and $Al(OH)_3$ on a silica gel. Their catalysts are composed of 5 mol % Ni, 5 mol% Al and 90 mol% SiO_2 and are activated under nitrogen at 450°C. Ethylene is oligomerized in a fixed-bed reactor at 230°C and the catalysts encounter stability issues under these conditions.[268] NiO/Al_2O_3-SiO_2 with various Al contents can also be obtained with similar performances by precipitation of nickel hydroxide obtained from an aqueous solution of nickel nitrate and ammonia onto a pre-synthesized aluminosilicate prepared by the hydrolysis of mixtures of $Si(OC_2H_5)_4$ (TetraEthylOrthoSilicate-TEOS), and Al(O*i*Pr)$_3$ in ammonia solution.[269] As was the case for a purely siliceous support, activity is induced by a layered silicate, here a nickel alumino layered silicate. Such NiO/SiO_2-Al_2O_3 catalysts proved to be active for the oligomerization of monoolefins[270,271] in general and especially for the selective dimerization of propene[272,273] and butenes[274] or mixtures thereof.[275] Concerning propylene, partial conversion of 30 wt% at 180°C under 25 bar on a 5 mol % NiO/SiO_2-Al_2O_3 (5 mol % Al_2O_3 on SiO_2) allows almost full selectivity to hexenes. In a similar way for oligomerization of butenes, selectivity for dimers of 95 wt% can be obtained at a partial butene conversion of 30 wt% at 100°C, even after catalyst regeneration under a nitrogen flow. Linear octenes and methylheptenes account for 60 wt% of the dimers. Both selectivities for propylene and butene dimerization are characteristics of a metallic mechanism. If the acidity of the catalyst is well-controlled, a minor contribution of acidic cationic mechanism towards either longer olefins or highly branched products like dimethylhexenes or even trimethylpentenes is observed.[276]

The effect of the composition of NiO/SiO_2-Al_2O_3 in terms of nickel and aluminum content was also investigated early on by Lapidus *et al.*[277] for ethylene and isobutene oligomerization before attempting precise correlations between the acidity and activity of the catalysts.[278] As terminal olefins can be isomerized on acidic sites,[279] the quest for alpha selectivity in the even numbered olefins appears to be difficult, although very attractive for the application of α-olefins in petrochemistry. Matsuda et al. relate the interest of a heterogeneous process for producing 1-butene and substitute the current titanium-based homogeneous catalytic system.[280] With acidic NiO-aluminosilicate, the rate of the isomerization of 1-butene was higher than that of ethylene dimerization, rendering access to 1-butene by this method extremely difficult.

Nicolaides et al.[281] tried to control the selectivity for 1-alkene products by modifying the time-on-stream, adding excess nickel, promoting with potassium and varying the Si/Al ratio (Figure 40).

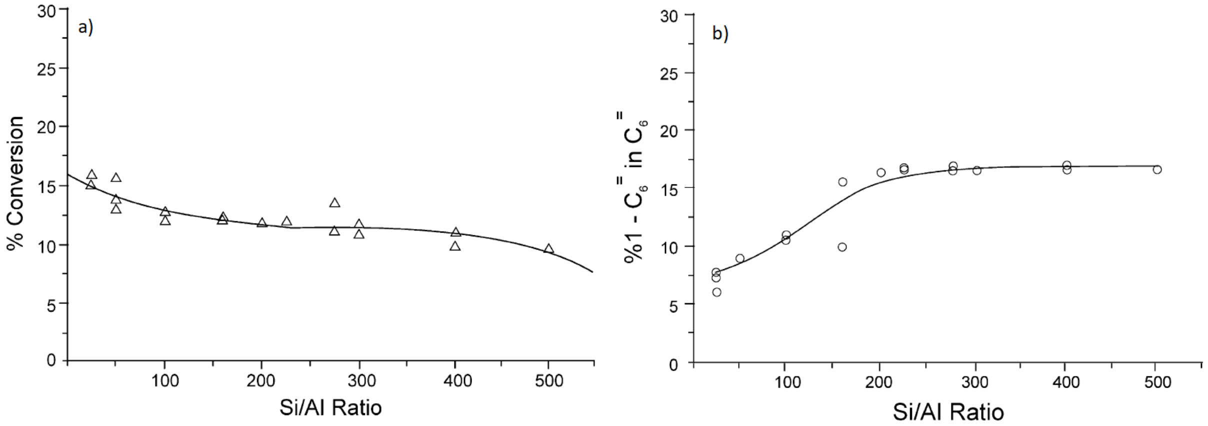


Figure 40. a) Ethene conversion and b) 1-Hexene selectivity as a function of Si/Al ratio of the support. T = 100 °C, P = 1.5 MPa, MHSV = 4 h^{-1}, and time-on-stream = 280 min. (Reproduced with permission from ref 281. Copyright 2003 Elsevier)

The highest 1-hexene contents in the hexene fraction, for instance, are obtained for catalysts having Si/Al ratios greater than 200, with some additional Ni and promotion with a small amount of potassium ions. This concept is transposable to the oligomerization of propylene : the use of carefully ion-exchanged amorphous supports could result in catalysts that have superior regioselectivity in propylene dimerization compared with many homogeneous systems.[282]

As Ni-exchanged silica-aluminas were then considered active enough to make them eligible for industrial development, systematic studies were carried out concerning various parameters of the ethylene oligomerization reaction that might govern activity, selectivity and stability.[283] Nickel concentration on the aluminosilicates and the conditions for oligomerization were carefully screened by Espinoza et al.[284,285] At low nickel contents, selective exchange of the nickel onto the most acidic sites occurs and a higher activity per site is recovered. Increasing the nickel concentration results in a shift to lighter products, but also increased the deactivation and decreased the activity recovery after regeneration. Single-event microkinetic modeling (SEMK) has been carried out by Toch et al.[286] with an amorphous Ni-SiO_2-Al_2O_3 free from strong acid sites after an experimental investigation varying temperature, total pressure, ethylene partial pressure, and space velocity. The model was attested to be significant and suitable for application to future rational catalyst design and industrial reactor optimization.

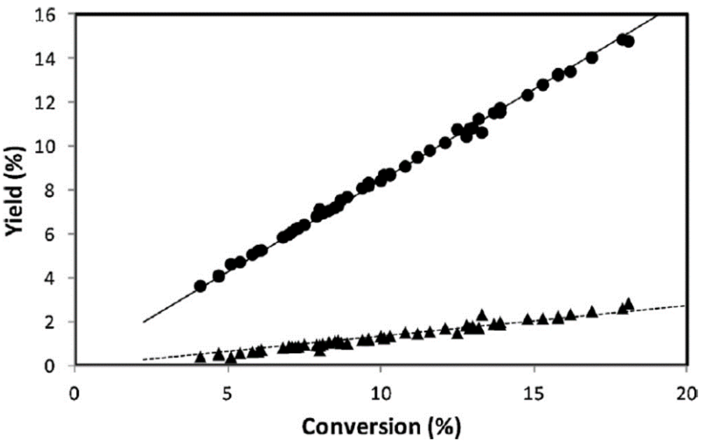


Figure 41. Experimental observations (symbols) and model simulations (lines) for butene yield (● and full line) and hexene yield (▲and dashed line) as function of ethylene conversion (443-503 K, 0.15-0.35 MPa) (Reproduced with permission from ref 286. Copyright 2015 Elsevier)

Recently, the use of amorphous alumino-silicates has gained interest for the valorization of specific olefin-rich refinery gases such as upgrading bio-syngas to gasoline-range hydrocarbons[287] or dilute ethylene feeds containing more impurities.[288] Recent commercialization of new amorphous aluminosilicates by Sasol, such as Siralox-30, prompted Hwang et al.[289] to use them for ethylene oligomerization and to maximize C_{10}^{+} selectivity for jet fuel production. Besides synthetic amorphous aluminosilicates, “natural” aluminosilicates have recently been described in the literature by Hulea et al.[290]. Bentonite, acid-washed montmorillonite and montmorillonite pillared clay were promoted by ion-exchange with nickel nitrate. The best catalyst combines high pore accessibility and lower acid density with a selectivity oriented towards linear C_4 and C_6 olefins.

Nickel-exchanged montmorillonite-based catalysts for olefin oligomerization had been developed in the late 1980s by Hüls AG[291] to implement the Octol process.[292] The Octol A version produces highly branched octenes for fuel applications. For chemical applications demanding a more linear octenes cut before hydroformylation reaction, the Octol B version is preferred. The main characteristics of n-butene oligomerization process and catalyst optimizations dedicated to industrial implementation are summarized well in a review by Wendt et al.[36]

Inspired by the sulfuration technique claimed by Shell, Gulf synthesized properly sulfided nickel-substituted mica-montmorillonite as the active catalyst for oligomerizing C_3 and C_4 olefins to fuel-range products from gasoline to jet-fuel.[293]

An original example has very recently been described by Shin et al.[294] with amorphous aluminosilicates as a support for nickel phosphide Ni_2P, aiming to mimic the homogeneous SHOP process which uses (P,O)-type ligands on nickel for full-range synthesis of α-olefins. $LiAlH_4$ is needed to activate the catalyst, which differs greatly from all other solids described in this section. A similar cooperation between Ni, P and O is highlighted, but nevertheless, the isomerization of α-olefins can not be avoided because of the Brønsted acidity of aluminosilicates, which hampers the selectivity of the process compared to the homogeneous SHOP counterpart.

As mentioned in many studies dealing with aluminosilicate supports, the acidity of the support/catalyst and the activity of the latter in olefin oligomerization seem to be correlated. Among other advantages, acidic amorphous aluminosilicate supports allow a decrease in nickel loading compared with siliceous carriers. Various operating conditions have been screened. High pressure and mild temperatures, around 30 bar and 100°C, appear to be the most suitable for selective olefin oligomerization.[295] Together with the rising success of zeolites in acid-catalyzed transformations in refineries,[296] their modularity in structure and acidic character has been taken advantage of as a carrier for nickel deposition and for use in olefin oligomerization.

Table 11. Amorphous Aluminosilicates (ASA)-supported nickel catalyst for olefin oligomerization

Ni precursor	ASA preparation	Deposition technique	Ni loading (%wt)	Activation	Olefin feed	T (°C)	P (bar)	Olefinic Products (wt%)	Performance	Ref
$Ni(NO_3)_2$	SiO_2 + $Al(NO_3)_3$ or Al_2SO_4	Impregnation	< 5	500°C Air	C_2	40	40	50 C_4+	Full conversion then deactivation	[257]
$Ni(NO_3)_2$	SiO_2 + $Al(NO_3)_3$ or Al_2SO_4	Impregnation	< 5	500°C Air	C_2 C_3	40-90	40-90	C_4-C_6	Full conversion then deactivation	[257]
$Ni(NO_3)_2$	SiO_2 + Al_2SO_4 then Na_2CO_3	Impregnation	0.7	-	1-C_4	80	55	82 C_8 14 C_{12}	0.54 $g_{oligomers}/g_{cata}/h$	[258]
$Ni(NO_3)_2$	SiO_2 + Al_2SO_4	Impregnation	1-10	-	C_2	275-300	1	Traces of C_4 45 C_6 15 C_8 25 C_{10}+	-	[259-264]
$NiSO_4$	Commercial ASA (13 wt%% Al)	Impregnation	2.7	540°C Air	C_2	100[a]	32	73 C_4 19 C_8	110 $g_{oligomers}/g_{cata}/h$	[265]
$Ni(NO_3)_2$	Commercial ASA (25 wt% Al)	Impregnation	3.6	540°C Air	C_2	150[b]	28	85 C_4 10 C_8	3.2 $g_{oligomers}/g_{cata}/h$	[267]
$Ni(NO_3)_2$	Commercial ASA (25 wt% Al) + DMDS (0,3 wt% S)	Impregnation	3.6	540°C Air	C_2	150[b]	28	43 C_4 28 C_6 13 C_8 7 C_{10}	1.9 $g_{oligomers}/g_{cata}/h$	[267]
$Ni(OH)_2$	SiO_2 + $Al(OH)_3$	Precipitation-Deposition	5	450°C N_2	90/10 v/v C_2/H_2	230	1	92 C_4	15 wt% conversion	[268]
$Ni(OH)_2$	SiO_2 + $Al(OH)_3$	Precipitation-Deposition	5	450°C N_2	90/10 v/v C_2/H_2	230	1	85 C_4	44 wt% conversion	[268]
$Ni(OH)_2$	SiO_2 + $Al(OH)_3$	Precipitation-Deposition	5	450°C N_2	90/10 v/v C_2/H_2	250	1	90 C_6	44 wt% conversion	[268]
$Ni(OH)_2$	$Si(OEt)_4$ + $Al(OPr)_3$ in NH_3 (5%mol Al)	Precipitation-Deposition	5	450°C N_2	C_3	180	25	99 C_6	30 wt% conversion	[272-276]
$Ni(OH)_2$	$Si(OEt)_4$ + $Al(OPr)_3$ in NH_3 (15%mol Al)	Precipitation-Deposition	5	450°C N_2	C_3	180	25	70 C_6 27 C_{7+}	30 wt% conversion	[272-276]
$Ni(OH)_2$	$Si(OEt)_4$ + $Al(OPr)_3$ in NH_3 (5%mol Al)	Precipitation-Deposition	5	450°C N_2	C_4	100	5	95 C_8	30 wt% conversion	[272-276]
$Ni(NO_3)_2$	SIRAL-30 (30/70 w/w SiO_2/Al_2O_3)	Ion-Exchange	4	550°C N_2	C_2	200	10	20 C_4 30 C_6 20 C_8 20 C_{10^+}	100 wt conversion	[289]
$Ni(NO_3)_2$	Montmorillonites	Ion-Exchange	1.1	500°C N_2	C_2	250	30	72 C_4 16 C_6	60-80 wt% conversion	[290]

								6 C_8		

[a] *Ethylene dissolved in pentane*

[b] *Ethylene dissolved in heptane*

5.3.2 *Zeolites*

Rapidly following the advent of amorphous aluminosilicates as carriers for nickel for the oligomerization of ethylene, nickel-promoted zeolites were also identified early on as suitable candidates. The main catalytic results are reported in Table 12. Many types of parent and modified zeolites have been investigated and are described in the following paragraphs, their performances being collected in Table 12. Zeolites are microporous crystalline materials that can display unique catalytic activities as well as shape selectivity properties for adsorption/separation processes. Like amorphous aluminosilicates, promotion with nickel is needed for selective oligomerization under mild conditions. Zeolites have served as well-defined model solids for the identification of the nickel active sites and for kinetic or DFT studies as detailed in Chapter 6.

In parallel with aluminosilicates, zeolites were first studied in the late 1960s by Eidus et al. beginning with Y and modified X and Y zeolites (NaY, CaX, CaY) as well as mordenite.[297] They were saturated with Ni ions for testing in the dimerization of ethylene. Performances are largely determined by the type of zeolite used. The butene fraction formed with such catalysts consisted almost completely of trans-2-butene, showing the strong isomerization activity of these acidic catalysts. NiHY and NiCaX were also compared in activity and selectivity by Lapidus et al., but the use of temperatures as high as 335°C renders interpretation difficult.[298] NiCaX and NiCaY-zeolites were also used as references for the first study concerning active site identification.[299,300] From these seminal studies up until now, Y zeolite is by far the most popular for nickel exchange and catalysis of olefin oligomerization. Other transition-metal exchanged zeolites such as RhY, RuY and CrY were tested.[301] Rh and Ni-exchanged zeolites were shown to be selective towards butenes formation. The zeolitic structure of NiY was more stable than that of RhY, because the Ni cation was more difficult to reduce to a metallic state than the Rh cation. Ethylene adsorption and diffusion kinetics were first studied on NiY zeolites.[302]

Nickel-exchanged 13X-zeolites were studied by Forni et al.for propylene[303] and butene[304] oligomerization, providing the first kinetic studies concerning the relative rate of isomerization, dimerization and codimerization as well as control of diffusion within the porous matrix.

Nickel-exchanged NaY zeolites were used by Heveling et al.for the transformation of ethylene to diesel-range products [305] At low temperatures (100-150°C), a Schulz-Flory type distribution was obtained at 35 bar and WHSV = 2 h^{-1}.

In order to again select oligomerization towards 1-butene, a constant challenge in heterogeneous ethylene oligomerization, Ng et al. investigated whether metallic, Lewis or Brønsted acidic sites of NiNaY (nickel-exchanged doped Y zeolite partially neutralized with Na) were involved in this isomerization step and in the dimerization of ethylene.[306] Treatments with pyridine and ammonia result in decreased activity but no improvement in selectivity to 1-butene. These results suggest that both the nickel and Brønsted acid sites are mandatory for the dimerization of ethylene. As with amorphous aluminosilicates, teh decorrelation of oligomerization and isomerization activities, which systematically lead to preferred 2-butene selectivity in productive conditions, is a challenge with such zeolites. Similarly, NiNaY catalyzed the oligomerization of butenes and were further exchanged with alkali and alkali-earth cations (NiMNaY).[307] Similar alkaline promotions were carried out by Mlinar et al. on nickel ion-exchanged Na-X zeolites for the oligomerization of propylene by alkali metal or alkaline earth-exchanged Ni-X (faujasite, Si/Al = 1.2).[308]

Dealumination of Y zeolite by the reaction of NH_4NaY with $SiCl_4$ is described, by Sohn et al., to modulate the acidity of the catalyst, with an optimal Si/Al ratio of 6.[309] Progressive dealumination of Y zeolites carried out by Hulea et al. have allowed their acidity to be modulated, and they specifically studied the influence of the pore size of the zeolites .[310] The most dealuminated zeolite NiY3 possessing the highest specific surface area outside micropores exhibits the best compromise between activity, stability and butenes selectivity. At 35°C, butene selectivity can even reach more than 90 wt%.

Following these observations on the influence of zeolite texture on catalytic performances, two zeolites from the MCM categories Ni-exchanged MCM-22 (Si/Al = 14) and MCM-36 (Si/Al = 26) were prepared by the same group for ethylene oligomerization.[311,312] MCM-22 has three porous networks relating to microporosity and possess a higher acidity than MCM-36, which possesses a more open porosity. Despite a higher acidity, Ni-MCM-22 is less active at any temperature. Textural properties like porosity have thus to be taken into account as a critical factor for activity and stability.

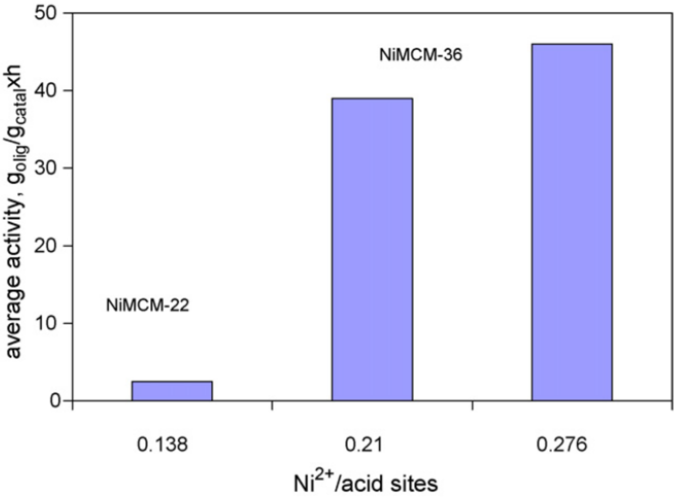


Figure 42. Effect of the Ni^{2+}/acid sites ratio on the catalytic activity of NiMCM-22 and -36 after 30 minutes (150°C, 40 bar) (Reproduced with permission from ref 311. Copyright 2008 Elsevier)

More recently, Martinez et al. proposed the use of bifunctional Ni-H-Beta, a rare example of the use of this nanocrystalline zeolite for olefin oligomerization.[313] Catalysts were prepared by ion-exchange or incipient wetness impregnation of a commercial H-Beta zeolite (Si/Al = 12) with $Ni(NO_3)_2$ solutions. Activity of the catalysts grows with nickel loading up to 2.5 wt% before leveling off. Brønsted acidic sites contribute in parallel to the metallic sites to produce branched octenes by carbocationic pathways. Surprisingly for such microporous zeolites (V_{micro} ~ 0.2 cm^3), no sign of deactivations were observed under the investigated conditions, even at relatively high ethylene conversions such as 60-80% within 10 hours on stream. The authors did not specify whether the improved stability is linked to the particular textural properties of Ni-H-Beta catalysts or to the operating conditions. The same group proposed a comparative study between this nanocrystalline Ni-H-Beta, a commercial aluminosilicate (Siralox 30) and a mesoporous mesostructured Ni/Al-MCM-41.[314] While the enhanced acidity of Ni-H-Beta orientates the selectivity towards higher liquid oligomers, the productivity is maximal for the most active mesoporous Ni/Al-MCM-41 under the same operating conditions as described above.

A systematic study by Resende et al. has recently been carried out with a similar Ni-Hβ catalyst on a continuous packed bed reactor.[315,316] Nickel nitrate was slowly dripped onto a commercial β zeolithe (ammonium form, Si/Al = 25). Parameter optimization led to a long-term experiment where ethylene conversion was found to be stable at 50% for several days.

Compared to its well-known success in refineries such as in the Fluid Catalytic Cracking process, ZSM-5 zeolites have rarely been mentioned as a support for nickel-promoted olefin oligomerization. Following a first patent by Mobil Oil Corp[317] in 1988 dedicated to ethylene-rich feedstocks, HNa-Ni/ZSM-5 (0.4-0.8 wt% Ni, SiO_2/Al_2O_3 17-80) were prepared and used for 1-butene dimerization in the search of linear octenes for petrochemistry.[318] The highest dimer selectivity and octens linearities were obtained for low-alumina ZSM-5 at 120°C and 80 bar. No form selectivity provided by the zeolitic structure was observed. On the contrary, the synthetic and natural mordenite channel structure seemed to influence the product distribution of n-butene dimerization, as unusually high selectivities for n-octenes and methylheptenes were found by Wendt et al.[319] ZSM-5 has recently been studied again by Bordiga et al. for high temperature deactivation studies between 150°C and 400°C.[320,321] Larger pore diameters are predicted to increase the desorption rate of surface species and limit deactivation.

The study of zeolites has allowed a deep understanding to be obtained of the parameters that govern activity and stability in ethylene oligomerization thanks to a broad variability of structural and textural properties by neutralization, dealumination or doping. A general trend is that microporous zeolites can suffer rapid deactivation by pore blockage caused by the formation of higher oligomers, leading to coking. This coking can also result from enhanced acidity at the surface of the micropores. Post-treatments with alkali ions for instance, or steaming, decrease surface acidity and open up the porous structure, to produce better, but still not sufficient stabilities while not dramatically affecting the activity or ethylene conversion rate. In this regard, the use of structured aluminosilicates with geometrically less constraining mesoporous networks appeared to be particularly attractive for obtaining active and also selective and more stable catalysts.

Table 12. Zeolite-supported nickel catalysts for ethylene oligomerization

Ni precursor	Zeolite	Deposition technique	Ni loading (wt%)	Activation	T (°C)	P (bar)	Products (wt%)	Performance $g_{oligomers}/g_{cata}/h$	Ref
$Ni(NO_3)_2$	NaY (Si/Al = 2.8)	Ion-Exchange	4.0	450°C Air	115	25	38 C_4 19 C_6 16 C_8 25 C_{10}	25.1	305
$Ni(NO_3)_2$	NaY (Si/Al = 1.5-3.0)	Ion-Exchange	5.6	400°C Air	70	40	67 C_4 33 C_6	0.4	306
$Ni(NO_3)_2$	Dealuminated Y (Si/Al = 6)	Ion-Exchange	1.5	550°C Air	50	40	3 C_4 2 C_6 2 C_8 1 C_{10+}	16.5	310
$Ni(NO_3)_2$	Dealuminated Y (Si/Al = 15)	Ion-Exchange	1.0	550°C Air	50	40	-	22.0	310
$Ni(NO_3)_2$	Dealuminated Y (Si/Al = 30)	Ion-Exchange	0.6	550°C Air	50	40	67 C_4 10 C_6 14 C_8 9 C_{10+}	31.9	310
$Ni(NO_3)_2$	Y	Ion-Exchange	5.6	400°C Air	60	28	67 C_4 13 C_6 6 C_8 15 C_{10+}	0.3	306
$NiCl_2$	Dealuminated Y (Si/Al = 32)	Ion-Exchange	0.6	-	20	0.4	67 C_4 13 C_6 6 C_8 15 C_{10+}	0.8	309
$Ni(NO_3)_2$	H-Beta (Si/Al = 12)	Ion-Exchange	2.5	550°C Air	120	26	38 C_4 8 C_6 14 C_8 15 C_{10}	nd. (75% conv.)	313

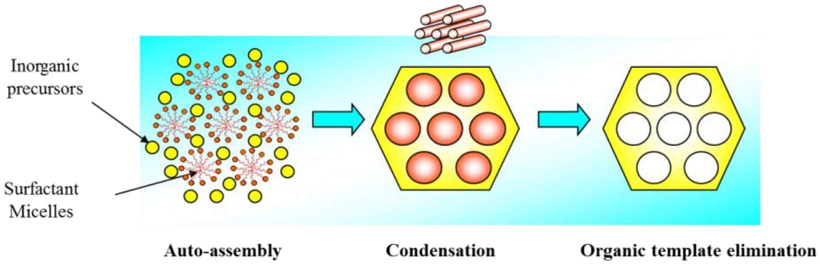
$Ni(NO_3)_2$	H-Beta (Si/Al = 12)	Impregnation	2.7	550°C Air	120	26	47 C_4 12 C_6 10 C_8 12 C_{10}	nd. (66% conv.)	[313]
$Ni(NO_3)_2$	H-Beta (Si/Al = 25)	Dripping	2.7	550°C Air	120	19	45 C_4 25 C_6 15 C_8 10 C_{10}	nd. (50% conv.)	[315,316]
$Ni(NO_3)_2$	MCM-22 (Si/Al = 14)	Ion-Exchange	0.6	550°C N_2	150	40	81 C_4 5 C_6 13 C_8 1 C_{10}	2.5	[312]
$Ni(NO_3)_2$	MCM-36 (Si/Al = 26)	Ion-Exchange	0.6	550°C N_2	150	40	45 C_4 25 C_6 15 C_8 15 C_{10}	39	[312]

5.3.3 *Mesoporous non-zeolitic aluminosilicates*

5.3.3.1 Olefin oligomerization

Mesoporous and mesostructured silicas have already been described in the first paragraph of this chapter and do not exhibit interesting performances for olefin oligomerization. The present paragraph thus focuses on mesoporous aluminosilicates, which possess pore diameters comprised between 2 and 50 nm, using the definition of the Interational Union of Pure and Applied Chemistry. Their performances in olefin oligomerization are collected in Table 13. Mesoporous materials can be obtained by treatment of microporous materials or by on-purpose synthesis thanks to the use of appropriately selected porogenic agents (Scheme 6).[322] Suitable treatments can then be applied in order to modulate the acidity, such as alumination or heteroatomic promotion. Pillar-layered structured (PLS) and molecular sieves such as M41S can thus be synthesized in a well-controlled manner and applied to numerous fields as catalysts, adsorbants or metal supports.

Scheme 6. Synthesis scheme for MCM-41 mesoporous materials



Hartmann et al.[323] described the synthesis of AlMCM-41 (Si/Al = 16) by the addition of sodium aluminate $NaAlO_2$ to the gel preparation mixture with sodium silicate Na_2SiO_3 and the surfactant CetylTrimethylAmmonium Chloride (CTAC).[324] This modification induces a three-fold enhancement of ethylene conversion which still remains particularly low, below 5 wt%.

No further investigations concerning these solids was mentioned until Hulea et al. looked at them again in 2004 for an in-depth research program on mesoporous materials promoted by nickel for ethylene oligomerization.[325] A first set of six catalysts from the MCM-41 category with Si/Al ratios comprised between 10 and 75 was synthesized. Mesoporous volume and mesopore diameters are similar within the set of catalysts. The higher the Si/Al ratio, the lower the global acidity of the catalyst measured by temperature programmed desorption using ammonia as a probe (TPD-NH_3).

The highest productivity was obtained for the highest Si/Al ratio, corresponding to the lowest acidity of the catalyst. More acidic catalysts deactivate faster because of the accumulation of heavy products. The influence of pore size was highlighted with two samples of Si/Al = 30 with a pore size of 37 and 86 Å. As expected, larger pores are beneficial for the diffusion of higher oligomers and result in lower deactivation rates.

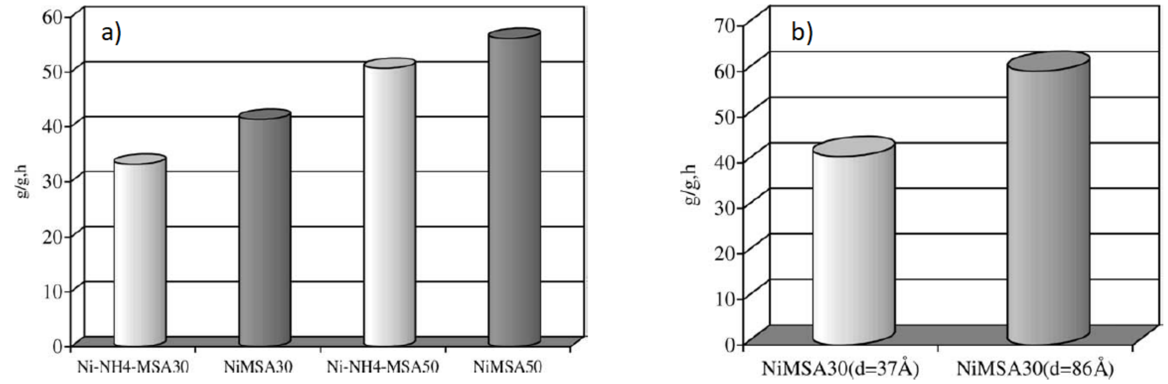


Figure 43. Effect of a) acidic properties and b) pore size on the catalytic activity of ethylene oligomerization at 150°C, 3.5 MPa after 60 minutes reaction time (Reproduced with permission from ref 325. Copyright 2004 Elsevier)

This same catalyst was later employed in a continuous stirred-tank reactor at a lower temperature without external start-up solvent.[326] At 30°C, butenes are the major products. Selectivity switches to C_6-C_{10} when the temperature is increased to 70°C. Overall oligomer production follows a Schulz-Flory distribution.

These results show the attraction of aluminating mesostructured and mesoporous catalysts, producing a broad variability in textural properties of the supports. The amount of aluminum introduced by alumination has a critical impact on the acidity, activity, selectivity and stability of the catalyst. This study shows that catalyst activity is not directly correlated to support acidity, in contrast to the studies described in the paragraph 5.3.1 dealing with other amorphous aluminosilicates. An optimal compromise between acidity, activity and stability could thus be attainable for efficient oligomerization catalysts.

A recent original study reports the stabilization of Ni/Al-MCM-41 by an extended ethylene liquid phase at low temperatures within MCM-41 channels.[327] Such a liquid phase facilitates solvation of the reactive transition state.

Following their study on NaX zeolites, Mlinar et al. carried out an equivalent alkali and alkaline-earth promotion of nickel-exchanged Al-MCM-41 for the gas-phase oligomerization of propylene at 180°C at near-atmospheric pressure.[328] The identity of the alkali metal cation had no significant impact on the catalytic activity or selectivity, except for Cs, which decreased the pore volume and resulted in a decreased activity and more linear products. This Cs effect can be looked at alongside that with NiCsNaY[307] zeolites, for which a greater linearity of the products was observed in butene oligomerization, presumably due to shape selectivity because of pore volume reduction caused in both cases by Cs.

The promising results of MCM-41 mesoporous materials were generalized to two other families of mesoporous families, namely MCM-48 and SBA-15.[329] MCM-48 belongs to the same M41S family as MCM-41, but displays a cubic phase rather than hexagonal. Their interwoven pore structure can produce better molecular diffusion in the pore channels.[330] SBA-15 was first synthesized by Zhao et al. in 1998.[331] It has a larger pore size and thicker pore wall than MCM-41, which exhibits improved hydrothermal and mechanical stability. AlMCM-41 was synthesized as described above by incorporation of alumina via $NaAlO_2$ upon synthesis of the gel with Na_2SiO_3. AlMCM-48 was also

prepared from $NaAlO_2$ but with a different silicon source, in this case TetraEthylOrthoSilicate (TEOS), by hydrothermal synthesis and with CTABr (CetylTrimethylAmmonium Bromide) as a surfactant. The Si/Al ratio is constant at 30 for all catalysts, resulting in equivalent acidities. They possess different average pore diameters: 8.5-9.0 nm for Ni/Al-MCM-41 and Ni/Al-SBA-15 and 2.7 for Ni/Al-MCM-48.
The results for ethylene oligomerization at 150°C and 35 bar in *n*-heptane indicate the impact of textural properties on catalytic activity. The three-dimensionnal interconnected channel structure of Al-MCM-48 showed higher activity than the one-dimensional MCM-41. Despite a larger pore size, Ni/Al-SBA-15 is less active than the MCM counterparts. The smaller BET surface area as well as the post-treatment alumination method could affect the nature of the catalytic sites and renders comparability with the other catalysts difficult. As a new catalyst for ethylene oligomerization, Ni/Al-SBA-15 was then investigated in more detail.

As a result, various methods for alumination by post-treatment of SBA-15 were investigated by using the pH-adjusting method using NH_4OH and NaOH.[332] New Al-SBA-15 with a Si/Al of 5 could be obtained while retaining the SBA-15 mesostructuration with $NaAlO_2$ as a post-alumination agent.[333,334] The textural properties are still significantly modified following alumination. For instance, the BET surface area is decreased from 740 to 440 m^2/g, as well as porous volume (1.05 to 0.75 ml/g). The average pore diameter is slightly reduced, from 8.4 to 7.9 nm.

At 35 bar, 150°C with heptane as solvent, Ni/Al-SBA-15 proved to be the most active among aluminosilicates from 155 to 175 $g_{oligomers}/g_{catalyst}/h$ and fairly stable. Ethylene conversion rises and butene selectivity decreases with increasing temperatures. Ethylene conversion is maintained above 80% over 80 hours, while selectivities are maintained, making Ni/Al-SBA-15 one of the most productive and stable catalysts for ethylene oligomerization.

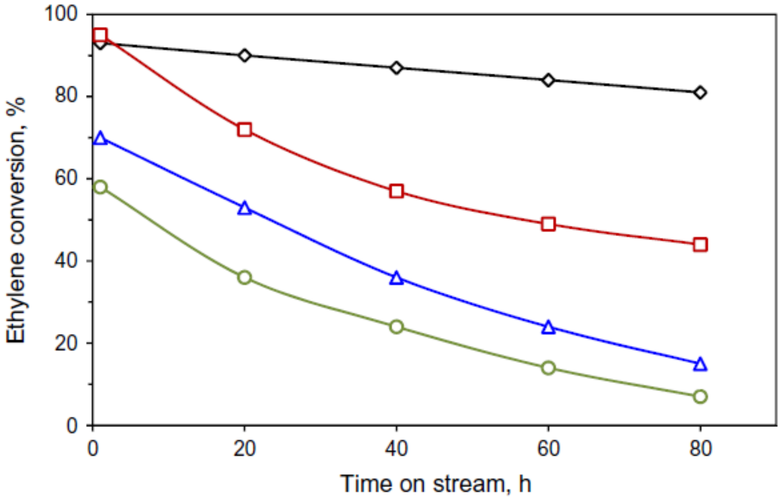


Figure 44. Activity profile of (◊) Ni-AlSBA-15 outperforming (□) Ni-MCM-41, (Δ) Ni-SiO_2-Al_2O_3 and (○) Ni-Y**.** (Reproduced with permission from ref 334. Copyright 2015 Elsevier)

As another family of mesoporous aluminosilicates, KIT-6 and Al-KIT-6 were chosen by Hwang et al.[335] for their similar 3D cubic pore structure to that of MCM-48[336] and their large pore diameter (4-12 nm), like SBA-15. Alumination with $NaAlO_2$ produces Na-Al-KIT-6 for further exchange with ammonium nitrate and nickel nitrate to produce Ni/Al-KIT-6 at 5 wt% Ni loading. Four different solids of Na-Al-KIT-6 exhibiting different calcining temperatures from 300°C to 900°C were obtained with this protocol. The most active catalyst was calcined at 300°C (Ni/Al-KIT-6(300)). Compared with 500°C and 700°C, it possesses the lowest Brønsted acidic site concentration and the highest Ni^{2+} site concentration. The decrease in calcining temperature of Al-KIT-6 seems to lead to intimate contact between Ni^{2+} and acid sites for an optimal metallic activity. The increase in calcining temperature shifted the selectivity towards acid-catalyzed oligomerization-cracking products such as odd-numbered carbon olefins.

5.3.3.2 Ethylene oligomerization within Ethylene-to-Propylene processes (ETP)

Hulea's group enriched the potential of Ni/Al-SBA-15 in direct Ethylene-to-Propene (ETP) conversion within a staged two-bed reactor for dimerization-metathesis cascade reactions.[337] At 80°C, a selectivity of 70% for butenes was obtained, 2-butene being the major isomer, and a 40% conversion of ethylene thanks to a high WHSV of 16.5 h^{-1}. Ethylene and 2-butenes can as a result be converted to propene at 80°C in the presence of MoO_3/Al-SBA-15. Following this, Hulea et al. looked for a cheaper alternative to Al-SBA-15 mesostructured mesoporous aluminated silicas and similar[338] commercial Grace-Davidson silicas further aluminated with the same method to produce a series of $AlSiO_2$ compounds. Oligomerization tests after 1 hour at 150°C, 35 bar in semi-batch mode indicated only a slightly reduced activity for Ni/$AlSiO_2$ compared with Ni/Al-SBA-15, but the "commercial" catalyst deactivated almost 15 times faster due to coking caused by the absence of mesostructuration.

Ni/Al-KIT-6 (Si/Al = 7) was also recently similarly described as transforming ethylene to propylene and 1-butene in a two-stage fixed bed reactor in association with Re_2O_7/Al_2O_3, both working at 60°C, 30 bar and a WHSV of 7.5 h^{-1} related to the oligomerization catalyst.[339] Of particular interest is the global selectivity to 1-butene and propylene formed after dimerization/metathesis. Partial conversion of ethylene in the dimerization step provides a higher ratio of butenes within oligomerization products, 1-butene within the butenes cut and a stoechiometric excess of ethylene on the metathesis catalyst. This excess participates in displacing the thermodynamic equilibria towards ethenolized products, which pushes the 2-butene conversion towards propylene and avoids the formation of 3-hexene by homometathesis of 1-butene.

Other two-step processes involving nickel-containing mesoporous aluminated silicas to produce clean fuels were evaluated. Ni/Al-MCM-41 catalysts were exploited in a two-step process for converting light olefins into long-chain hydrocarbons in the distillate range. Olefins containing even numbers of carbon atoms were first produced thanks to metallic oligomerization with the aforementioned catalyst. A second step with H-MCM-41 produced longer chain hydrocarbons with high productivity.[340] Jet-fuel range olefins could also be produced by combining the oligomerization of ethylene over Ni/Al-SBA-15 (1.9 wt% Ni and Si/Al = 9 prepared by alumination of SBA-15 with $NaAlO_2$) with subsequent co-oligomerization of the liquid oligomer mixtures over an Amberlyst-35 acidic ion-exchange resin catalyst.[341] Full-conversion of ethylene was achieved in the first step at 200°C, 10 bar, WHSV = 0.375 h^{-1} for 60 hours. Co-oligomerization was operated at 100°C under 30 bar N_2 and 24 hours with 98% selectivity for C_5^+, including 42% C_{10}^+.

5.3.3.3 Conclusions regarding mesoporous materials

Mesoporous catalysts exhibit structural and textural properties that fit well with olefin oligomerization requisits. Porosity and acidity can easily be tuned to present improved compromises between activity and stability. The highest performing catalysts under optimized conditions produce a Schulz-Flory distribution of even-numbered olefins, with butene selectivity around 50%. As some acidity seems to be required for activity, the isomerization of primary terminal olefins to internal olefins reaches equilibrium. Branched olefins like hexenes or octenes issuing from codimerization of ethylene and/or butenes are also present, as is the case with nickel-catalyzed homogeneous oligomerizations.

All these studies concerning adaptations of aluminosilicates from amorphous to microporous/mesoporous zeolites, and further to mesoporous aluminosilicates in general, is informative about the critical factors governing activity and stability. Acidity, average pore diameter, porosity distribution, and Ni^{2+}/acid sites ratio are examples of key parameters. In terms of potential industrialization ability, that is to say a viable compromise between productivity and stability, mesoporous materials present an attractive solution thanks to the versatility of the preparations of siliceous materials using various alumination techniques. In this regard, particular attention should be paid to the following: extrapolation of material synthesis, processability with external solvents to deal with the exothermicity of the oligomerization, etc.

Zeolites, amorphous aluminosilicates and, more recently, mesoporous and mesostructured aluminosilicates have thus had tremendous success as carriers for nickel oxide applied to olefin oligomerization. The intrinsic acidity of aluminosilicates can often be a hurdle because of deactivation to a greater or lesser extent. Aluminas exhibit lower acidities while frequently possessing mesoporosity. In this respect, they have also witnessed interest in academic and industrial groups in order to obtain active and stable catalysts for olefin oligomerization. The strategies for obtaining such active catalysts for olefins are described in the following section.

Table 13. Mesoporous ASA-supported nickel catalysts for olefin oligomerization

Ni precursor	Mesoporous material	Deposition technique	Ni loading (wt%)	Activation	Olefinic feed	T (°C)	P (bar)	Products (wt%)	Performance	Ref
$NiCl_2$	Aluminated MCM-41	Ion-Exchange	0.84 wt%	450°C Vacuum	C_2	70	1	> 99 C_4	4.5 wt% conversion	[323]
$Ni(NO_3)_2$ in EtOH	Aluminated MCM-41 Si/Al = 26.2 d = 37 Å	Ion-Exchange	0.5 wt%	550°C Air	C_2	150	35	50 C_4 22 C_6 19 C_8 9 C_{10}	41 $g_{oligomers}/g_{catalyst}/h$	[325]
$Ni(NO_3)_2$ in EtOH	Aluminated MCM-41 Si/Al = 25.7 d = 86 Å	Ion-Exchange	0.5 wt%	550°C Air	C_2	150	35	50 C_4 22 C_6 19 C_8 9 C_{10}	60 $g_{oligomers}/g_{catalyst}/h$	[325]
$Ni(NO_3)_2$	Aluminated MCM-41 Si/Al = 20	Ion-Exchange	1.0 wt%	500°C Air	C_3	180	1	99.5	6 $C_3/Ni_{ion}/min$	[328]
$Ni(NO_3)_2$	Aluminated MCM-48 Si/Al = 30	Ion-Exchange	0.5 wt%	550°C Air	C_2	150[a]	35	42 C_4 37 C_6 14 C_8 7 C_{10}	113 $g_{oligomers}/g_{catalyst}/h$	[329]
$Ni(NO_3)_2$	Aluminated SBA-15 Si/Al = 30	Ion-Exchange	0.5 wt%	550°C Air	C_2	150[a]	35	49 C_4 31 C_6 12 C_8 8 C_{10}	63 $g_{oligomers}/g_{catalyst}/h$	[329]
$Ni(NO_3)_2$	Aluminated SBA-15 Si/Al = 7	Ion-Exchange	2.6 wt%	550°C Air	C_2	150[a]	35	49 C_4 31 C_6 12 C_8 8 C_{10}	175 $g_{oligomers}/g_{catalyst}/h$	[332]
$Ni(NO_3)_2$	Aluminated KIT-6 Si/Al = 16.1	Ion-Exchange	5.0 wt%	400°C Air	C_2	120[a]	40	59 C_4 20 C_6	94 wt% conversion	[335]
$Ni(NO_3)_2$	Aluminated SiO_2 Si/Al = 6.5	Ion-Exchange	2.0 wt%	550°C Air	C_2	150[a]	35	56 C_4 31 C_6 10 C_8 3 C_{10}	130 $g_{oligomers}/g_{catalyst}/h$	[338]

[a] Ethylene dissolved in heptane

5.4 Aluminas Ni/Al_2O_3

Alumina supports (Al_2O_3) are first mentioned in 1945 in a single example in the seminal patented work by Phillips[15], but their activity was about one-twentieth that of the siliceous catalyst. Thanks to current knowledge, it appears that the nickel precursor and nickel loading were not adapted to the characteristics of aluminic supports. In fact, in contrast to aluminosilicates in general, the use of classical neutral precursors such as nickel nitrate, widely used with aluminosilicates, does not provide active catalysts for olefin oligomerization under mild conditions when deposited on Al_2O_3.[217] Because neutral precursors do not provide supplementary acidity, it can be assumed that the intrinsic acidity of the support is not sufficient to create a suitable environment for nickel active sites under mild conditions. To compensate for the loss of acidity compared to aluminosilicates, three main strategies have been investigated in patents and literature :

- Adapting the nickel precursor or nickel-containing solution to deposition techniques
- Adapting the synthesis of alumina
- Adapting the post-treatment of alumina after synthesis

The performances of the corresponding catalysts are gathered in Table 14.

5.4.1 *Acidity provided by the nickel precursor*

5.4.1.1 $NiCl_2$

The use of $NiCl_2$ as a nickel precursor on alumina was described in 1988 by Chauvin et al.[20] It was systematically compared with the use of nickel nitrate $Ni(NO_3)_2$ and nickel sulphate $NiSO_4$. The influence of the nature of the anion and the anion-to-nickel ratio was investigated with or without the addition of salts. After impregnation, calcining of the catalyst completely decomposed the nitrate, part of the chloride was left on the support and the sulfate was fully maintained. The actual nature of the catalyst thus strongly depends on the nickel precursor used. Benchmark silica and aluminosilicate supports were also used. Ni loadings were chosen to be between 1 and 4wt%. At 40°C and 40 bar, $Ni(NO_3)_2$ deposited on SiO_2 or Al_2O_3 leads to inactive catalysts for liquid-phase propene oligomerization. $NiSO_4$ deposited on SiO_2 has low activity at 22 wt% conversion of propene, while intermediate conversion of 65 wt% was obtained with $Ni(NO_3)_2$ on SiO_2-Al_2O_3. These two examples can provide clues as to the influence of the acidity provided solely by the precursor in the former case and solely by the support in the latter. $NiSO_4$ and $NiCl_2$ deposited on Al_2O_3 are the most active, reaching almost full conversion of propylene, and exhibit better stability than $Ni(NO_3)_2/SiO_2$-Al_2O_3. The $NiCl_2/Al_2O_3$ turned out to be the most selective catalyst for dimerization, but its activity decreased after 3 regeneration tests at 500°C. Since primary calcining of fresh catalyst already removes part of the chloride from the surface as gaseous hydrogen chloride, it is likely that additional chloride is lost after calcining regeneration at the same temperature, showing the critical impact of chloride content on catalyst acidity and indirectly on its activity. For these reasons, plus the fact that $NiSO_4/Al_2O_3$ showed an equivalent activity without being as selective, an large amount of research work focused on the use of $NiSO_4$ as a nickel precursor deposited on alumina.

5.4.1.2 $NiSO_4$

Heterogeneous catalysts of the $NiSO_4/Al_2O_3$ type enjoyed great success in the 1990s in the literature, notably by Sohn et al.'s group, and patents from IFP and BASF concerning ethylene, propene as well as butene oligomerization. Concerning ethylene oligomerization, the selective production of butenes was a common target for the different research groups. $NiSO_4/Al_2O_3$ catalysts have also been used as reference catalysts for the investigation of the nature of the active sites, the relationship between acidity and activity, as well as the large-scale processability potential.

Since the stoechiometric ratio between nickel and sulfur is imposed by the nature of the precursor ($NiSO_4$), the impact of the Ni/S ratio has been studied by Chauvin et al.[20] This ratio has on one hand been modulated to higher values by mixing $NiSO_4$ with $Ni(NO_3)_2$. On the other hand, it was reduced by mixing $NiSO_4$ and $(NH_4)_2SO_4$ or $Al_2(SO_4)_3$. A mixture of $Ni(NO_3)_2$ and H_2SO_4 to mimic $NiSO_4$ is also proposed by BASF. Patents from IFP[342–344] and later BASF[38] conclude that the preferred ratio is comprised between 0.2 and 0.8 in orderto optimize catalyst selectivity for ethylene, propylene and butene oligomerization.

Like Chauvin et al., Cai et al. also studied propylene[345] and ethylene[346,347] oligomerization with $NiSO_4/Al_2O_3$. Catalysts were prepared by impregnation of $NiSO_4$ at 2.5-10 wt% Ni loading on a commercial alumina having a specific surface area of 197 m^2/g and a pore volume of 0.45 ml/g. Under mild conditions, 30°C, 25 bar, almost full conversion of propylene was obtained. Ethylene was oligomerized with the same catalysts at 50°C. Poisoning with NaOH and CO led to strong or even total deactivation of the catalyst, proving the importance of the acid and metallic sites.

$NiSO_4/Al_2O_3$ catalysts were also extensively studied by Sohn et al.[348] for the selective dimerization of ethylene to butenes. Al_2O_3 powder is commercially available and characterized by a specific surface area of 240 m^2/g. Ten catalysts with $NiSO_4$ loading varying from 2 wt% to 100 wt% were prepared and tested at 20°C, 0.4 bar in a batch mode under a slight ethylene pressure. Increasing the $NiSO_4$ loading from 2 to 20 wt% resuleds in a constant increase in activity, which decreased above 20 wt%. These results are not in accordance with previous catalytic activities observed by IFPEN and BASF, even though the nature of the alumina can have a critical impact on catalysis. Only butenes were detected in the gas phase, including 1-butene as major product at the beginning of the reaction. Ethylene conversion must therefore be too low to observe codimerization to hexenes, and only primary products were detected. The high catalytic activity of 20 % $NiSO_4/Al_2O_3$ was attributed to the increase in the total and strength of acidity due to the addition of $NiSO_4$. The asymmetric stretching frequency of the S=O bonds by infrared spectroscopy of the catalysts was related to the acidic properties and then to the activity.[349]

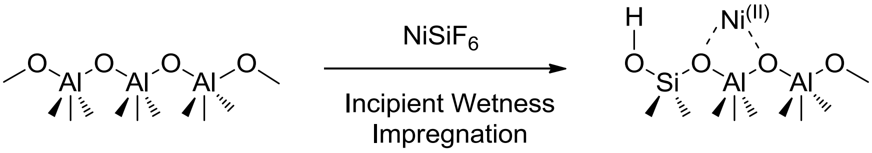
Like Ni/Al-SBA-15 in association with Mo/Al-SBA-15 for one-pot transformation of ethylene to propylene, $NiSO_4/Al_2O_3$ was associated with Re_2O_7/Al_2O_3 for selective dimerization-metathesis reactions at 50°C at atmospheric pressure,[350] inspired by a Russian patent that claimed to develop $Re_2O_7/NiO/B_2O_3/Al_2O_3$ for the same reaction.[351]

$NiCl_2$ and $NiSO_4$ deposited on Al_2O_3 seems to induce an interesting dimer selectivity compared to NiO/SiO_2-Al_2O_3 that rather produces a larger Schulz-Flory-like distribution with significant amounts of hexenes, octenes and decenes, which can ultimately lead to accelerated deactivation. This peculiarity, brought to light by Chauvin et al.,[20] was not fully understood, but striking similarities were observed by comparing the products spectra between homogeneous and heterogeneous catalysts. $NiSO_4/Al_2O_3$ is the heterogeneous catalyst giving the closest product distribution to the homogeneous process known as Dimersol® E and G developed by IFPEN, respectively for the selective dimerization of ethylene and propylene catalyzed by the association of a naked nickel complex and an alkylaluminum. These similarities drove us to design an active non-acidic heterogeneous catalyst with a specific non-innocent precursor $NiSiF_6$ that could bring the nickel active site in the most favorable electronic environment for active ethylene oligomerization.

5.4.1.3 *The specific case of $NiSiF_6$*

Recently, comparisons between homogeneous and heterogeneous product distribution with $NiSO_4/Al_2O_3$ catalysts led us to reconsider the need for a global acidity of the catalyst to turn it into an active oligomerization promoter. The first clue is that the addition of $NiSO_4$ to Al_2O_3 produces fewer acidic sites of a lower strength than all the previously described aluminosilicates, namely zeolites, modified zeolites or mesoporous materials. Instead of depositing a small quantity of nickel atoms onto an aluminosilicate prone to deactivation because of global acidity, we had the idea of bringing silicon atoms within the nickel precursor in the hope of creating a stoichiometric aluminosilicate cluster around the Ni (Scheme 7).

Scheme 7. Expected effect of Al_2O_3 impregnation with $NiSiF_6$ to create a nickel-aluminosilicate pocket



As the dealuminating agent to replace the aluminum with silicon in the zeolite, SiF_6^{2-} was the anion of choice, and $NiSiF_6$ is a commercially available salt thereof. As expected from the design, $NiSiF_6/Al_2O_3$ was the first non-acidic catalyst which could oligomerize ethylene under mild conditions between 50-70°C without witnessing any deactivation, in strong contrast to all the catalysts listed above.[217] The intrinsic activity of the nickel atoms is enhanced and implies a large distribution of isomerized and co-dimerized products obtained by metallic pathways, reducing the butene selectivity compared with $NiSO_4/Al_2O_3$. More in-depth characterizations would be needed to fully understand the effect of silicon and fluorine atoms in proximity to the nickel active site.

5.4.2 *Acidity brought by sulfation of alumina*

An alternative to the acidity supplied by the precursor is the use of sulfated alumina. Instead of being present as $NiSO_4$ or as a sulfate containing salt in the metallic impregnation solution, sulfate can be supplied by alumination of the support before or after the deposition of nickel. Reference publications on these solids were reported by Zhang et al.[352,353]. The catalyst support is a nonporous fumed alumina possessing a specific surface area of 102 m^2/g. Nickel is either introduced by impregnation of a $Ni(NO_3)_2$ solution or by ion exchange with a nickel ammonium complex prepared by dissolving $Ni(NO_3)_2$ in ammonium hydroxide at a pH of 11. Both catalysts containing 1.5 to 3.5 wt% of Ni are dried at 120°C for 4 hours and calcined at 500°C for 4 hours. After that, sulfation is carried out by impregnation of a solution of $(NH_4)_2SO_4$ to reach 5.7 wt% sulfate loading. In the micro-reactor, the ethylene pressure is low at 0.7 bar, and so is the temperature, at 6°C. The catalysts still deactivate rapidly by adsorption of high molecular weight oligomers. Non-sulfated aluminas are inactive towards ethylene oligomerization. At such low pressure, ethylene conversion is high, more than 95 wt%. Nevertheless, selectivity remains centered on butenes, and especially 1-butene and 1-hexene, which is surprising compared with all previously described catalysts, which describe increasing 1-butene isomerization and codimerizations to branched hexenes with increasing ethylene conversion. Associated productivities are low under these very mild conditions and not representative of scalable productive conditions.

In the slurry mode in semi-open batch containing heptane, as described frequently by Hulea et al. with mesoporous materials or Nicolaides et al. with aluminosilicates[354], catalyst stability is improved by oligomer washing with the solvent at 6°C. At 50°C, catalysts deactivate much faster after 2 hours. The stability of this type of catalysts thus appears to be worse than mesoporous aluminosilicate materials containing nickel, which have stabilities of dozens of hours.

At any temperature, selectivities remain extremely high for 1-butene and 1-hexene with only traces of unidentified isomers which could be 2-butenes, internal and branched hexenes.

Only one attempt at higher pressure was carried out at 2 bar instead of 0.7 bar, which led to similar results. Sulfated aluminas thus appear to be very unstable catalysts, preventing their use under production conditions without being strongly deactivated. Even when operated in a liquid phase at 50°C, rapid deactivation is witnessed. These results inspired the licensing company AMT to patent their use in a reactive distillation mode under the same mild conditions for ethylene oligomerization.**[355]**

The catalysts described in these two articles by Zhang et al. were also thoroughly characterized by by Davydov et al. using FT-IR spectroscopy [356] and confirmed the importance of covalently bonding sulfate groups to the support on the activity of the catalyst. In-depth analysis of these results are detailed in chapter 6 dedicated to the determination of the active sites on the various nickel-containing heterogeneous catalysts.

In conclusion, aluminas are revealed as a versatile alternative to acidic aluminosilicates as activity can be provided by the precursor or by simple modification of the support. A deeper understanding of the oligomerization pathway could also lead to rational design of active sites by putting silicon and nickel in proximity. Depending on the nickel precursor and the nature of the aluminic supports, various selectivities can moreover be obtained from a high selectivity to butenes with $NiSO_4/Al_2O_3$ to a broad distribution of olefins with $NiSiF_6/Al_2O_3$.

Table 14. Alumina-supported nickel catalyst for olefin oligomerization (deposition technique = impregnation)

Ni precursor	Alumina	Ni loading (wt%)	Activation	Olefinic feed	T (°C)	T (°C)	Products (wt%)	Performance	Ref
$NiCl_2$	Commercial Alumina 207 m²/g; 0.51 ml/g	3.9	500°C Air	C_3	40	40	89 C_6	97 wt% conversion	20
$NiSO_4$	Commercial Alumina 207 m²/g; 0.51 ml/g	3.6	500°C Air	C_3	40	40	66 C_6	97 wt% conversion	20
$NiSO_4$	Commercial Alumina 197 m²/g; 0.45 ml/g	8	500°C Air	C_3	30	25	60 C_6	98 wt% conversion	345
$NiSO_4$	Commercial Alumina 197 m²/g; 0.45 ml/g	3.5	500°C Air	C_2	50	25	-	15 kPa drop pressure after 1 h	345
$NiSO_4$	Commercial Alumina 240 m²/g	6.4	500°C Air	C_2	20	0.4	100 C_4	1.4 $g_{oligomers}/g_{cata}/h$	349
$NiSO_4$	Commercial Alumina 200 m²/g; 0.47 ml/g	3.0	550°C Air	C_2	70^a	40	85 C_4 14 C_6 2 C_8	95 wt% conversion	217
$NiSiF_6$	Commercial Alumina 200 m²/g; 0.47 ml/g	0.7	550°C Air	C_2	70^a	40	62 C_4 26 C_6 12 C_8	75 wt% conversion	217
$NiSO_4$	Commercial Alumina 200 m²/g; 0.47 ml/g	3.0	550°C Air	1-C_4	70^a	40	100 C_8	13 wt% conversion	217
$NiSiF_6$	Commercial Alumina 200 m²/g; 0.47 ml/g	0.7	550°C Air	1-C_4	70^a	40	100 C_8	17 wt% conversion	217

5.5 NiO/Other supports

Besides the extensive studies on aluminosilicates and aluminic supports, many other supports have been investigated, mainly inspired by the solid acids frequently encountered in academic and industrial research into acid-catalyzed reactions for refining, petrochemistry or biomass upgrading.

As first reporters of mesostructured materials like Ni-MCM-41 or Ni/Al-MCM-41, Hartmann and Kevan have also used the electron spin resonance technique to characterize silicoaluminophosphates (SAPO-n with n = 5, 8, 11).[357] No reaction occurs with NiH-SAPO-34 and selectivity to butenes is quite low with NiH-SAPO-5, 8 and 11 at 80°C. Many side-products are formed, whereas ethylene conversion remains below 10 wt%. The decrease in channel size from 14-ring SAPO-8 to 12-ring SAPO-5 and 10-ring SAPO-11 causes a larger amount of side products to be formed because of slower product diffusion out of the channels, as could be also witnessed with microporous zeolites.

A patent by Mobil[358] describes silica pillared vacancy titanates (VTM) and compares their activites with NiO/ZSM-5 (Mobil[317]) and NiO/SiO_2-Al_2O_3 (Shell[359]). Catalytic tests were carried out in an autoclave at 150°C in the presence of dodecane. Ethylene was introduced at 35 bar and the pressure drop was measured after 3 hours. The oligomerization of ethylene catalyzed by Ni/VTM was poorly selective towards butenes; only 13 wt% of the overall products and 18 wt% of C_{16}^+ were co-produced. The productivity was similar to that of the aluminosilicates chosen as a comparative example under the same condition,s but Ni/VTM produced much heavier products.

Concomitantly with the investigation of $NiSO_4/Al_2O_3$, Sohn et al. developed many variations of this system. NiO-TiO_2 prepared by precipitation were active only after treatment with H_2SO_4 for ethylene oligomerization.[360] As expected, the catalytic activity of NiO-TiO_2/SO_4 was correlated with the increase in acid strength. Infra-red spectra indicated that sulfate anions are coordinated to Ti^{4+} and Ni^{2+}. Activating thermal treatment before the test should not exceed 400°C because of a structural change from the amorphous phase to the crystalline phase and a decrease in surface area. $NiSO_4/ZrO_2$ also proved active for ethylene oligomerization.[361,362] Aqueous solutions of $NiSO_4$ were impregnated onto ZrO_2. An interaction between $NiSO_4$ and ZrO_2 changes the transition of zirconia from amorphous to tetragonal. Like the sulfation of NiO-TiO_2, the activity is correlated to the enhancement of acidity provided by the sulfate group contained in the nickel precursor. Tungstated zirconias promoted with nickel were prepared by coprecipitation of $Ni(OH)_2$ and $Zr(OH)_4$ and subsequent impregnation of $(NH_4)_6(H_2W_{12}O_{40})$.[363,364] The most active catalyst was loaded with 25 wt% NiO and 15 wt% WO_3. The same results were obtained when impregnating $(NH_4)_6(Mo_7O_{24})$ with 15 wt% MoO_3. The formation of $Zr(MoO_4)_2$ phases were detected by XRD. Again, naked NiO-ZrO_2 without WO_3 or MoO_3 was inactive, like NiO-TiO_2. In contrast, $NiSO_4/TiO_2$-ZrO_2 was active at room temperature at 20 wt% loading with Ni and again, the correlation between acidity and activity can be concluded from this study.[365,366]Zirconia promoted with iron oxide was prepared by adding ammonia slowly to a mixed aqueous solution of an iron nitrate and zirconium oxychloride and used as a support for the impregnation of 15 wt% of $NiSO_4$.[367] A similar transition of zirconia was observed. The addition of Fe_2O_3 up to 5 mol% enhanced the acidity and surface area to provide the catalyst with enough activity to oligomerize ethylene at room temperature. $NiSO_4/Fe_2O_3$ alone was also active for ethylene oligomerization with a maximum activity at a high nickel loading of 20 wt%.[368] Zirconia has also been promoted by cerium after the coprecipitation of zirconium oxychloride and cerium nitrate and impregnating the resulting solid with $NiSO_4$.[369] The maximum activity was achieved with 10 wt% $NiSO_4$ and only 1 mol% CeO_2. CeO_2 plays a similar role to Fe_2O_3 by stabilizing zirconia, enhancing the specific surface area and increasing the acidity.

Two nickel-containing zincosilicates (Ni-CIT-6 and Ni-Zn-MCM-41) are synthesized and compared with two zeolite-derived catalysts Ni-HiAl-BEA and Ni-USY. They are used as catalysts to oligomerize propylene into hexenes and nonenes.[370] The oligomerization of propylene is carried out between 180 and 250°C, at atmospheric pressure. Under these conditions, all of the catalysts are active and present conversions of propylene ranging from 3 to 16 wt%. Zincosilicates exhibited higher selectivities to dimers and trimers than aluminosilicates, whereas the latter produced cracking hydrocarbons. Zincosilicates thus exhibited higher linear-to-branched hexene isomer ratios (typically 1.0-1.5). The mesoporosity of Ni-Zn-MCM-41 allows the catalyst to exhibit the best reaction behavior.

Similar overall information can be obtained from these supports: some acidity helps the nickel site to be active, and the mesoporosity of the catalysts avoids blocking of the pores and a premature deactivation of the catalyst. It is nonetheless interesting to highlight the large diversity of the materials that are able to promote olefin oligomerization when nickel is deposited on them.

5.6 Conclusion and challenges

Heterogeneous nickel-catalyzed oligomerization has attracted great attention in the development of ever more active and selective catalysts, mainly towards ethylene, propylene and butene transformations, to provide immobilized versions of efficient homogeneous catalytic systems. Starting from silica supports with low activity and high nickel loadings, increasing knowledge in material science has led to improved performances with reduced percentages of nickel when deposited on or impregnated into aluminosilicates (amorphous, crystalline and/or mesoporous aluminosilicates) and aluminas. An adequate choice of nickel precursors and aluminic carriers has enabled oligomerization under milder conditions with better selectivities for dimerization, especially for ethylene, for which dimer selectivity is hard to achieve. Despite the tremendous progress made in the last few years, homogeneous ethylene and propylene dimerization is still preferred for industrial implementation when specific selectivity in terminal olefins or in dimers, trimers or tetramers are demanded. Butene dimerization is the only reaction where a technological choice exists in both homogeneous and heterogeneous modes. Regarding ethylene oligomerization, the selectivity towards short and overall terminal olefins at high conversions still remains a serious challenge in nickel heterogeneous systems. Since active nickel catalysts are often composed of an acidic surface (aluminosilicates, sulfated alumina), 1-butene isomerization to 2-butenes readily occurs. Surface acidity also favors the cationic oligomerization of reactive olefins such as propylene or butenes, resulting in coke formation and catalyst deactivation. An ideal compromise between controlled acidity and meso/macroporosity to avoid pore filling, as well as the precise localization of promoters, for example placing silicon in the proximity of the nickel center, are critical parameters for active and stable catalysts.

As an efficient and rare catalyst inducing selectivity for butenes, especially 2-butene, $NiSO_4/Al_2O_3$ could be used to compete with homogeneous Phillips catalysts $NiCl_2(PBu_3)_2$ for the production of 1-butene and 2-butene mixtures with limited hexene production. Nevertheless, in the case of ethylene conversion with high productivities in heterogeneous mode, exothermicity of the reaction has to be dealt with and represents a tough challenge that cannot yet address existing process technologies. Homogeneous technologies indeed allow an easier evacuation of the heat of reaction, rendering processability feasible at high selectivities. Process innovation thus has to be carried out in parallel with the improvement in catalyst stability and selectivity..

Questions about the nature of the nickel active sites in heterogeneous catalysis have long been under debate, as along with those regarding the mechanistic pathways that can be followed to rationalize observed selectivities. Exciting improvements in the fields of analytical techniques, being ex situ, in situ or operando, combined with the exponentially growing power of surface molecular modelization and DFT calculations, has recently brought about a renewed interest in the identification of the active sites governing the reactivity and selectivity of olefin oligomerization. The parallels that can be drawn between homogeneous and heterogeneous catalysis can be taken advantage of in order to gain a deeper insight into the identification of the actual active sites and the determination of the mechanism governing selectivity.

6 Active Sites and Mechanism(s)

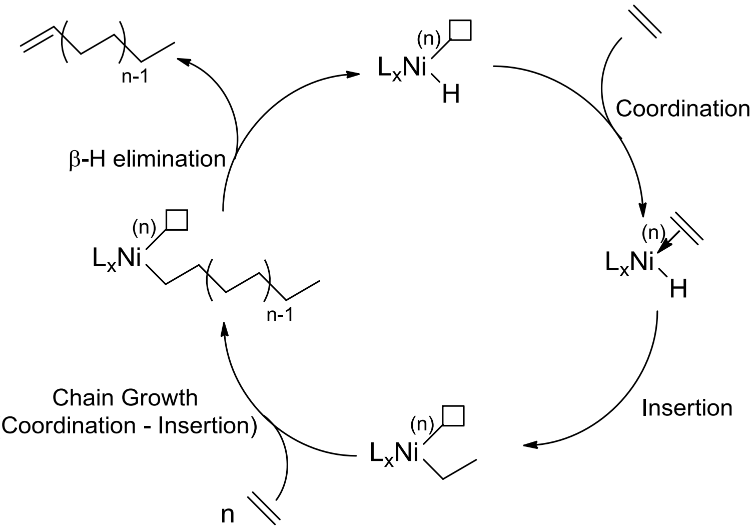
6.1 Introduction

The generation of active species to trigger nickel-catalyzed olefin dimerization and oligomerization has been widely studied in homogeneous and heterogeneous catalysis since the discovery of the "nickel effect" by Ziegler.[7,17,52,129,371–376] As well-defined isolated species, homogeneous complexes have generally been easier to characterize than supported nickel oxides which exist in different oxidation states within various nickel nanoparticle sizes. Nearly all of the homogeneous investigations refer to the presence of a nickel(II) hydride or an alkyl species as a common feature lying at the heart of olefin catalytic transformations. Nickel alkyl species have only very recently been proposed as promoters of olefin oligomerization in heterogeneous catalysis. The absence of alkylaluminum activators and the variety of nickel oxidation states on the surface of oxide supports have long rendered a clear-cut conclusion elusive.

6.2 Mechanisms

The catalytic mechanism associated with nickel-hydride and nickel-alkyl species is the well-known Cossee-Arlman mechanism, proposed long ago for homogeneous catalysis and more recently for heterogeneous catalysis. The corresponding catalytic cycle is described for the transformation of ethylene (Scheme 8). The cycle starts with a nickel hydride species, and involves three main elemental steps: olefin coordination, olefin insertion into the nickel hydride or alkyl intermediate, and β-H elimination, providing the corresponding oligomer, and regenerating the active species. For each nickel alkyl intermediate generated along this mechanism, two competitive paths exist, *i. e.* propagation through ethylene insertion, or termination by means of β-H elimination, leading to a Schulz-Flory distribution.[377] Controlling this competition is the key to further industrial developments. Favoring chain growth would lead to highly linear long chain oligomers, as occurs in the SHOP process, while promotion of the termination step would generate 1-butene, a major comonomer in the polyethylene industry. It is worth mentioning that no industrial processes for 1-butene production have emerged so far either in homogeneous catalysis or in heterogeneous catalysis, highlighting the difficulty in controlling such processes and understanding how to promote one elementary step compared with another. The competition between insertion and elimination has been scrutinized for selected systems, through DFT and kinetic studies (Section 6.5). Nonetheless, these studies have not offered clear perspectives regarding what is mandatory to make a highly effective and selective catalyst pop out. Additionally, many side reactions are interlinked with this ideal catalytic cycle. As an example, isomerization is readily carried out by nickel hydride species, or co-oligomerization between ethylene and the longer olefins produced. However, and despite its importance, a distinct lack of detailed studies exists which measures and compares the kinetics of all these elemental steps. This deficiency is likely to be due to the high level of challenge set by this study. One of these difficulties is that long olefins, such as hexenes in ethylene oligomerization, may be produced through different pathways, hampering determination of the mechanism using the product distribution analysis.

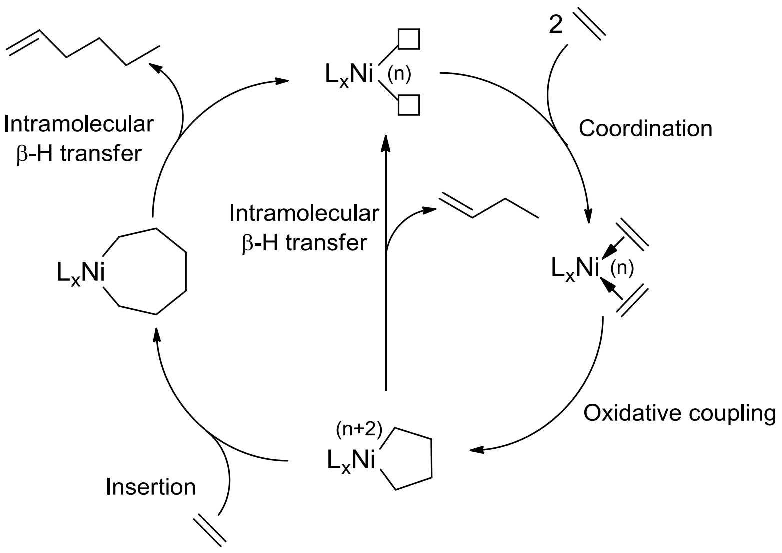
Scheme 8. Cossee-Arlman mechanism.



Within this type of mechanism, co-oligomerization reactions occurring at high ethylene conversions have to be taken into account, althoughthey are often underestimated in academic studies.

The Cossee-Arlman mechanism is often put into perspective with the metallacyclic mechanism. The latter postulates an active species having two vacant sites, allowing the coordination of two ethylene molecules. Thus, oxidative coupling occurs by the formation of a nickellacyclopentane. Further intramolecular β-H transfer leads to 1-butene release and regeneration of the active species. However, the nickellacyclopentane may also react with an extra molecule of ethylene, leading to higher nickellacycles that can degrade to 1-hexene and the active species. This mechanism is described for other transition metals such as titanium and chromium,[378] while for nickel, no clear experimental evidence has been provided. Only DFT models suggest that a metallacyclic mechanism could be energetically feasible, as described in paragraph 6.5.

Scheme 9. Metallacyclic mechanism.



As detailed previously, the oligomerization mechanism and nickel active sites are intimately connected. Mechanistic propositions in heterogeneous catalysis have only recently emerged, with dissonant opinions as regards a Cossee-Arlman or a concerted oxidative coupling mechanisms. Most recent studies tend to rule out the oxidative coupling eventuality and propose a common mechanism between a homogeneous and a heterogeneous mechanism. It is thus worthwhile detailing those studies for both types of catalysis.

Based on experimental results and product selectivities, Feldblyum et al.[379] and Chauvin et al.[20] suspected equivalent mechanisms in both the homogeneous and heterogeneous nickel-based oligomerization of propylene. Inspired by this study, we carried out a systematic comparison of homogeneous ($Ni(acac)_2$/EADC) and heterogeneous catalysis ($NiSO_4/Al_2O_3$ and $NiSiF_6/Al_2O_3$) to enrich mechanistic understanding thanks to a thorough analysis of primary and secondary product distributions obtained for ethylene oligomerization under similar thermal and pressure conditions. Product distributions only differed in the more pronounced amount of isomerized products on the more acidic heterogeneous catalyst. These results have led us to postulate a common mechanistic proposition based on a degenerate polymerization mechanism or Cossee-Arlman and active sites proposition. [217]

An experimental investigation used to build a Single-Event MicroKinetic (SEMK) model was carried out by Toch et al.[286] The model was developed on the assumption that a Cossee-Arlman mechanism involving a nickel-ethyl species was predominant. Experimental results described and fitted well with the model without systematic deviations.

Andrei et al. have proposed a mechanism involving a metallacyclic pathway,[333] which was unprecedented in nickel supported-catalyzed oligomerization. A diversity of nickellacycles have been investigated by a quantum mechanical perspective on heterogeneous MCM-41, including some energetically reachable nickel clusters on specific 3T and 2T sites. No comparison with Cossee-Arlman mechanism was provided.[380]

A big step forward in dispelling doubt was provided by Brogaard and Olsbye based on an exhaustive density functional theory (DFT) study.[381] Every conceivable pathway was scanned energetically from ethylene to 1-butene on SSZ-24 zeolite with a well-defined structure. Of all of them, Ni^{2+} active sites implicated in a Cossee-Arlman mechanism appeared to be the most plausible. A sacrificial ethylene molecule induces the formation of the desired Ni-ethyl species (Figure 45). The acidity of the support can play a role in olefin protonation to favor the first insertion of ethylene. By analogy, this association could play a role in external activation in homogeneous catalysis. The synergetic effect of acid sites and nickel sites has recently been highlighted for MCM-56 and ITQ-1 zeolites.[382]

As energetically unattainable metallacyclic pathway has been ruled out, as it has been in homogeneous catalysis with Ni(II) based catalysts. Even though SSZ-24 zeolite is a representative zeolite framework for fundamental investigation, this zeolite structure has never been investigated experimentally for olefin oligomerization and experimental counterparts to DFT calculations would have been desirable.

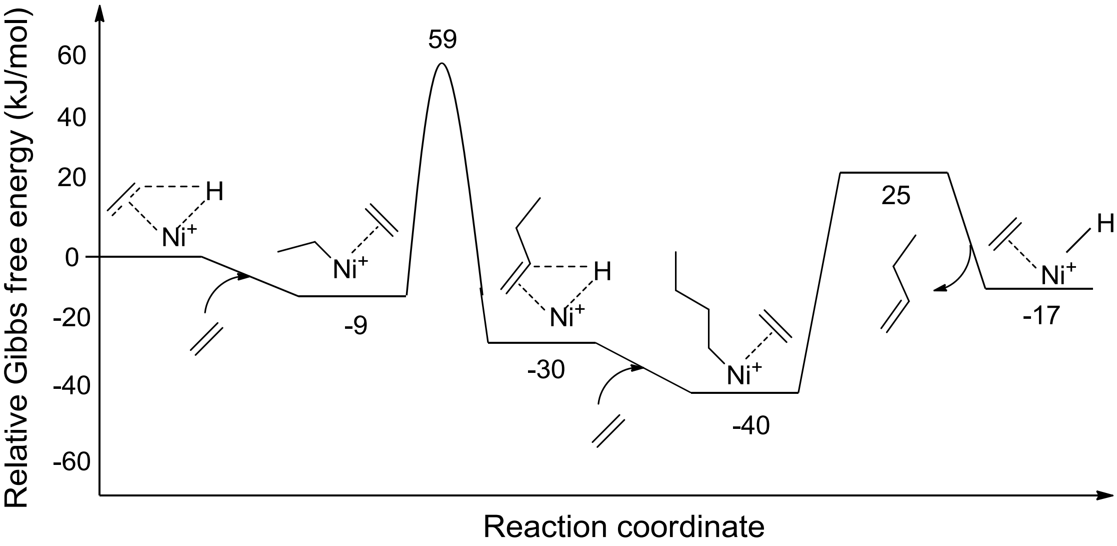


Figure 45. Mechanistic proposition for Ni/SSZ-24 catalyzed ethylene oligomerization based on DFT

An experimental study concluding a Cossee-Arlman mechanism was thus later provided by the same authors in collaboration with Berlier et al., relying on a FTIR spectroscopy study with CO as the probe molecule. [383] Gounder et al. go along with this opinion thanks to a multi-technique experimental investigation using Ni-exchanged Beta zeolites.[384] Selective poisoning assays with Li^+, NH_4^+ combined with the use of zincosilicate supports and H_2-D_2 scrambling unequivocally provide evidence for a Cossee-Arlman mechanism as the main route for alkene dimerization.

In parallel, by comparing the selectivities obtained with Ni/zeolites and Ni/mesoporous materials, Martinez et al. explain that Schulz-Flory linear primary products are formed through a mechanism similar to homogeneous Cossee-Arlman pathway, whereas branched C_{6+} olefins rely more on acidic carbocationic mechanisms promoted by surface acidity. Online analysis using mass-spectrometry and FTIR-CO spectroscopy allowed the authors to propose a Cossee-Arlman-type mechanistic pathway via a sacrificial ethylene activation on the support.[385] Most recent studies thus converge their experimental, theoretical and analytical observations towards divalent nickel atoms activated by a sacrificial ethylene and by the support to promote a degenerated polymerization mechanism, or Cossee-Arlman mechanism.

More interestingly again, even if a common mechanism is postulated, the way to give rise to the active sites differs greatly. In heterogeneous catalysis, no alkylaluminum is needed and the controlled synthesis of nickel-alkyl precatalyst has never been reported. Since mechanism and active sites natures are intimately correlated, the next paragraphs are devoted to the quest of active site identification in homogeneous catalysis first, and then in heterogeneous catalysis.

6.3 Active site nature and generation in homogeneous and heterogeneous catalysis

Several activation methods have been developed under homogeneous conditions depending on the precatalyst considered. A series of milestones accompanied the quest for more stable, active and selective catalysts over more than 60 years, and progress in the comprehension of the fundamental mechanisms involved. Three main classes may indeed be described to generate the active Ni-H or Ni-C species: i) non-organometallic nickel complexes requiring an alkyl aluminium activator to form Ni-C or Ni-H bond or ii) organonickel precatalysts requiring an activator to form the catalytically active species, and iii) readily active single-component organonickel species under ethylene pressure and possible heating. It should be noted that Ni(0) precursors can also be considered with some Lewis acid activators, although clean and easy-to-characterize activation processes are accessible.

Compared with homogeneous catalysis, the identification of Ni active sites responsible for ethylene oligomerization and the determination of which mechanism occurs with Ni-based heterogeneous catalysts has witnessed fewer comprehensive studies. Despite more than seven decades of experimental olefin oligomerization, a clear-cut determination of the actual nickel active sites before ethylene coordination and during oligomerization process has yet to be unequivocally claimed. Most intriguing is that nickel active site generation in heterogeneous catalysis does not demand alkylaluminum co-catalysts of any sort, unlike Ziegler-type homogeneous systems, which are activated with alkylaluminum species. This highlights, if necessary, the critical role of the support. The preparation of nickel-containing catalysts without exception involves impregnation, deposition or exchange with Ni(II) salts or precursors. After that, high-temperature treatment for activation is systematically required and complicates the localization and distribution of nickel atoms.[386]

6.3.1 *Activation in homogeneous catalysis*

6.3.1.1 First class of catalytic systems: Ziegler type systems consisting of non-organometallic Ni complexes and activators

The first of the three main classes of activations, *i.e.* the Ziegler activation, is the most conventional path in academia and industry. It consists in the reaction of a nickel salt with an organometallic compound, usually an organoaluminum. In fact, a limited number of synthetic steps are required to access the components, and the associated *in situ* catalytic procedures are efficient and easy to scale up. But *in situ* catalyst activation greatly complicates comprehensive active catalyst studies, since the highly reactive species formed are believed to be ionic pairs, which are difficult to isolate. However, contradicting reports also exist, mentioning neutral or sometimes bimetallic species, further underlining a diversity of active complexes. They also highlight that the role of the co-catalyst is crucial during the whole catalytic process, although this is difficult to grasp. To illustrate the diversity of possible active species according to the nature of the co-catalyst and Ni precursors, some selected examples are given below and summarized in Table 15. Pozdeeva et al. published an electrochemical study of a catalytically active Ni system, formed by [Ni(acac)$_2$], in the presence of phosphines or phosphites and $AlEt_3$ as co-catalyst.[387] A comparison with the electrochemical properties of model compounds led them to the conclusion that no nickel reduction occurred and that the active catalyst may be tentatively assigned to a bimetallic species, $[NiEtL_3][AlEt_4]$. Nickel K-edge XAS studies on the efficient propylene dimerization catalyst $[NiCl_2(PEt_3)_2]$, activated by $Al_2Me_3Cl_3$, reported by Evans et al., show the presence of two carbon and two phosphorous atoms in the first coordination sphere and a Ni-Al distance of 2.97 A, indicative of a Ni-C-Al interaction.[388] In line with these observations, Dent, Hagelstein et al. observed the presence of Ni-C-Al interactions by EXAFS experiments on $[NiCl_2(PEt_3)_2]$ and $AlEt_3$, or $Al_2Me_3Cl_3$ samples.[389]

With $[Ni(acac)]_2$ under catalytically relevant conditions, *i.e.* in presence of $AlEt_2OEt$ and 1-hexene, XAS studies performed by Salvini et al. highlighted the alkyl exchange between the aluminum and the nickel, leading to [NiR(alkene)(acac)] as the main species.[390] De Souza et al. used EXAFS to study the well-known catalytic system $[Ni((1,4\text{-bis}(2,6\text{-diisopropylphenyl})\text{-acenaphtenediimine}))Cl_2]$ associated with MAO in the presence of 1-decene.[391] The first coordination sphere presents two carbon and two nitrogen atoms. The low number of carbon atoms measured, compared with the expected cationic intermediate $[Ni(\alpha\text{-diimine})(R)(1\text{-decene})]^+$, is explained by the presence of multiple nickel species, some being unsaturated, like $[Ni(\alpha\text{-diimine})(R)]^+$. Interestingly, a Cl atom is localized at *ca.* 3.5 Å, probably indicative of an ion pair in close contact.

Direct protonation of Ni(0) complexes is also suitable for the generation of active species. Spencer et al., as an example, have prepared a series of cationic ethylnickel complexes, stabilized by β-agostic interaction, by addition of HBF_4 to $[Ni(P,P)(\eta^2\text{-}C_2H_4)]$ in which (P,P) = $t\text{Bu}_2P(CH_2)_2Pt\text{Bu}_2$, $t\text{Bu}_2P(CH_2)_3Pt\text{Bu}_2$ or $o\text{-}(t\text{Bu}_2PCH_2)_2C_6H_4$, and demonstrated that an ethylene migratory insertion step occurs during this process.[392]

A dicationic nickel(II) complex $[Ni(MeCN)_6][(BF_4)]_2$ has been reported by de Souza et al. as an effective ethylene oligomerization catalyst when associated to $AlEt_3$ or $AlEt_2Cl$,[393] however no further information regarding the nature of the active catalyst involved was reported.

Table 15 : Importance of the role of the co-catalyst : examples of characterized active species formed by the reaction of Ni(II) precursors and different co-catalysts

Ni(II) precursors	Co-catalyst	Identified Active species	Characterization method
$Ni(acac)_2$ + L= phosphine or phosphite	$AlEt_3$	$[NiEtL_3][AlEt_4]$ Cationic Ni-C	Electrochemistry
$NiCl_2(PEt_3)$	$Al_2Me_3Cl_3$	Ni-C-Al bimetallic species	K-edge XAS
$Ni(acac)_2$	$AlEt_2OEt$	[NiR(alkene)(acac)] Neutral Ni-C	XAS
$[Ni((1,4\text{-bis}(2,6\text{-diisopropylphenyl})\text{-acenaphtenediimine}))Cl_2]$	MAO	$[Ni(\alpha\text{-diimine})(R)(1\text{-decene})]^+$ Cationic Ni-C	EXAFS

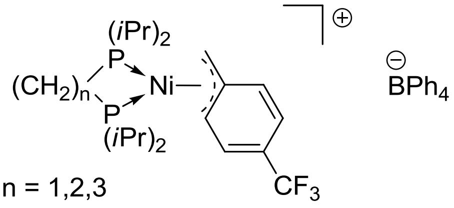
Another way of generating Ni-active species is to start with Ni complexes already containing a Ni-carbon bond. Activation of these organometallic complexes is carried out by addition of a co-catalyst that often generates cationic active complexes.

6.3.1.2 Second class of catalytic systems : organometallic Ni complexes requiring an activator

η^3-Allylnickel halide complexes, thanks to their great stability and their η^3 to η^1 coordination switch offering a vacant site, have been widely employed as precatalysts since the origins of nickel-catalyzed oligomerization. The seminal work by Wilke et al. described the ^1H NMR detection of an active bimetallic complex, [Ni(η^3-allyl)(μ-X)Al(R)$_n$X$_{3-n}$] where X = Cl, Br or I, and n = 0, 1, 2.[373] A family of more active phosphine-based species have also been reported, including the X-ray structural determination of some of these complexes, such as [Ni(η^3-allyl)(PCy$_3$)(μ-Cl)Al(Me)Cl$_2$].[394] Additional phosphine incorporation or use of bis(diphenylphosphino)ethane as a ligand leads to inactive systems unless an excess of alkylaluminum halide is used. A possible hypothesis to explain this phenomenon considers that the active species has to contain only one coordinated phosphine ligand. The nature of the bridging halide atom (μ-X) in such bimetallic structures is of tremendous importance, as it influences the strength of the interactions involved and thus the reactivity of the system. Webster et al. confirmed, by using EXAFS, the bimetallic nature of the species formed by reaction of [Ni(η^3-C$_3$H$_5$)(PPh$_3$)Br] with AlEt$_3$ and, in contrast to the previous report, four carbon and one phosphorus atoms in the coordination sphere, as in [Ni(η^3-allyl)(PPh$_3$)(μ-C$_2$H$_5$)AlEt$_2$X] (with X = Br or Et).[395]

Maruya et al. compared the impact of the use of BF$_3$.Et$_2$O and NaBPh$_4$ as activators on a [Ni(PPh$_3$)$_2$(1-naphthyl)Br] complex. They led, respectively, to a selective ethylene dimerization catalyst and a weakly active species, suggesting a crucial role for the halogen, probably remaining in the coordination sphere.[396]

As an example of the effect of the ligand structure, Campora et al. described the synthesis of readily active cationic η^3-benzylnickel complexes **85** bearing diphosphine ligands. These species were obtained by oxidative addition of benzyl chloride on Ni(0), followed by halogen abstraction with NaBPh$_4$.[397] The product distribution depends on the bite angle of the disphosphine ligand. Large amounts of polymer were obtained with 1- and 2-carbon spacers between the two phosphorous atoms, while 3-carbon spacer-based catalysts produced up to C$_{22}$ oligomers. Non-coordinating anions are also successfully introduced with thallium salts, such as TlPF$_6$, leading to isolable but also active allyl- and methallylnickel complexes, as reported by Tkatchenko and co-workers.[398]

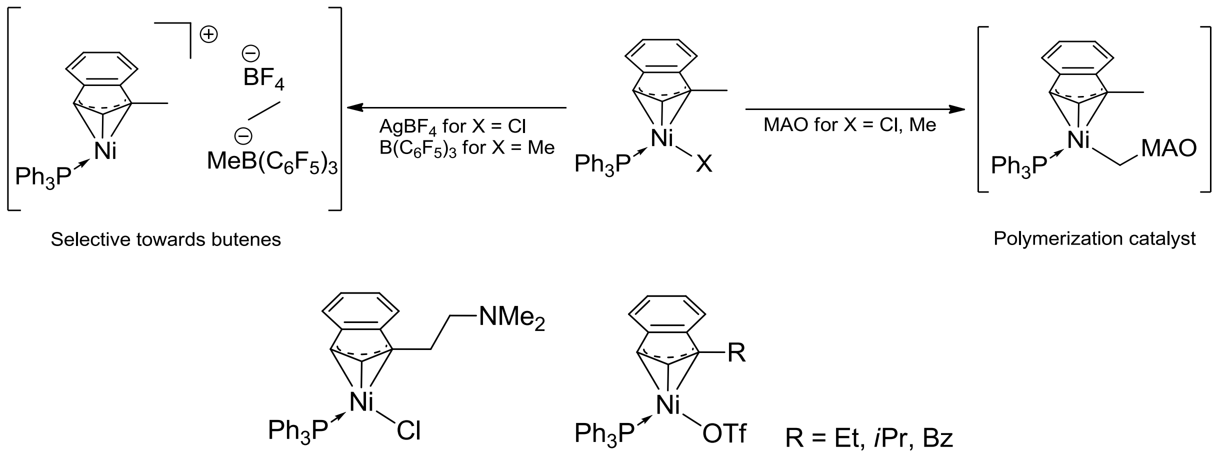


85

Figure 46. Examples of isolated cationic allylnickel complexes

Collins et al. studied the activation of [Ni(1-Me-Ind)(PPh$_3$)X] (X = Cl or Me) that are inert towards ethylene.[399] However, chloride and methyl abstraction from the corresponding precatalysts with AgBF$_4$ and B(C$_6$F$_5$)$_3$ respectively led to active species, producing butenes. These species are likely to be the cationic [Ni(1-Me-Ind)(PPh$_3$)]$^+$, with BF$_4^-$ or MeB(C$_6$F$_5$)$_3^-$ as counter-ions (Scheme 10). The active species is suspected to be the cationic Ni–H species, which can occur by insertion of ethylene into the Ni–Ind bond followed by beta-H elimination to give the corresponding vinyl indene. In contrast, the addition of MAO to either chloride or methyl complexes provides a species displaying ^{1}H and ^{31}P NMR chemical shifts, similar to [Ni(1-Me-Ind)(PPh$_3$)Me], although it is active for ethylene polymerization. A non-cationic bimetallic nickel-aluminum structure with a bridging methyl group is proposed to be the active species, the MAO weakening the Ni-Me bond. Similar observations are reported by Groux's group with functionalized indenyl complex.[400,401]

Scheme 10. Activation of [Ni(1-Me-Ind)(PPh$_3$)X]



The use of Na(BAr$_f$)$_4$ ((BAr$_f$)$_4$ = B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4^-$) is extensively described by Brookhart et al. [51,402] to access cationic allylnickel complexes. As an example, phenacyldiarylphosphine-based cationic nickel species with (BAr$_f$)$_4^-$ as the counter-ion were isolated (Figure 47).[403] Modification of the diarylphosphino moiety demonstrate the impact of the steric hindrance on the catalytic outcome. Bulkier ligands lead to polymer formation, while less hindered phenyl groups steered towards butenes. This phenomena is recurrent in nickel-[404] or even iron-based[405] oligomerization/polymerization catalysis.

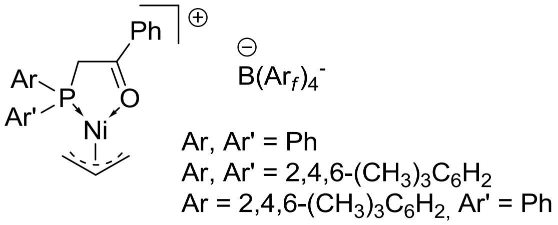


Figure 47. Examples of isolated cationic allylnickel complexes

Cationic alkyl- or arylnickel complexes bearing phosphines appear also as suitable candidates for ethylene transformation. A series of [Ni(2,4,6-Me$_3$C$_6$H$_2$)(CH$_3$CN)(PR$_3$)$_2$][BF$_4$] complexes with R = Et, Bu, *i*Bu or Bz (benzyl), formed by reacting the corresponding nickel halide with TlBF$_4$, presents interesting turnover numbers towards ethylene.[406] Surprisingly, Tkatchenko et al. also mention that the corresponding neutral nickel halide complexes catalyze ethylene, although turnover numbers are more modest.

Another source of cationic alkylnickel catalysts is the corresponding dialkylnickel complexes. Brookhart and co-workers reported effective alkyl abstraction on diimine-[407] or diphosphine-based[408] complexes by protonation with a Brønsted acid, H(OEt$_2$)BAr$_F$. This reaction leads to the cationic nickel species, characterized at low temperatures by NMR spectroscopy (Figure 48).

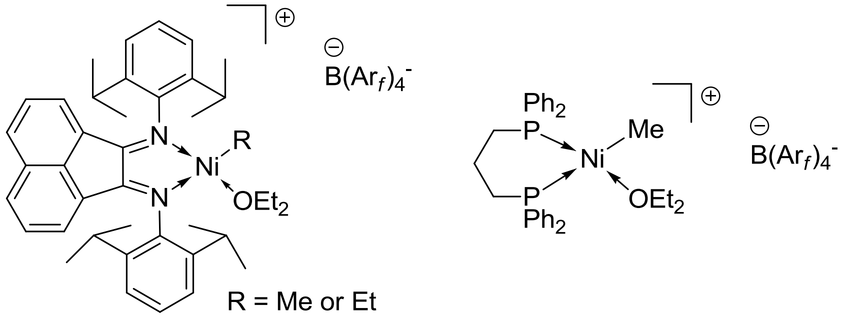


Figure 48. Examples of isolated cationic alkylnickel complexes

Finally, the last class of isolated Ni-active species consists of neutral or zwitterionic organometallic complexes. No co-catalysts are needed for activation of these systems.

6.3.1.3 Third class of catalytic systems : single site organometallic complexes

Single-component catalysts are defined by the absence of a co-catalyst to trigger their reactivity towards olefins. They are generally built with a bidentate anionic ligand and present a metal-carbon bond. The cornerstone of this class of catalysts is based on anionic (P,O) ligands, as reported by Keim (Figure 49).[409] Such well-defined active species are obtained by reaction of ylide $Ph_3P{=}CH{-}C(O){-}Ph$ with [Ni(cod)$_2$]/PPh$_3$ or [Ni(PPh$_3$)$_4$]. The corresponding allyl- and cyclopentadienyl-based complexes bearing the same P,O ligands may be obtained from a nickel(II) source, *i.e.* [Ni(η^3-allyl)$_2$] and [Ni(η^5-cyclopentadienyl)$_2$], respectively.[410,411] Active nickel hydride P,O-based complexes, although observable,[412] are rather unstable species.[413] However, the introduction of PCy$_3$ during the synthesis with $Ph_2PCH_2C(CF_3)_2OH$ and [Ni(cod)$_2$] enabled the stabilization and X-ray determination of [Ni($Ph_2PCH_2C(CF_3)_2O$)(PCy3)H].[414]

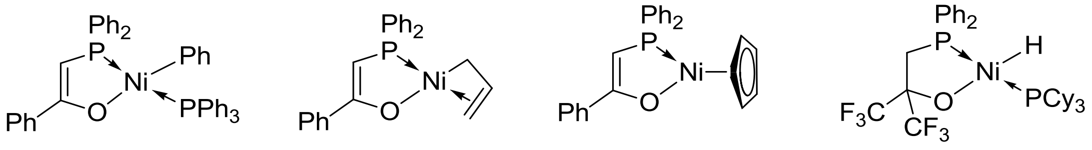
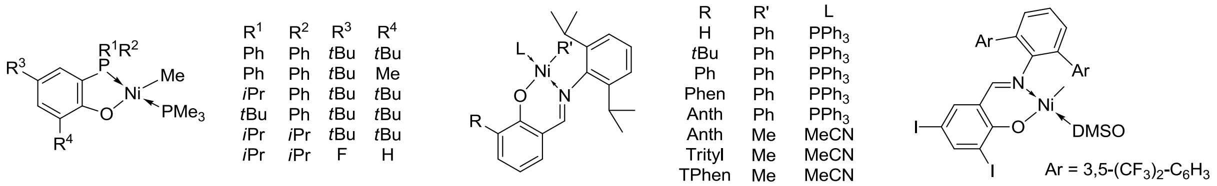


Figure 49. Examples of single site organometallic active nickel complexes

Numerous single-component organonickel compounds are obtained by reacting the well-known [Ni(cod)$_2$] precursor with protic ligands, and are generally isolated as cyclooctenyl complexes. However, the formation of such active species is not straightforward. One path consists in the formation of a nickel hydride, followed by migratory insertion into the alkene. Zetterberg et al., supported by deuterium labelling experiments, envisaged an alternative path where nickel(0) is proposed to increase the basicity of the 1,5-cyclooctadiene, allowing direct protonation of one of the alkenes by a weak acid, namely 1,1,1,5,5,5-hexafluoroacetylacetone.[415]

Phenoxy-based single-component catalysts have also been developed (Figure 50). (P,O) chelate complexes are synthesized from phosphanylphenols and [NiMe(PMe$_3$)(μ-OMe)]$_2$, as reported by Heinicke, Klein, Keim et al.[416] Meanwhile, Grubbs et al. reported the replacement of the phosphino moiety with an imino functional group containing a harder heteroatom (N instead of P), by reaction of the corresponding sodium phenolates and [NiClPh(PPh$_3$)$_2$].[56,417] [NiBrAr(L)$_2$] (Ar = *p*-tolyl or Ph and L = PPh$_3$, PCy$_3$ or PBz$_3$) as the source of nickel to generate readily active species in association with a bidentate anionic ligand such as pyridine-carboxylate or pyridine-acetate has been extensively used.[418] Mecking et al. reported closely related structures obtained from [Ni(Me)$_2$(TMEDA)] and the iminophenol.[419]



R^1	R^2	R^3	R^4
Ph	Ph	*t*Bu	*t*Bu
Ph	Ph	*t*Bu	Me
*i*Pr	Ph	*t*Bu	*t*Bu
*t*Bu	Ph	*t*Bu	*t*Bu
*i*Pr	*i*Pr	*t*Bu	*t*Bu
*i*Pr	*i*Pr	F	H

R	R'	L
H	Ph	PPh_3
*t*Bu	Ph	PPh_3
Ph	Ph	PPh_3
Phen	Ph	PPh_3
Anth	Ph	PPh_3
Anth	Me	MeCN
Trityl	Me	MeCN
TPhen	Me	MeCN

Figure 50. Examples of neutral active nickel complexes bearing bidentate monoanionic ligands

The gap between neutral and cationic active species is filled by the introduction of zwitterionic active species. Described by Bazan et al., the addition of one equivalent of $B(C_6F_5)_3$ to the neutral benzylnickel complex, bearing a 2-(diphenylphosphino)benzoate ligand, increases the electrophilicity of the nickel center by formation of the zwitterionic (P,O)-based complexes, readily active for ethylene oligomerization (Figure 51).[420,421] Similarly, they also reported the formation of the zwitterionic O,N-based complexes.[422] Compared to the neutral catalysts based on 4-(2,6-diisopropylphenylimino)acetylacetonate, a 100-fold higher activity was measured. The increase in the nickel electrophilicity is likely to enhance olefin insertion. This strategy, *via* zwitterionic species, may also promote ethylene oligomerization over other reactions, as demonstrated by Breuil et al. with outer-sphere Lewis acid addition onto secondary phosphine oxide-based complexes.[102]

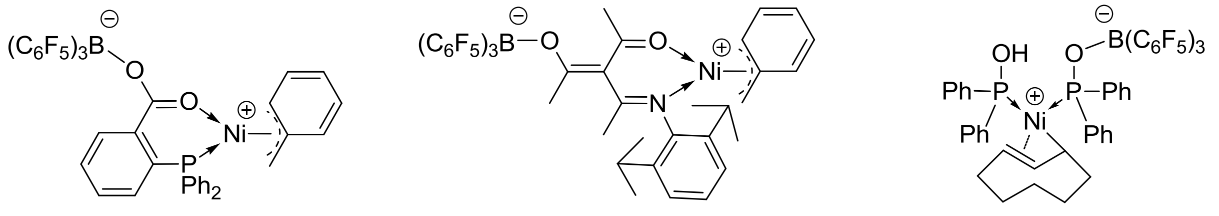


Figure 51. Zwitterionic (P,O)-based isolated active complexes

All these examples relate to cationic, zwitterionic or neutral Ni(II) active species having a Ni-C bond as an entry point into the catalytic cycle.

All of the previously described nickel catalysts are Ni(II) complexes. The final active species contain a Ni-C bond into which the first olefin insertion can occur. The consideration of other Ni oxidation states as active species or the absence of metal-carbon bond is an ongoing and strongly debated process.

Nickel(0) complexes have been employed for olefin oligomerization. Dekker and de Hann, for example, reported a catalyst arising from [Ni(POPh$_3$)$_4$] and a Lewis acid as $AlCl_3$ in chlorobenzene, although no further description of the active species is given.[423]

Kraikivskii et al. studied, by using EPR, the reaction of $AlBr_3$ with [Ni(PPh$_3$)$_4$] or [Ni(P(OPh)$_3$)$_4$] leading to Ni(0) oxidation, and the formation of neutral Ni(I) bromide complexes which are inert towards ethylene.[424] A different outcome is raised by the authors when, in presence of $BF_3.Et_2O$, a cationic Ni(I) with BF_4^- as the counter-ion is formed and proposed to be the relevant active catalyst.[425] Additionally, alcohols are presented by Saraev et al. as promoters of such Ni(0) systems,[426] making possible the generation of an active Ni(II) hydride and/or a coordinatively unsaturated cationic Ni(I) species, described as being ten times more active catalysts than the Ni(II) hydride.[427] Based on a related system, Kraikivskii et al. proposed that when [Ni(cod)$_2$] is reacted with $BF_3.Et_2O$, ethylene can be dimerized with a Ni(I)/Ni(III) metallacyclic mechanism.[428] Schmidt et al. focused on the same [Ni(PPh$_3$)$_4$] - $BF_3.Et_2O$ system, but he postulated the presence of a Brønsted acid impurity that could form the catalytically active Ni(II) hydride species.[429] Increase of Brønsted acid content and its effect over time, from the reaction of $BF_3.Et_2O$ with water (as a solvent impurity), was demonstrated in a more detailed study.[66] A complementary study carried out on phosphine- and diimine-based nickel complexes with various oxidation states (0, +1 and +2) associated with Lewis acid consolidated the role of Ni(II) hydride as an active catalyst, with the oxidation of Ni(0) species and disproportionation of Ni(I) being emphasized.[67]

6.3.2 *Active site identification in heterogeneous catalysis*

Compared with homogeneous catalysis, the identification of Ni active sites responsible for ethylene oligomerization and the determination of which mechanism occurs with Ni-based heterogeneous catalysts has witnessed few comprehensive studies. Despite more than seven decades of experimental olefin oligomerization, a clearcut determination of the actual nickel active sites before ethylene coordination and during the oligomerization process is still to be unequivocally claimed, if possible. Most intriguing is that nickel active site generation in heterogeneous catalysis does not demand an alkylaluminum co-catalyst of any sort, unlike Ziegler-type homogeneous systems, which are activated with alkylaluminum species. This highlights, if necessary, the critical role of the support. Preparations of nickel-containing catalysts without exception involve the impregnation, deposition or exchange with Ni(II) salts or precursors. After that, high-temperature treatment for activation is systematically required and complicate the localization and distribution of nickel atoms.[386]

Nickel active site identification for heterogeneous catalysts had been attempted earlier, but the debate about their nature has only recently closed in on the goal. The formation of active sites on inorganic supports, generally acidic supports like aluminosilicates or modified aluminas, has impelled many research groups to investigate how nickel could be activated for oligomerization. The main reason for this ongoing debate is the different electronic configurations like Ni(0), Ni(I) or Ni(II) that can be adopted by nickel atoms after thermal activation. An arsenal of analytical, theoretical and experimental methodologies has thus been employed in order to shed light on active sites generation. Recent tremendous progresses on *in-situ* and operando in-depth characterization has drawn homogeneous and heterogeneous implementations closer, eventually leading to exquisite catalyst optimization.

Lapidus et al. published a seminal work with crystalline and amorphous Ni-aluminosilicates.[430] In this study, the solids containing only Ni(0) were all inactive with ethylene at 150-250°C. The conditions for catalyst pretreatment and their effect on catalyst activity let the authors assume that only Ni(II) oxide on zeolite surface or ionic Ni^{2+} in an exchanged position in the cavities are reactive. This assumption was rapidly contradicted by Yashima et al., who mentioned that Ni(0), well dispersed in a zeolite matrix, could be the active site, supported by IR (Infra-Red) and ESR (Electron Spin Resonance) measurements.[301] ESR, IR and CO adsorption measurements have also allowed Ni(I) obtained by partial reduction of Ni(II) by reaction with ethylene to be proposed. Such species are also detected for propylene oligomerization, which is proposed to proceed via dual catalysis with acidic sites. Since Ni(I) species are not observed for 1-butene oligomerization, the oligomerization mechanism was hypothesized to be solely acidic.

Che et al.[299] confirmed, by EPR (Electronic Paramagnetic Resonance), the presence of monomeric paramagnetic Ni(I) species dispersed in X-type zeolites where surface oxygens act as a ligand for ethylene and propylene dimerization. EPR spectroscopy was also used by Elev et al.[300] to characterize NiCaY zeolites. Thermal and photo-assisted reduction in hydrogen resulted in the formation of Ni^+ ions.[431] A linear relationship between the rates of ethylene conversion and Ni^+ was found for the photoactivated catalysts. Studies by Kevan et al.on other zeolites such as mordenite, ferrierite[432] or clinoptilolite[433] led to the same conclusions.

Based on product selectivities at different conversions, Feldblyum et al.[379] and Chauvin et al.[20] suspected equivalent Ni(II)-H and Ni(II)-ethyl active sites to be responsible for catalytic activity in both the nickel-based homogeneous and heterogeneous oligomerization of propylene.

In view of the IR results for CO adsorption, Sohn et al. also concluded that low-valent nickel associated with an acidic site was responsible for ethylene oligomerization activity with $NiSO_4/Al_2O_3$.[349] FTIR spectroscopy on similar Ni(II)-exchanged sulfated alumina[356] was simultaneously described by Davydov et al. to establish the role of isolated Ni(I) species as active sites. Formation is proposed by a reduction process, in which the acidic support is involved by proton transfer induced by covalently-bonded sulfate ions on the surface.

Monovalent Ni^+ or dehydrated Ni^{2+} were also proposed by Lallemand et al. relying on a combination of CO-FTIR analyses and EPR spectroscopy.[434] An original ^{13}C-NMR study of propylene dimerization at low temperatures on NiO/SiO_2 concluded that propylene was complexing with Ni^{2+} ions.[435]DFT studies by Brogaard and Olsbye[381] claim that the most plausible active sites on SSZ-24 zeolite were Ni^{2+} active sites. A sacrificial ethylene molecule induces the formation of the desired Ni-ethyl species with protonic assistance from the support, as shown in Figure 52.

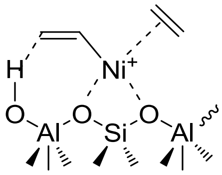


Figure 52. DFT-computed intermediate proposed in nickel active site generation in a SSZ-24 zeolite framework[26]

Most recently, Brogaard et al. proposed a mobile Ni(II) complex hosted in the same SSZ-24 zeolite to be the active site for ethylene oligomerization based on DFT and micro-kinetic modeling from continuous flow experimental studies.[436] The reversible adsorption of two ethylene molecules on Ni-alkyl species creates a mobile active site in the zeolite pores, highlighting an additional connection between heterogeneous and homogeneous catalysis thanks to zeolite echange properties for metallic ions.

Ni^{2+} contained in microporous/mesoporous aluminosilicate was confirmed as the active species by the author in collaboration with Berlier et al., thanks to a FTIR spectroscopy study with CO as probe molecule. Ni sites grafted onto silanol sites and NiO particles are suspected to be spectators.[383] Ni^{2+} cations were also recently identified by Gounder et al. using Ni-exchanged Beta zeolites.[384]

In parallel, Martinez et al. question the fact that ion-exchanged Ni^{2+} cations are the unique active Ni species.[437] They propose that under-coordinated Ni^{2+} species interacting with surface hydroxyls of aluminosilicates should contribute to the high activity of the solid catalysts. Coexistence of different Ni speciation participating in a unique type of mechanism underline the complexity of these systems. More recently, focusing on Ni-beta catalysts, Ni^{2+} grafted onto acidic silanols were described by the same group to be the most likely active species, compared with nickel atoms in ion-exchange positions. Online analysis by mass-spectrometry and FTIR-CO spectroscopy allowed the authors to propose a nickel vinyl-hydride to be a plausible intermediate obtained by a sacrificial ethylene activation on the support.[385]

Operando studies are flourishing in many homogeneous and heterogeneous applications in order to get a deeper insight into active sites and reaction mechanism. Considering the intrinsic complexity of these systems, they have also provided, and will still provide, major assistance in resolving the question of active sites and mechanisms.

Operando magnetic resonance has, for instance, been carried out to follow the oligomerization of ethylene catalyzed by Ni/SiO_2-Al_2O_3 at 110°C, 28 bar.[438] Even though acquisition of the spectra during the course of the reaction can only inform about ethylene conversion and product distribution, it is a proof-of-concept that such a reaction of interest can be followed spectroscopically at high temperatures and pressures.

First-of-a-kind operando EPR and in situ XAS analysis was recently carried out by Brückner et al. for butene oligomerization from the raffinate III under industrally representative conditions (80°C, 16 bar).[439] The critical impact of pressure was highlighted since no activity was observed below 2 bar because of unactive Ni(0) formation. A Ni(I)/Ni(II) redox shuttle was identified as the active site and enabled a more reliable butene dimerization mechanism to be proposed. This influential operando study paves the way for in-depth complex spectroscopic investigation, rising to the challenge of the quest to precisely identify active sites in heterogeneous catalysis.

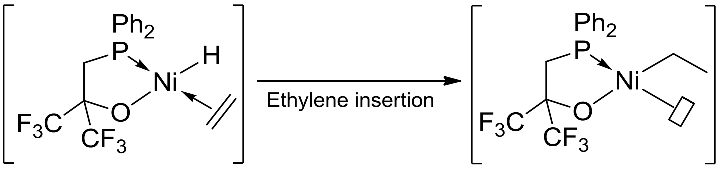
The debate about the oxidation state and the valence of the nickel atoms has thus long existed and is still animated. Monovalent nickel ions were first proposed as active sites and divalent species propositions are appearing more and more in the literature. The evolution of characterization techniques, operando and DFT methodologies has allowed a deeper insight into nickel speciation and implications in the genesis of active sites to be gained. In heterogeneous catalysis, this active sites= identification was more recently linked with oligomerization mechanism. Most recent studies thus converge their experimental, theoretical and analytical observations towards divalent nickel atoms activated by a sacrificial ethylene and by the support in order to promote a degenerated polymerization mechanism, or Cossee-Arlman mechanism, with similar active sites and mechanisms, as with homogeneous complexes. The only difference is the activation step between homogeneous and heterogeneous catalysts to induce the olefin insertion and oligomerization.

6.4 Study of the reactivity of some active species with ethylene: towards first step mechanism elucidation

Naturally, as illustrated in the previous section, the choice of the ligand plays a tremendous role in the catalytic outcome, by influencing the different steps of the catalytic cycle. In this section, special attention is paid to the intermediates involved and the mechanism elucidation, always supported by characterization techniques, kinetic studies and DFT calculations. In the case of organonickel and nickel hydride active species, the mechanisms are generally well–established, although whether the nickel hydride is involved or not in the catalytic cycle remains a question.

^{1}H NMR studies carried out by Keim et al. revealed that the reaction of $Ph_2PCH_2C(CF_3)_2OH$ with $[Ni(cod)_2]$ leads to the formation of a hydride species. In the presence of ethylene, this hydride species readily disappears, along with formation of a new signal, assigned to an alkylnickel complex (Scheme 11).[414] Starting from different (pseudo)allylnickel complexes illustrated as cyclopentadienyl complexes bearing the same P,O ligand, Keim demonstrated that the product distribution was similar in all cases, only differing by the temperature required for the activation of the catalyst. This was clearly indicative of the absence of the allyl group in the active catalyst.[410]

Scheme 11. ^{1}H NMR study of the reactivity of nickel hydride with ethylene

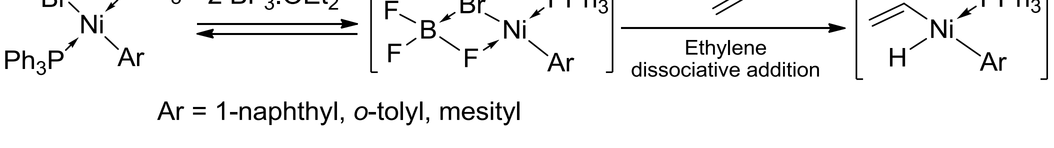


Hasanayn, Krogh-Jespersen, Goldman et al. have extensively studied the ligand's *trans* effect on the migratory insertion into the intermediates, $[Ni(X,Y)(CH_2CH_3)(C_2H_4)]$, (X,Y) being an anionic bidentate ligand as a phosphino-enolate.[440] A low activation barrier was measured for ethyl migration when the ethyl group is located *trans* to a "strong *trans* influence" ligand. Moreover, isomerization in order to place the ethyl group in the preferred position for posterior migration is facile, making repetition of ethylene coordination/insertion globally favorable, compared with catalysts having symmetrical bidentate ligands with either "strong" or "weak *trans* influence".

The use of GC or GC-MS analysis for primary insertion products is well established for olefin oligomerization.[131,418,441] The vinylic or butenyl products formed after one or two ethylene insertions consolidate the generally established Cossee-Arlman mechanism, *i.e.* coordination of the olefin followed by insertion. The ESI-MS study, by Santos and Rojas, of cationic active allyl species in the presence of ethylene supports the nickel hydride as an intermediate of the catalytic cycle.[442]

Another path is proposed by Maruya et al., who studied the catalytic system formed by $[Ni(PPh_3)_2(\sigma\text{-aryl})Br]$ and BF_3 (Scheme 12).[443] No vinylic products were observed, suggesting that the aryl group is retained on the nickel center. Observation of an isotopic exchange between C_2H_4 and C_2D_4 also supports the idea of the formation of a hydride species. Furthermore, the absence of evolution of the hydrogen atomic fraction in ethylene or butenes after C_2D_4 dimerization suggests hydrides do not arise from the catalytic system or the solvent, *i.e.* dichloromethane. In this alkyl-free process, the authors propose a hypothesis similar to one described in heterogeneous nickel oligomerization, namely, a dissociative addition of ethylene to generate H-Ni-CH=CH$_2$ without the use of an external activator.[383]

Scheme 12. Catalytic system formed by $[Ni(PPh_3)_2(\sigma\text{-aryl})Br]$ and BF_3



The debate around a possible metallacyclic path in nickel oligomerization is still open. Several decades ago, and just as the sole example, Grubbs et al. reported the synthesis of the nickel metallocyclopentane $[Ni(PPh_3)_3(CH_2CH_2CH_2CH_2)]$ and its degradation into 1-butene or ethylene.[444–446] Moreover, by subjecting the ethylene adduct $[Ni(PPh_3)_2(C_2H_4)]$ to ethylene pressure, at low temperatures, the authors observed the formation of the nickellacycle $[Ni(PPh_3)_2(CH_2CH_2CH_2CH_2)]$ [447]. They also showed that $[Ni(PPh_3)_3(CH_2CH_2CH_2CH_2)]$ is able to catalytically dimerize ethylene, which tends to demonstrate the reversibility of the process.[448] Schmidt et al. studied the reactivity of $[Ni(PPh_3)_2(C_2H_4)]$ with ethylene. Low activity was obtained (TON = 7 $mol_{C2H4}.mol_{Ni}^{-1}$). The authors suggest that the origin of such activity may be due to the presence of remaining traces of alkylaluminum in the synthesis of the Ni(0) complex.[66]

6.5 Kinetics and DFT studies

6.5.1 *Ethylene oligomerization*

Numerous kinetic studies support the Cossee-Arlman mechanism, ethylene insertion not only being a key step, but also being the rate-determining step. In line with this idea, Peuckert and Keim reported a kinetic study of the oligomerization of ethylene, catalyzed by $[Ni(Ph_2PCH_2COO)(\eta^3\text{-}C_8H_{13})]$, and producing a Schulz-Flory product distribution. The results obtained supported a Michaelis-Menten-type mechanism, where the ethylene insertion was the rate-determining step, with an energy barrier of *ca.* 17 kcal.mol^{-1}.[54] Ahmed et al. also developed a kinetic model for ethylene oligomerization, in this case catalyzed by a diphenylphosphinoacetate-based catalyst.[449] A good fit is observed when first-order in ethylene is assumed for the initiation, propagation and also termination steps, meaning that β-H transfer to the monomer is considered. Starting from the well-defined cationic methylnickel complex **86**, Berkefeld and Mecking monitored, using NMR spectroscopy, the formation of the corresponding Ni-ethyl intermediate, and determined a pseudo-first-order rate constant for ethylene insertion (Scheme 13).[419]

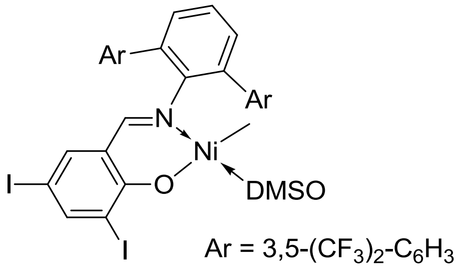


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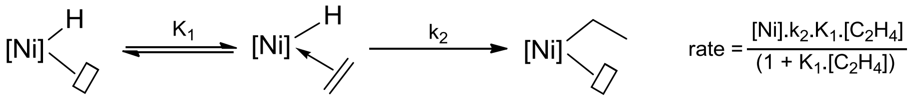
Figure 53 : Cationic methylnickel complex synthesized by Berkefeld and Mecking

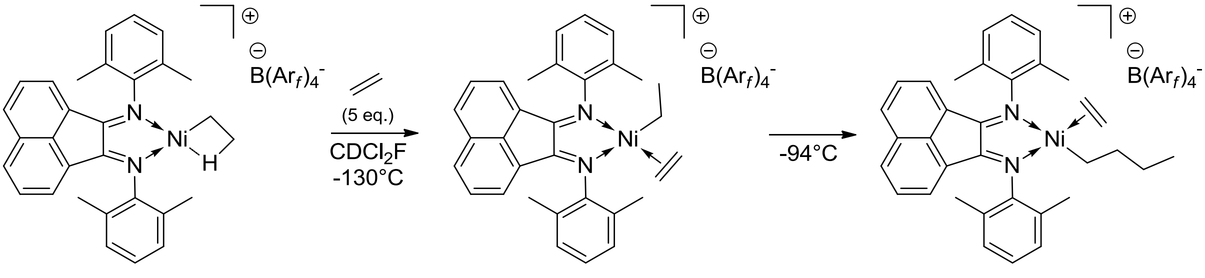
Scheme 13 : Kinetic model for ethylene oligomerization



$$\text{rate} = \frac{[Ni].k_2.K_1.[C_2H_4]}{(1 + K_1.[C_2H_4])}$$

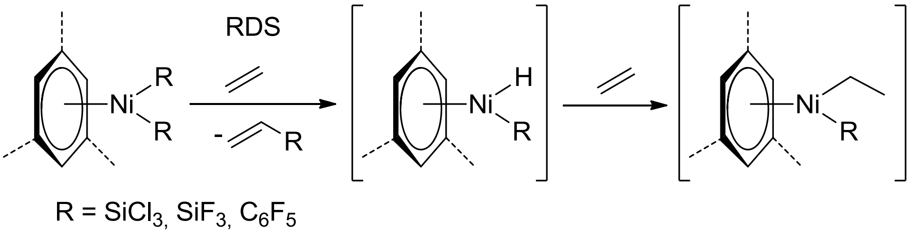
For diimine-based complexes activated by MMAO, Brookhart et al.[404] observed turnover numbers that were independent of ethylene pressure, thus indicating that the Ni(diimine)(alkyl)(olefin) is the catalyst resting state, with propagation rates controlled by the rate of the migratory insertion reaction. Assuming that all of the nickel halide precursor is converted into the active catalyst, the energy barrier for the migratory insertion step is around 16 kcal.mol^{-1}. Focusing on an active species study, the authors reported the quantitative formation of the cationic [Ni(diimine)(C_2H_5)(η^2-C_2H_4)] generated in situ at -130°C. (Step 1, Scheme 14).[407] Upon increasing the temperature to -94°C, ethylene insertion was observed, with an energy barrier of *ca.* 13 kcal.mol^{-1}.

Scheme 14. Brookhart type complex reactivity with ethylene



Kinetics that were first-order in ethylene were observed by Klabunde et al. with [Ni(η^6-arene)R_2] (arene = benzene, toluene, mesitylene and R = SiF_3, $SiCl_3$, C_6F_5), who proposed that the rate determining step was Ni-H formation.[450] It should be noted that this step is not part of the catalytic cycle (Scheme 15).

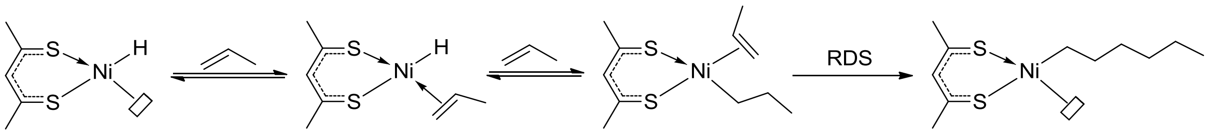
Scheme 15. Ni-H formation from [Ni(η^6-arene)R_2]



6.5.2 *Propylene and 1-butene oligomerization*

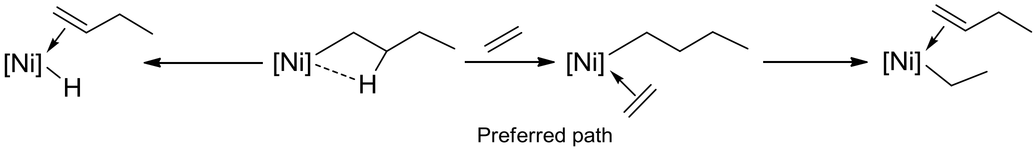
Examples of kinetic studies for the oligomerization reaction of higher olefins are scarce. For propylene oligomerization, Sukakibara et al. described kinetics which were first-order in olefin concentration for a catalytic system based on [Ni(acac)$_2$] associated with three equivalents of PPh_3 and activated by $Et_3Al_2Cl_3$. The energy barrier was measured at *ca.* 16 kcal.mol^{-1}.[451] The kinetic study carried out by Brown et al. on the pentane-2,4-dithionato-based complex, associated with diethylaluminum chloride, revealed kinetics which were second-order in olefin concentration for 1-butene or propylene oligomerization (Scheme 16).[452,453] They suggested that the rate-determining step is the insertion of the second molecule of alkene into the nickel-alkyl bond. A fast reversible equilibrium exists between the nickel-alkyl and the nickel-hydride species.

Scheme 16. Kinetic study of propylene dimerization with pentane-2,4-dithionato-based catalysts



Ziegler et al. calculated the ethylene dimerization path for [Ni(acac)H] using DFT.[454–456] Insertion of ethylene into the Ni-H or the Ni-ethyl bonds are facile and exothermic steps. While chain termination by β-H elimination is an endothermic step, calculations for alternative paths suggest a preferred β-H transfer to ethylene. Similar observations have been reported by Musaev and Morokuma for cationic diimine-based alkylnickel catalysts.[457] Siegbahn et al. carried out DFT calculations on the cationic model $[Ni(HN=CH-CH=NH)(CH_2CH_3)(C_2H_4)]^+$.[458] An exothermic energy barrier, of *ca.* 11 $kcal.mol^{-1}$, was found for the insertion step, in agreement with highly active diimine-based polymerization catalysts. The mechanistic model has also been calculated by Sunoj et al.for cationic species $[Ni(PMe_3)(_\eta{}^3\text{-allyl})]^+$ [459] After ethylene insertion and elimination of 1,4-pentadiene, they identified that the nickel-ethyl intermediate is thermodynamically and kinetically favored over the nickel hydride. The metal-assisted β-hydride transfer to coordinated ethylene is the preferred elimination path. Hieringer et al. modeled the insertion reaction of 1-butene on cationic $[Ni(L)_2(butyl)]^+$ (L = PH_3, PMe_3 or NHC N,N'-dimethylimidazol-2-ylidene) as the rate determining step of the overall catalytic process, in line with the previous studies on ethylene.[460] Insertion into the Ni-$C_{terminal}$ bond is slightly preferred over the Ni-$C_{internal}$ bond, supporting the favoured production of linear or monobranched C_8 products (Scheme 17).

Scheme 17. Modeled insertion reaction of 1-butene on cationic $[Ni(L)_2(butyl)]^+$

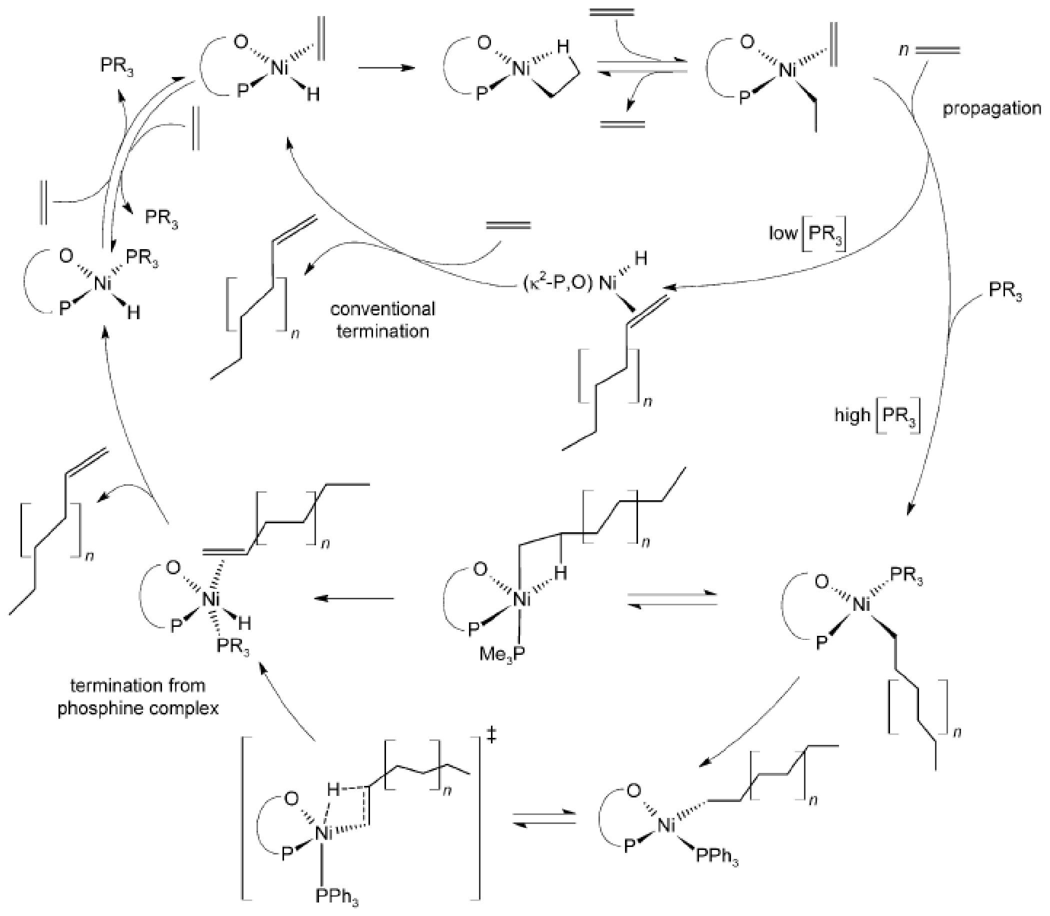


The isomerization ability of nickel catalysts is well documented, easily demonstrated with long terminal alkenes, and is responsible for the production of most of the internal alkenes.[461,462] In particular, hydride nickel(II) complexes have been proven to be isomerizing catalysts.[463] However, such a reaction is rarely put into perspective with the primary oligomerization reaction, and levers to undermine it are rarely discussed.. The key is probably at the chemical level, working around the catalyst environment.

6.5.3 *DFT calculation : Cossee-Arlman versus metallacyclic mechanism*

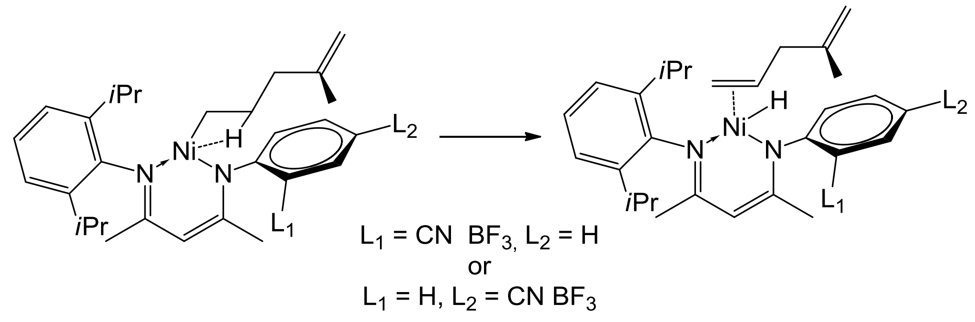
Jensen et al. developed thorough DFT studies on chain termination pathways, for SHOP-type catalysts (Scheme 18).[464] The calculated mechanism, involving β-hydride elimination followed by olefin dissociation, occurs with pentacoordinate intermediates with an additional coordinated phosphine. This supports the experimental observations where the olefinic chain decreases as the phosphine's concentration, or basicity, increases. These calculations are equally in agreement with the limited degree of branching and isomerization recorded in these catalytic systems. Further theoretical work on different systems bearing a (P,O), (O,O), (N,O) or (P,N) anionic ligands discriminates catalysts through ΔG between propagation and termination steps, being 0 $kcal.mol^{-1}$ for oligomerization and above 7 $kcal.mol^{-1}$, favoring propagation for polymerization.[465]

Scheme 18. Phosphine influence on catalytic cycles studied by DFT (Reproduced with permission from ref. 464 Copyright 2014 John Wiley & Sons)



Rojas, Toro-Labbé et al. studied the Cossee-Arlman mechanism for neutral methallylnickel bearing an anionic NacNac ligand (1,3-diketimine) functionalized by a cyano group (Scheme 19).[466] They supported the impact of co-catalyst Lewis Acids (LA), $B(C_6F_5)_3$ and BF_3, on polymer or short chain oligomer formation respectively. In respect of the latter, agostic interaction and β-H elimination are facilitated by the electronic properties and steric influence of the co-catalyst, interacting with the cyano group.

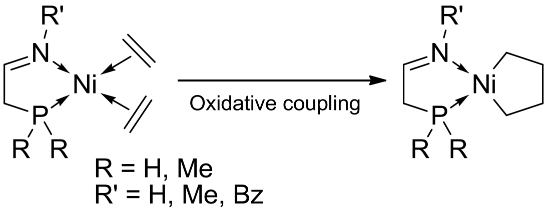
Scheme 19. Rojas et al. study on termination pathway in Cossee-Arlman mechanism



Development of a critical DFT model is paramount for a better understanding and even predictive ambitions. Adamo et al. carried out an extensive study on the exchange-correlation function, basis set, and model size for the Cossee-Arlman mechanism.[467] In the case of cationic phosphino-iminophosphorane-based nickel catalysts, they concluded that this latest parameter is crucial and it impacts the energy calculations and chemical interpretation tremendously. Moreover, they reported their attempt to link molecular descriptors to the prediction of selective ethylene dimerization catalysts by comparing the ΔG of the ethylene insertion and butene elimination steps, on the butyl intermediates.[468] Unfortunately, no clear correlation could be established.

Considering that the nature of the active catalyst formed during the activation process is still elusive, an enlightened computational approach involves the comparison between different potentially operative mechanisms. Adamo et al. thus studied the different phosphino-iminophosphorane-based nickel intermediates and their role in the Cossee-Arlman and in the metallacyclic mechanisms (Scheme 20).[469] For the latter, featuring the change in the nickel oxidation state during the oxidative coupling of two molecules of ethylene to form the nickellacyclopentane, the authors calculated that the activation barrier is reduced while the oxidation state increases (*ca.* 50 kcal.mol^{-1} for Ni(0), 39 kcal.mol^{-1} for Ni(I), and 20 kcal.mol^{-1} for Ni(II)), thus rendering the dicationic Ni(II) intermediate the most suitable for oxidative coupling. However, because the key step prior to entering a catalytic mechanism is the activation process, the authors modeled the MAO activation of the dihalide nickel precursor by $AlMe_3$ and showed that cationic alkylnickel(II) is the most likely intermediate.

Scheme 20. Imino-phosphorane Ni complexes and their role in metallacycle formation

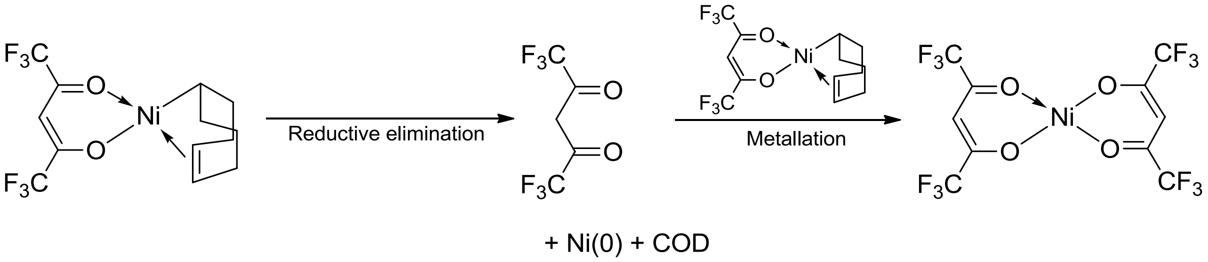


Bernardi, Bottoni et al. have considered, using DFT calculation , the cycloaddition of two molecules of ethylene, modeled by the approach of a C_2H_4 to $[Ni(PH_3)_2(C_2H_4)]$ or $[Ni(PH_3)_2(C_2H_4)_2]$.[470] The C-C coupling does not take place on the nickel center, but on the ligated ethylene, leading to a biradical transition state. The corresponding activation energies were 37.0 and 35.8 kcal.mol^{-1}, respectively, with prior cyclization to form the nickellacyclobutane.

6.6 Deactivation pathways

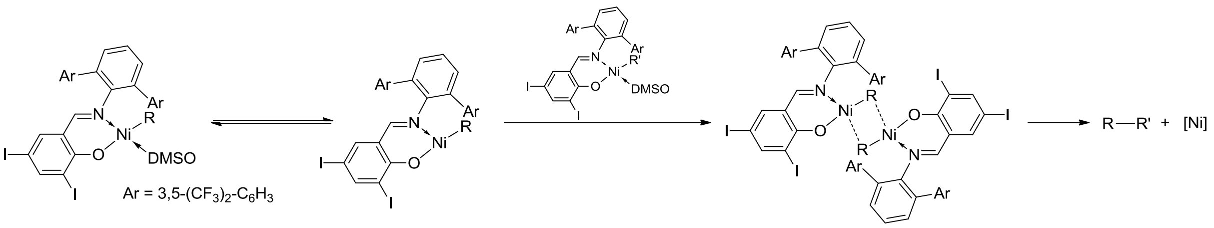
There are many deactivation pathways, depending on the nickel catalyst considered. For organonickel compounds, one possible pathway is reductive elimination leading to black nickel(0), as shown by Behr et al. with fluorinated acetyacetonate-based complexes (Scheme 21).[471] A second step as a direct consequence is metallation leading to the bis-ligated inactive species. These two successive deactivation pathways have been reviewed by Matt et al. for anionic (P,O) ligands.[57]

Scheme 21. Possible deactivation pathway for fluorinated-acetylacetonate Ni octadienyl catalysts



Another relevant decomposition route is bimolecular elimination. Mecking et al. demonstrated that their Ni-Me(DMSO) complex is prone to homocoupling, leading to ethane formation, while no comparable observation could be made for Ni-alkyl (alkyl > Me), which has longer hydrocarbonated chains (Scheme 22).[419] However, heterocoupling was observed between Ni(II)-Me and Ni(II)-Et, to form propane, or between Ni(II)-Et and Ni(II)-H, producing ethane. Hydrolysis of Ni(II)-alkyls as a possible decomposition pathway is not specifically observed for this system, while the corresponding TMEDA-based nickel complex,[472] although inactive towards ethylene, breaks down in the presence of water. Carbon monoxide is also described as a poison in olefin oligomerization, although its effect is reversible.[473] Butadiene is also described as a catalyst inhibitor, probably forming an η^3-allyl resting state.[396,413]

Scheme 22. Deactivation pathway involving heterocoupling



The previous paragraphs show that nickel active molecular species can be diverse, depending on the catalyst precursors (nature of the ligand, oxidation state of the metal, etc.) and activation mode. Nevertheless, the main identified active species involve Ni(II) complexes bearing Ni-C or Ni-H bonds into which the olefin can insert. These species can be neutral (anionic ligand), cationic or zwitterionic. Mechanisms associated with these species are of Cosse-Arlman type (migratory-insertion), with the insertion of olefin often being a rate determining step. Non-organometallic Ni species with different oxidation states can also be considered as active species. Cationic Ni(I) species formed from Ni(0) oxidation have been reported, although not fully characterized. A metallacyclic mechanism involving oxidative coupling on the Ni center is proposed to account for ethylene activation and transformation. Computational approaches can provide insights into comparing the different operative mechanism pathways.

7 Conclusion

Olefin oligomerization catalyzed by nickel is a broad and dynamic topic, as shown by the broad scope of this review and the literature covered. Since the “nickel effect” discovered by Holzkamp more than 60 years ago, different milestones have marked the path of the quest for more active, selective, stable and tunable nickel catalysts, in making use of homogeneous or heterogeneous technologies or the development of new concepts to support the catalytic system (polymers, metal–organic framework, inorganic porous materials, ionic liquids…).

Regarding homogeneous systems, the choice and design of the ligand, but also of the nickel precursor and its activation mode naturally play a tremendous role in the catalytic outcome. In early work, phosphine ligands were studied the most; they are still applied today in industrial technologies to control oligomerization selectivity. Nevertheless, we can see an evolution towards a diversification of the type of ligand, mono- or multi-dentate, containing different heteroelements, opening the way to quite limitless coordination modes. Some classes of ligands have emerged, derived from the model of (P,O) SHOP-like ligands or from the α-diimine based ones. However, the evaluation of the huge number of catalytic systems reported is still very often based on trial-and-error methodology. Heterogeneous nickel-catalyzed oligomerization has taken advantage of the increasing knowledge in material science from simple silicas to tailored mesoporous aluminosilicates to improve activity and stability. Acidity and porosity are both critical factors in obtaining active and stable catalysts. In this context, secondary reactions such as isomerization and codimerization hampers α-olefin and linear selectivity, which remains the privilege of homogeneous catalysis for ethylene and propylene oligomerization. Aluminosilicates with controlled porosity and acidity, as well as the adequate choice of non-innocent nickel precursors on mesoporous alumina, constitute promising candidates for high-performance olefin oligomerization. Ethylene dimerization still suffers from severe limitations with heterogeneous catalysis technologies to cope with the high exothermicity of the reaction. Process innovation here is highly desired in order to make a major breakthrough in this domain and compete with the selectivity and processability of homogeneous catalysis.

Supported by advanced characterization, kinetic studies, DFT calculations as well as isolation of well-defined active nickel intermediates, the mechanisms in play are in some cases quite well-established for homogeneous and heterogeneous catalytic systems, standing pretty clearly in favor of the Cossee-Arlman mechanism. However, in many other cases, relationships between nickel pre-catalyst structure and reactivity are not fully rationalized, and questions remain. Debate concerning the occurrence of a Cossee-Arlman or concerted oxidative coupling via a metallacyclic intermediate mechanism is still open, as well as[474] the nature and particularly the oxidation state of the active species. The parallels that can be drawn between homogeneous and heterogeneous catalysis can be taken advantage of in order to gain a deeper insight into the identification of the actual active sites and the determination of the selectivity-governing mechanism. The development of highly selective processes for the formation of α-olefins employing nickel-based catalysts thus remains a major challenge academically and industrially.

AUTHOR INFORMATION

Corresponding Authors

Hélène Olivier-Bourbigou, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, BP 3, 69360 Solaize, France, orcid.org/0000-0002-0337-4652, e-mail: helene.olivier-bourbigou@ifpen.fr

Maria Fernandez Espada Pastor, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, BP 3, 69360 Solaize France, orcid.org/0000-0002-2806-4095, e-mail : maria.fernandez-espada-pastor@ifpen.fr

Damien Delcroix, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, France, BP 3, 69360 Solaize, France, orcid.org/0000-0001-6119-6105, e-mail : damien.delcroix@ifpen.fr

Authors

Pierre-Alain Breuil, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, BP 3, 69360 Solaize France, orcid.org/0000-0001-6788-8663

Lionel Magna, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, BP 3, 69360 Solaize France, orcid.org/0000-0003-3050-6144

Typhène Michel, IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, BP 3, 69360 Solaize France, orcid.org/0000-0002-9020-0334

Notes

The authors declare no competing financial interest

Biographies

Hélène Olivier-Bourbigou obtained her PhD in Chemistry from the University of Paris VI under the guidance of Prof. Henri Kagan and Yves Chauvin after a top engineering school degree in Chemistry and post-graduate degree in Organic Chemistry (University of Rennes, France) and in Petroleum Science (IFP School, France). In 1988, she joined as a post-doc researcher the group of Prof. M. F. Lappert at the University of Sussex (UK). She was appointed scientist researcher at IFP Energies nouvelles in the Homogeneous Catalysis group in 1989 then Head of the Department from 2003 to 2019. She has been the leader of different projects dealing with fundamental studies as well as the development of new processes in petrochemistry. She is now Program Manager of the fundamental research at IFPEN.

Pierre-Alain Breuil graduated from the Ecole Nationale Supérieure de Chimie de Paris (Chimie ParisTech) in 2005. He next worked on supramolecular catalysts and asymmetric hydrogenation under the guidance of Prof. Joost Reek at the University of Amsterdam, in Netherlands, where he obtained his PhD in 2009. In 2010, he joined IFP Energies nouvelles as an R&D engineer. His current research interests are focused on the development of new catalysts and chemical processes for petrochemistry.

Lionel Magna graduated from Ecole Supérieure de Chimie Physique Electronique de Lyon (ESCPE) in 1997 and received his PhD degree in chemistry from the University Claude Bernard (Lyon) in 2000 under the supervision of Jean-Marie Basset and Yves Chauvin. His PhD thesis was focused on the use of ionic liquids for two-phase catalysis using palladium complexes. In 2001, he joined the department of molecular catalysis of IFP Energies nouvelles (IFPEN) for a post-doctoral stay working on olefin hydroformylation with H. Olivier-Bourbigou. Lionel obtained a permanent position at IFPEN Lyon in 2002. He's currently in charge of the development of new catalysts and processes in the fields of refining and petrochemistry. He particularly explored olefin oligomerization reaction using homogeneous catalysts.

Typhene Michel graduated from Ecole Supérieure de Chimie Physique Electronique de Lyon (ESCPE) in 2009. She joined then the group of Prof. Dr. F. E. Kühn at the Technical University of Munich, where she obtained her PhD in 2012. Her PhD dealt with catalytic epoxidation of terpenes with Rhenium catalysts. In 2013, she worked at UnaveraChemLab and developed the synthesis of intermediate and active pharmaceutical ingredients. In 2015, Typhene joined IFP Energies nouvelles as an R&D engineer. Her current research interests are focused on the development of catalysts and chemical processes for petrochemistry.

María F. Espada completed her studies in Universidad de Sevilla in 2010. Then, she joined the group of Prof. Ernesto Carmona, where she obtained her PhD with International Distinction (2015) in fundamental organometallic chemistry, under the supervision of Prof. Carmona and Dr. Manuel L. Poveda, after spending a visiting stay with Prof. Cameron Jones (Monash University, Melbourne, Australia, 2013). In 2016 she moved to Toulouse (France), to join the group of Dr. Nicolas Mézailles (LHFA, 2016-2018) as a postdoctoral researcher, to work on dinitrogen activation and functionalization mediated by Mo centers. She then enlisted the IFP Energies nouvelles (2018) to work in catalytic olefin oligomerization as an R&D engineer, where she got a permanent position in 2019, focusing on biomass valorization.

Damien Delcroix graduated from the Ecole Nationale Supérieure de Chimie de Montpellier in 2007. He obtained his PhD in 2011 under the supervision of Dr. Didier Bourissou and Prof. Blanca Martin Vaca working on organocatalyzed ring-opening polymerization of lactones and cyclic carbonates towards biodegradable polymers. In 2012 he joined IFP Energies nouvelles as a post-doctoral fellowship to convert lignocellulosic biomass into oxygenated valuable monomers. He then got a position there in 2013 as an R&D engineer to focus on biomass valorization and transformation of small olefins by metallic oligomerization and metathesis with homogeneous and heterogeneous catalysts.

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ABBREVIATIONS USED

SHOP : Shell Higher Olefin Process
WHSV : Weight Hourly Space Velocity
ZSM : Zeolite Socony Mobil
MCM : Mobil Composition of Matter
KIT : Korea Advanced Institute of Science and Technology
SBA : Santa Barbara Amorphous
VTM : Vacancy Titanate Material
BEA : Zeolite Beta
USY : Ultra Stable Y Zeolite
XAS : X-Ray Adsorption Spectroscopy
FTIR : Fourier Transform InfraRed Spectroscopy
LAO : Linear Alpha Olefin
XPS : X-Ray Photoelectron Spectrometry
DFT : Density Functional Theory
MAO : MethylAluminOxane
MMAO : Modified MethylAluminOxane
PMAO-IP : PolyMethylAluminOxane-Improved Performance

REFERENCES

(1) Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H. Role of Homogeneous Catalysis in Oligomerization of Olefins: Focus on Selected Examples Based on Group 4 to Group 10 Transition Metal Complexes. *Catal. Lett.* **2015**, *145*, 173–192.

(2) Forestière, A.; Olivier-Bourbigou, H.; Saussine, L. Oligomerization of Monoolefins by Homogeneous Catalysts. *Oil & Gas Science and Technology - Rev. IFP* **2009**, *64*, 649–667.

(3) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. Dimerization of Ethylene to Butene-1. *Catal. Today* **1992**, *14*, 1–124.

(4) Bianchini, C.; Giambastiani, G.; Luconi, L.; Meli, A. Olefin Oligomerization, Homopolymerization and Copolymerization by Late Transition Metals Supported by (Imino)Pyridine Ligands. *Coord. Chem. Rev.* **2010**, *254*, 431–455.

(5) Speiser, F.; Braunstein, P.; Saussine, L. Catalytic Ethylene Dimerization and Oligomerization: Recent Developments with Nickel Complexes Containing P,N-Chelating Ligands. *Acc. Chem. Res.* **2005**, *38*, 784–793.

(6) Keim, W. Oligomerization of Ethylene to α-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP). *Angew. Chem. Int. Ed.* **2013**, *52*, 12492–12496.

(7) Mecking, S. Cationic Nickel and Palladium Complexes with Bidentate Ligands for the C-C Linkage of Olefins. *Coord. Chem. Rev.* **2000**, *203*, 325–351.

(8) Olivier-Bourbigou, H.; Forestière, A.; Saussine, L.; Magna, L.; Favre, F.; Hugues, F. Olefin Oligomerization for the Production of Fuels and Petrochemicals. *Oil & Gas European J.* **2010**, 97–102.

(9) Raubenheimer H. G. Nickel - Not Evil but Catalytically Friendly: Olefin Oligomerization with Nickel Complexes. *S. Afr. J. Chem.* **1998**, *51*, 73–78.

(10) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169–1204.

(11) Wang, S.; Sun, W.-H.; Redshaw, C. Recent Progress on Nickel-Based Systems for Ethylene Oligo-/Polymerization Catalysis. *J. Organomet. Chem.* **2014**, *751*, 717–741.

(12) Wang, Z.; Liu, Q.; Solan, G. A.; Sun, W.-H. Recent Advances in Ni-Mediated Ethylene Chain Growth: N-Imine-Donor Ligand Effects on Catalytic Activity, Thermal Stability and Oligo-/Polymer Structure. *Coord. Chem. Rev.* **2017**, *350*, 68–83.

(13) Zhang, B.; Wang, Y.; Wang, G.; Cao, J.; Sun, S.; Xing, L.; Sun, Y.; Han, Y. Oligomerization and Polymerization of Ethylene Initiated by Novel Ni(II)-Based Acetyliminopyridine Complexes as Single-Site Catalysts. *J. Nat. Gas Chem.* **2007**, *16*, 64–69.

(14) Nicholas, C. P.; Laipert, L.; Prabhakar, S. Oligomerization of Light Olefins to Gasoline: An Advanced NMR Characterization of Liquid Products. *Ind. Eng. Chem. Res.* **2016**, *55*, 9140–9146.

(15) Bailey, G. C.; Reid, J. A. US Patent US2381198, 1945.

(16) Sivaram, S. The Ziegler Catalysts. Serendipity or Systematic Research? *Resonance - Journal of Science Education* **2017**, *22*, 985–1006.

(17) Fischer K.; Jonas K.; Misbach P.; Stabba R.; Wilke G. The Nickel Effect. *Angew. Chem. Int. Ed.* **1973**, *12*, 943–1026.

(18) Wilke G. Contribution to Homogeneous Catalysis : 1955-1980. *J. Organomet. Chem.* **1980**, *200*, 349–364.

(19) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D. *et al.* Allyl-Transition Metal Systems. *Angew. Chem. Int. Ed.* **1966**, *5*, 151–266.

(20) Chauvin, Y.; Commereuc, D.; Hugues, F.; Thivolle-Cazat, J. Nickel-Based Heterogeneous Catalysts for Olefin Oligomerization. *Appl. Catal., A* **1988**, *42*, 205–216.

(21) Chauvin, Y.; Gaillard, J. U.S. Patent 3,728,283, 1973.

(22) Chauvin, Y.; Commereuc, D.; Gaillard, J.; Léger, G.; Phung, N. H. U.S. Patent 4,283,305, 1981.

(23) Zuech, E. A. U.S. Patent 3,485,881, 1969.

(24) Carter, O. C. U.S. Patent 4,176,086, 1979.

(25) Heckelsberg, L. F. U.S. Patent 4,317,948, 1982.

(26) Carter, C. O. U.S. Patent 4242531, 1980.
(27) Kent, A. G.; Lawrenson, M. J.; Macalpine, D. K. U.S. Patent 4,835,328 A1, 1969.
(28) Sato, H.; Uchida, K.; Tojima, H. U.S. Patent 4,992,610 A1, 1991.
(29) Itagaki, M.; Suzukamo, G.; Yamamoto, M. U.S. Patent 6,388,160 B1, 2002.
(30) Nojiri, M.; Misono, M. Recent Progress in Catalytic Technology in Japan, a Supplement. *Appl. Catal., A* **1993**, *93*, 103–122.
(31) Glockner, P. W.; Keim, W.; Mason, R. F. U.S. Patent 3,647,914, 1972.
(32) Bauer, R.; Chung, H.; Barnett, K. W.; Glockner, P. W.; Keim, W. U.S. Patent 3,686,159, 1972.
(33) Mason, C. U.S. Patent 3,676,523, 1972.
(34) Kister, A. T.; Lutz, E. F. U.S. Patent 4,020,121, 1977.
(35) Nierlich, F.; Wildt, T.; Droste, W.; Obenaus, F. U.S. Patent 5,177,882, 1993.
(36) Albrecht, S.; Kiessling, D.; Maschmeyer, D.; Nierlich, F.; Wendt, G. Oligomerization of n-Butenes. *Chemie Ingenieur Technik* **2005**, *77*, 695–709.
(37) Schulze, J.; Homann, M. *C4-Hydrocarbons and Derivatives, Resources, Production, Marketing: Oligomerization of n-Butenes*; Springer-Verlab: Berlin-Heidelberg, 1989.
(38) Walter, M.; Heidemann, T. U.S. Patent 7,259,285 B1, **2007**.
(39) Nomura, K.; Ishino, M.; Yamamoto, M.; Suzukamo, G.; Itagaki, M. U.S. Patent 5,349,115, 1994.
(40) Chauvin, Y.; Commereuc, D.; Hirschauer, A.; Hugues, F.; Saussine, L. FR Patent 2,611,700, 1987.
(41) Commereuc, D.; Hugues, H.; Forestière, A.; Olivier-Bourbigou, H. U.S. Patent 6,444,866, B1, 2002.
(42) Wasserscheid, P.; Keim, W. World Patent 9,847,616 A1, 1998.
(43) Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; Wang, L.; Yang, Z.-Y. U.S. Patent 5,880,323, 1999.
(44) Svejda, S. A. World Patent 200010945 A1, 2000.
(45) Zhao, B.; Berluche, E.; Kacker, S.; Canich, J. M. World Patent 2003102005, 2003.
(46) Zhao, B.; Squire, K. R.; Kacker, S.; Canich, A. M. U.S. Patent 7,160,834 B2, 2007.
(47) Gibson, V. C.; Tomov, A. T. U.S. Patent, 0,094,588 A1, 2006.
(48) Bansleben, D. A.; Friedrich, S. K.; Younkin, T. R.; Grubbs, R. H.; Wang, C.; Li, R. T. U.S. Patent, US6410664 B1, 2002.
(49) Doetterl, M.; Alt, H. G.; Schmidt, R. U.S. Patent, 20120136189 A1, 2012.
(50) Peitz, S.; Bayrak, Z.; Behr, A.; Geilen, F.; Maschmeyer, D.; Stochniol, G.; Winterberg, M.; Boing, C. World Patent WO104185 A1, 2015.
(51) Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, M. A.; Coughlin, E. B.; Ittel, S. D. *et al.* World Patent WO9623010, 1996.
(52) Bogdanovic, B.; Henc, B.; Karmann, H.-G.; Nüssel, H.-G.; Walter, D.; Wilke, G. Olefin Transformations Catalyzed by Organonickel Compounds. *Ind. Eng. Chem.* **1970**, *62*, 34–44.
(53) Nowlin G.; Burnie G.; Lyons H. D. U.S. Patent 2,969,408, 1961.
(54) Peuckert, M.; Keim, W. A New Nickel Complex for the Oligomerization of Ethylene. *Organometallics* **1983**, *2*, 594–597.
(55) Johnson, L. K.; Killian C. M.; Brookhart M. New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and α-Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.
(56) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. Neutral Nickel(II)-Based Catalysts for Ethylene Polymerization. *Organometallics* **1998**, *17*, 3149–3151.
(57) Kuhn, P.; Semeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. Structure-Reactivity Relationships in SHOP-Type Complexes: Tunable Catalysts for the Oligomerization and Polymerization of Ethylene. *Dalton Trans.* **2007**, 515–528.
(58) Camacho, D. H.; Guan, Z. Designing Late-Transition Metal Catalysts for Olefin Insertion Polymerization and Copolymerization. *Chem. Commun.* **2010**, *46*, 7879–7893.
(59) Budagumpi, S.; Keri, R. S.; Biffis, A.; Patil, S. A. Olefin Poly/Oligomerizations by Metal Precatalysts Bearing Non–Heterocyclic N–Donor Ligands. *Appl. Catal., A* **2017**, *535*, 32–60.
(60) Delferro, M.; Marks, T. J. Multinuclear Olefin Polymerization Catalysts. *Chem. Rev.* **2011**, *111*, 2450–2485.
(61) Gao, R.; Sun, W.-H.; Redshaw, C. Nickel Complex Pre-Catalysts in Ethylene Polymerization: New Approaches to Elastomeric Materials. *Catal. Sci. Technol.* **2013**, *3*, 1172.

(62) Gibson, V. C.; Spitzmesser, S. K. Advances in Non-Metallocene Olefin Polymerization Catalysis. *Chem. Rev.* **2003**, *103*, 283–315.

(63) Luk, Y.-Y. G.; Foucher, D. A.; Gossage, R. A. Recent Advances in the Homogeneous Polymerisation of Olefins Mediated by Nickel Complexes. *Comptes Rendus Chimie* **2013**, *16*, 573–579.

(64) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. FI Catalysts for Olefin Polymerization- A Comprehensive Treatment. *Chem. Rev.* **2011**, *111*, 2363–2449.

(65) Mu, H.; Pan, L.; Song, D.; Li, Y. Neutral Nickel Catalysts for Olefin Homo- and Copolymerization: Relationships between Catalyst Structures and Catalytic Properties. *Chem. Rev.* **2015**, *115*, 12091–12137.

(66) Titova, Y. Y.; Belykh, L. B.; Rokhin, A. V.; Soroka, O. G.; Schmidt, F. K. Catalysis of Dimerization and Oligomerization Reactions of Lower Alkenes by Systems Based on $Ni(PPh_3)_2(C_2H_4)$ and $Ni(PPh_3)_nCl$ (n = 2 or 3). *Kinet. Catal.* **2014**, *55*, 35–46.

(67) Schmidt, F. K.; Titova, Y. Y.; Belykh, L. B. The Role of Phosphine and 1,2-Diimine Complexes of Nickel in the Oxidation States 0, +1, and +2 in the Catalyzed Di-, Oligo-, and Polymerization of Ethylene. *Kinet. Catal.* **2016**, *57*, 61–71.

(68) McGuinness, D. Alkene Oligomerisation and Polymerisation with Metal-NHC Based Catalysts. *Dalton Trans.* **2009**, 6915–6923.

(69) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. Nickel(II) Heterocyclic Carbene Complexes as Catalysts for Olefin Dimerization in an Imidazolium Chloroaluminate Ionic Liquid. *Organometallics* **2002**, *21*, 175–181.

(70) Sun, H. M.; Shao, Q.; Hu, D. M.; Li, W. F.; Shen, Q.; Zhang, Y. Indenylnickel(II) N-Heterocyclic Carbene Complexes: Synthesis via Indene Elimination and Catalytic Activity for Ethylene Dimerization. *Organometallics* **2005**, *24*, 331–334.

(71) Li, W.-F.; Sun, H.-M.; Chen, M.-Z.; Shen, Q.; Zhang, Y. Synthesis and Catalytic Activity of Neutral Salicylaldiminato Nickel(II) Complexes Bearing a Single N-Heterocyclic Carbene Ligand. *J. Organomet. Chem.* **2008**, *693*, 2047–2051.

(72) Hameury, S.; Fremont, P. de; Breuil, P.-A. R.; Olivier-Bourbigou, H.; Braunstein, P. Synthesis and Characterization of Oxygen-Functionalised-NHC Silver(I) Complexes and NHC Transmetallation to Nickel(II). *Dalton Trans.* **2014**, *43*, 4700–4710.

(73) Hameury, S.; Fremont, P. de; Breuil, P.-A. R.; Olivier-Bourbigou, H.; Braunstein, P. Synthesis and Characterization of Palladium(II) and Nickel(II) Alcoholate-Functionalized NHC Complexes and of Mixed Nickel(II)-Lithium(I) Complexes. *Inorg. Chem.* **2014**, *53*, 5189–5200.

(74) Hameury, S.; Fremont, P. de; Breuil, P.-A. R.; Olivier-Bourbigou, H.; Braunstein, P. Bis(ether-functionalized NHC) Nickel(II) Complexes, Trans to Cis Isomerization Triggered by Water Coordination, and Catalytic Ethylene Oligomerization. *Organometallics* **2015**, *34*, 2183–2201.

(75) Milani, J. L. S.; Casagrande, A. C. A.; Livotto, P. R.; Casagrande, O. L., JR. Synthesis and Characterization of Ether-Imine-Furfural [ONO] Nickel(II) Complexes and their Application in Oligomerization of Ethylene. *Appl. Catal., A* **2016**, *523*, 247–254.

(76) Speiser, F.; Braunstein, P.; Saussine, L. Dinuclear Nickel Complexes with Bidentate N,O Ligands: Synthesis, Structure, and Catalytic Oligomerization of Ethylene. *Inorg. Chem.* **2004**, *43*, 4234–4240.

(77) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitola, E.; Leskelä, M. Pyridinylimine-Based Nickel(II) and Palladium(II) Complexes: Preparation, Structural Characterization and Use as Alkene Polymerization Catalysts. *J. Organomet. Chem.* **2000**, *606*, 112–124.

(78) Rishina, L. A.; Kissin, Y. V.; Lalayan, S. S.; Gagieva, S. C.; Kurmaev, D. A.; Tuskaev, V. A.; Bulychev, B. M. New α-Diimine Nickel Complexes-Synthesis and Catalysis of Alkene Oligomerization Reactions. *J. Mol. Catal. A: Chem.* **2016**, *423*, 495–502.

(79) Tuskaev, V. A.; Gagieva, S. C.; Kurmaev, D. A.; Zvukova, T. M.; Fedyanin, I. V.; Bulychev, B. M. Synthesis, Characterization and Ethylene Oligomerization Behavior of New Nickel(II) Octofluoro-α-Diimine Complex. *Inorg. Chim. Acta* **2016**, *442*, 167–171.

(80) Laine, T. V.; Lappalainen, K.; Liimatta, J.; Aitola, E.; Löfgren, B.; Leskelä, M. Polymerization of Ethylene with New Diimine Complexes of Late Transition Metals. *Macromol. Rapid Commun.* **1999**, *20*, 487–491.

(81) Chandran, D.; Byeon, S. J.; Suh, H.; Kim, I. Effect of Ion-Pair Strength on Ethylene Oligomerization by Divalent Nickel Complexes. *Catal. Lett.* **2013**, *143*, 717–722.

(82) Chandran, D.; Lee, K. M.; Chang, H. C.; Song, G. Y.; Lee, J.-E.; Suh, H.; Kim, I. Ni(II) Complexes with Ligands Derived from Phenylpyridine, Active for Selective Dimerization and Trimerization of Ethylene. *J. Organomet. Chem.* **2012**, *718*, 8–13.

(83) Antonov, A. A.; Semikolenova, N. V.; Talsi, E. P.; Matsko, M. A.; Zakharov, V. A.; Bryliakov, K. P. 2-Iminopyridine Nickel(II) Complexes Bearing Electron-Withdrawing Groups in the Ligand Core: Synthesis, Characterization, Ethylene Oligo- and Polymerization Behavior. *J. Organomet. Chem.* **2016**, *822*, 241–249.

(84) Zhang, N.; Wang, J.; Huo, H.; Chen, L.; Shi, W.; Li, C.; Wang, J. Iron, Cobalt and Nickel Complexes Bearing Hyperbranched Iminopyridyl Ligands: Synthesis, Characterization and Evaluation as Ethylene Oligomerization Catalysts. *Inorg. Chim. Acta* **2018**, *469*, 209–216.

(85) Suo, H.; Zhang, Y.; Ma, Z.; Yang, W.; Flisak, Z.; Hao, X.; Hu, X.; Sun, W.-H. 2-Chloro/Phenyl-7-Arylimino-6,6-Dimethylcyclopenta[b]pyridylnickel Chlorides: Synthesis, Characterization and Ethylene Oligomerization. *Catal. Commun.* **2017**, *102*, 26–30.

(86) Mukherjee, S.; Patel, B. A.; Bhaduri, S. Selective Ethylene Oligomerization with Nickel Oxime Complexes. *Organometallics* **2009**, *28*, 3074–3078.

(87) Tayade, K. N.; Mane, M. V.; Sen, S.; Murthy, C. N.; Tembe, G. L.; Pillai, S. M.; Vanka, K.; Mukherjee, S. A Catalytic and DFT Study of Selective Ethylene Oligomerization by Nickel(II) Oxime-Based Complexes. *J. Mol. Catal. A: Chem.* **2013**, *366*, 238–246.

(88) Suo, H.; Zhao, T.; Wang, Y.; Ban, Q.; Sun, W.-H. N-(2,2-Dimethyl-1-(Quinolin-2-yl)Propylidene)arylaminonickel Complexes and their Ethylene Oligomerization. *Molecules* **2017**, *22*, 630/1-630/9.

(89) Wang, S.; Du, S.; Zhang, W.; Asuha, S.; Sun, W.-H. Nickel(II) Complexes Bearing 4-Arylimino-1,2,3-Trihydroacridines: Synthesis, Characterization, and Ethylene Oligomerization. *ChemistryOpen* **2015**, *4*, 328–334.

(90) Wang, S.; Zhang, W.; Du, S.; Asuha, S.; Flisak, Z.; Sun, W.-H. Propyl Substituted 4-Arylimino-1,2,3-Trihydroacridylnickel Complexes: Their Synthesis, Characterization and Catalytic Behavior Toward Ethylene. *J. Organomet. Chem.* **2015**, *798*, 408–413.

(91) Ainooson, M. K.; Guzei, I. A.; Spencer, L. C.; Darkwa, J. Pyrazolylimine Iron and Cobalt, and Pyrazolylamine Nickel Complexes: Synthesis and Evaluation of Nickel Complexes as Ethylene Oligomerization Catalysts. *Polyhedron* **2013**, *53*, 295–303.

(92) Hao, P.; Song, S.; Xiao, T.; Li, Y.; Redshaw, C.; Sun, W.-H. Highly Active 8-Benzoxazolyl- or 8-Benzothiazolyl-2-Alkylquinolinylnickel(II) Complexes for Ethylene Dimerization and Vinyl Polymerization of Norbornene. *Polyhedron* **2013**, *52*, 1138–1144.

(93) Ortiz de la Tabla, L.; Matas, I.; Palma, P.; Alvarez, E.; Campora, J. Nickel and Palladium Complexes with New Phosphinito-Imine Ligands and Their Application as Ethylene Oligomerization Catalysts. *Organometallics* **2012**, *31*, 1006–1016.

(94) Zhang, S.; Pattacini, R.; Jie, S.; Braunstein, P. A Phosphino-Oxazoline Ligand as a P,N-Bridge in Palladium/Cobalt or P,N-Chelate in Nickel Complexes: Catalytic Ethylene Oligomerization. *Dalton Trans.* **2012**, *41*, 379–386.

(95) Zhang, S.-M.; Pattacini, R.; Braunstein, P. Reactions of a Phosphinoimino-Thiazoline-Based Metalloligand with Organic and Inorganic Electrophiles and Metal-Induced Ligand Rearrangements. *Organometallics* **2010**, *29*, 6660–6667.

(96) Ghisolfi, A.; Fliedel, C.; Rosa, V.; Monakhov, K. Y.; Braunstein, P. Combined Experimental and Theoretical Study of Bis(diphenylphosphino)(N-Thioether)amine-Type Ligands in Nickel(II) Complexes for Catalytic Ethylene Oligomerization. *Organometallics* **2014**, *33*, 2523–2534.

(97) Cooley, N. A.; Green, S. M.; Wass, D. F.; Heslop, K.; Orpen, A. G.; Pringle, P. G. Nickel Ethylene Polymerization Catalysts Based on Phosphorus Ligands. *Organometallics* **2001**, *20*, 4769–4771.

(98) Song, K.; Gao, H.; Liu, F.; Pan, J.; Guo, L.; Zai, S.; Wu, Q. Syntheses, Structures, and Catalytic Ethylene Oligomerization Behaviors of Bis(phosphanyl)aminenickel(II) Complexes Containing N-Functionalized Pendant Groups. *Eur. J. Inorg. Chem.* **2009**, 3016–3024.

(99) Boulens, P.; Lutz, M.; Jeanneau, E.; Olivier-Bourbigou, H.; Reek, Joost N. H.; Breuil, P.-A. R. Iminobisphosphines to (Non-)Symmetrical Diphosphinoamine Ligands: Metal-Induced Synthesis of Diphosphorus Nickel Complexes and Application in Ethylene Oligomerisation Reactions. *Eur. J. Inorg. Chem.* **2014**, *2014*, 3754–3762.

(100) Aluri, B. R.; Peulecke, N.; Peitz, S.; Spannenberg, A.; Mueller, B. H.; Schulz, S.; Drexler, H.-J.; Heller, D.; Al-Hazmi, M. H.; Mosa, F. M. *et al.* Coordination Chemistry of New Selective Ethylene Trimerisation Ligand $Ph_2PN(iPr)P(Ph)NH(R)$ (R = iPr, Et) and Tests in Catalysis. *Dalton Trans.* **2010**, *39*, 7911–7920.

(101) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. Efficient and Selective Nickel-Catalyzed Addition of H-P(O) and H-S Bonds to Alkynes. *J. Am. Chem. Soc.* **2004**, *126*, 5080–5081.

(102) Lhermet, R.; Moser, E.; Jeanneau, E.; Olivier-Bourbigou, H.; Breuil, P.-A. R. Outer-Sphere Reactivity Shift of Secondary Phosphine Oxide-Based Nickel Complexes: From Ethylene Hydrophosphinylation to Oligomerization. *Chem. - Eur. J.* **2017**, *23*, 7433–7437.

(103) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S. *et al.* Ethylene Tetramerization: a New Route to Produce 1-Octene in Exceptionally High Selectivities. *J. Am. Chem. Soc.* **2004**, *126*, 14712–14713.

(104) Aluri, B. R.; Peulecke, N.; Müller, B. H.; Peitz, S.; Spannenberg, A.; Hapke, M.; Rosenthal, U. Synthesis, Coordination Chemistry, and Catalysis of the First 1,2-Bis(diphenylphosphino)-1,2-diphenylhydrazine, $Ph_2PN(Ph)N(Ph)PPh_2$. *Organometallics* **2010**, *29*, 226–231.

(105) Meng, X.; Le Zhang; Chen, Y.; Jiang, T. Silane-Bridged Diphosphine Ligands for Nickel-Catalyzed Ethylene Oligomerization. *React. Kinet., Mech. Catal.* **2016**, *119*, 481–490.

(106) Huang, Y.; Le Zhang; Wei, W.; Alam, F.; Jiang, T. Nickel-Based Ethylene Oligomerization Catalysts Supported by PNSiP Ligands. *Phosphorus, Sulfur, and Silicon and the Related Elements* **2018**, *193*, 363–368.

(107) Wei, W.; Yu, B.; Alam, F.; Huang, Y.; Cheng, S.; Jiang, T. Ethylene Oligomerization Promoted by Nickel-Based Catalysts with Silicon-Bridged Diphosphine Amine Ligands. *Transit. Met. Chem.* **2018**, *822*, 104.

(108) Ulbrich, Ana H. D. P. S.; Campedelli, R. R.; Milani, J. L. S.; dos Santos, Joao H. Z.; Casagrande, Osvaldo de L., Jr. Nickel Catalysts Based on Phenyl Ether-Pyrazol Ligands: Synthesis, XPS Study, and Use in Ethylene Oligomerization. *Appl. Catal., A* **2013**, *453*, 280–286.

(109) Wang, K.; Patil, A. O.; Zushma, S.; McConnachie, J. M. Ethylene Oligomerization Using Nickel Dithiolene Complexes $Ni(S_2C_2R_2)_2$ (R = Ph, CF_3) and the Crystal Structure of $Ni[S_2C_2(CF_3)_2]_2$. *J. Inorg. Biochem.* **2007**, *101*, 1883–1890.

(110) Bayón, J.C.; Claver, C.; Masdeu-Bultó, A. M. Homogeneous Catalysis with Transition Metal Complexes Containing Sulfur Ligands. *Coord. Chem. Rev.* **1999**, *193-195*, 73–145.

(111) Schaarschmidt, D.; Kuehnert, J.; Tripke, S.; Alt, H. G.; Goerl, C.; Rueffer, T.; Ecorchard, P.; Walfort, B.; Lang, H. Ferrocenyl Phosphane Nickel Carbonyls: Synthesis, Solid State Structure, and their Use as Catalysts in the Oligomerization of Ethylene. *J. Organomet. Chem.* **2010**, *695*, 1541–1549.

(112) Obuah, C.; Jordaan, J. H. L.; Darkwa, J. (Ferrocenylpyrazolyl)Nickel(II)-Catalysed Ethylene Oligomerisation. *Catal. Sci. Technol.* **2016**, *6*, 4814–4823.

(113) Dresch, L. C.; Araujo, B. B. de; Casagrande, Osvaldo de L., Jr.; Stieler, R. A Novel Class of Nickel(II) Complexes Containing Selenium-Based Bidentate Ligands Applied in Ethylene Oligomerization. *RSC Adv.* **2016**, *6*, 104338–104344.

(114) Oliveira, L. L. de; Campedelli, R. R.; Kuhn, Maria C. A.; Carpentier, J.-F.; Casagrande, O. d. L. Highly Selective Nickel Catalysts for Ethylene Oligomerization Based on Tridentate Pyrazolyl Ligands. *J. Mol. Catal. A: Chem.* **2008**, *288*, 58–62.

(115) Oliveira, L. L. de; Campedelli, R. R.; Bergamo, A. L.; dos Santos, Ana H. D. P.; Casagrande, O. d. L. Substituted Tridentate Pyrazolyl Ligands for Chromium and Nickel-Catalyzed Ethylene Oligomerization Reactions. Effect of Auxiliary Ligand on Activity and Selectivity. *J. Braz. Chem. Soc.* **2010**, *21*, 1318–1328.

(116) Small, B. L.; Brookhart, M. Iron-Based Catalysts with Exceptionally High Activities and Selectivities for Oligomerization of Ethylene to Linear α-Olefins. *J. Am. Chem. Soc.* **1998**, *120*, 7143–7144.

(117) Britovsek, George J. P.; Gibson, V. C.; McTavish, S. J.; Solan, G. A.; White, Andrew J. P.; Williams, D. J.; Kimberley, B. S.; Maddox, P. J. Novel Olefin Polymerization Catalysts Based on Iron and Cobalt. *Chem. Commun.* **1998**, 849–850.

(118) Fan, R.-Q.; Fan, R.-J.; Lv, Z.-W.; Yang, Y.-L.; An, F.; Gu, D.-M. Synthesis, Crystal Structure and Catalytic Performance of Bis(imino)pyridyl Nickel Complexes. *J. Coord. Chem.* **2007**, *60*, 919–927.

(119) Lee, G. M.; Appukuttan, V. K.; Suh, H.; Ha, C.-S.; Kim, I. Nickel(II) Dibromide Complexes Bearing Bis(benzimidazolyl)amine and Bis(benzimidazolyl)pyridine Ligands for Ethylene Oligomerizations. *Catal. Lett.* **2011**, *141*, 1608–1615.

(120) Zhang, W.; Wang, Y.; Yu, J.; Redshaw, C.; Hao, X.; Sun, W.-H. 2-(N-Alkylcarboxamide)-6-Iminopyridyl Palladium and Nickel Complexes: Coordination Chemistry and Catalysis. *Dalton Trans.* **2011**, *40*, 12856–12865.

(121) Zhang, J.; Liu, S.; Li, A.; Ye, H.; Li, Z. Nickel(II) Complexes Chelated by 2,6-Pyridinedicarboxamide: Syntheses, Characterization, and Ethylene Oligomerization. *New J. Chem.* **2016**, *40*, 7027–7033.

(122) Nyamato, G. S.; Alam, M. G.; Ojwach, S. O.; Akerman, M. P. (Pyrazolyl)-(Phosphinoyl)pyridine Iron(II), Cobalt(II) and Nickel(II) Complexes: Synthesis, Characterization and Ethylene Oligomerization Studies. *J. Organomet. Chem.* **2015**, *783*, 64–72.

(123) Ojwach, S. O.; Guzei, I. A.; Benade, L. L.; Mapolie, S. F.; Darkwa, J. (Pyrazol-1-ylmethyl)pyridine Nickel Complexes: Ethylene Oligomerization and Unusual Friedel-Crafts Alkylation Catalysts. *Organometallics* **2009**, *28*, 2127–2133.

(124) Nyamato, G. S.; Ojwach, S. O.; Akerman, M. P. Unsymmetrical (Pyrazolylmethyl)pyridine Metal Complexes as Catalysts for Ethylene Oligomerization Reactions: Role of Solvent and co-Catalyst in Product Distribution. *J. Mol. Catal. A: Chem.* **2014**, *394*, 274–282.

(125) Ulbrich, Ana H. D. P. S.; Bergamo, A. L.; Casagrande, Osvaldo de L., Jr. Oligomerization of Ethylene Using Tridentate Nickel Catalysts Bearing Ether-Pyrazol Ligands with Pendant O- and S-Donor Groups. *Catal. Commun.* **2011**, *16*, 245–249.

(126) Dresch, L. C.; Junges, C. H.; Casagrande, O. d. L.; Stieler, R. Nickel Complexes Supported by Selenium-Based Tridentate Ligands and Their Use as Effective Catalyst Systems for Ethylene Dimerisation. *J. Organomet. Chem.* **2018**, *856*, 34–40.

(127) Boudier, A.; Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H.; Braunstein, P. Nickel(II) Complexes with Imino-Imidazole Chelating Ligands Bearing Pendant Donor Groups (SR, OR, NR2, PR2) as Precatalysts in Ethylene Oligomerization. *J. Organomet. Chem.* **2012**, *718*, 31–37.

(128) Nyamato, G. S.; Ojwach, S. O.; Akerman, M. P. Ethylene Oligomerization Studies by Nickel(II) Complexes Chelated by (Amino)pyridine Ligands: Experimental and Density Functional Theory Studies. *Dalton Trans.* **2016**, *45*, 3407–3416.

(129) Mecking, S. Olefin Polymerization by Late Transition Metal Complexes-A Root of Ziegler Catalysts Gains New Ground. *Angew. Chem. Int. Ed.* **2001**, *40*, 534–540.

(130) Gomes Carneiro, T. M.; Dupont, J.; Luke, M.; Matt, D. The Preparation of Keim's Ethylene Oligomerization Catalyst. An Introductory Experiment in Organometallic Chemistry. *Quim. Nova* **1988**, *11*, 215–217.

(131) Boulens, P.; Pellier, E.; Jeanneau, E.; Reek, Joost N. H.; Olivier-Bourbigou, H.; Breuil, P.-A. R. Self-Assembled Organometallic Nickel Complexes as Catalysts for Selective Dimerization of Ethylene into 1-Butene. *Organometallics* **2015**, *34*, 1139–1142.

(132) Heinicke, J.; Basvani, K. R.; Jones, P. G. α-Phosphino Amino Acids: Synthesis, Structure, and Reactivity of Phosphaprolines. *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 678–682.

(133) Song, L.; Song, S.; Huang, J. Synthesis, Characterization and Ethylene Oligomerization Behavior of Neutral Nickel Complexes Bearing N-Fluorinated Phenyl Salicylaldiminato Chelate Ligands. *Chin. J. Chem.* **2012**, *30*, 1119–1126.

(134) Wang, J.; Zhang, N.; Li, C. Q.; Shi, W. G.; Lin, Z. Y. Nickel Complexes Based on Hyperbranched Salicylaldimine Ligands: Synthesis, Characterization, and Catalytic Properties for Ethylene Oligomerization. *J. Organomet. Chem.* **2016**, *822*, 104–111.

(135) Wang, J.; Zhang, N.; Li, C.; Shi, W.; Lin, Z. Synthesis and Ethylene Oligomerization of Hyperbranched Salicylaldimine Nickel Complexes. *Adv. Polym. Technol.* **2018**, *37*, 629–636.

(136) Li, C.; Wang, F.; Lin, Z.; Zhang, N.; Wang, J. Novel Nickel Complexes with Hyperbranched Structure: Synthesis, Characterization and Performance in Ethylene Oligomerization. *Inorg. Chim. Acta* **2016**, *453*, 430–438.

(137) Zhang, N.; Fu, Z.; Jiang, Y.; Guo, D.; Chen, L.; Wang, J. Synthesis of Novel Structure Based Low Generation Branched Salicylaldimine Nickel Complexes and Their Catalysis of Ethylene Oligomerization. *ChemistrySelect* **2018**, *3*, 10428–10433.

(138) Cheisson, T.; Cao, T.-P.-A.; Le Goff, X. F.; Auffrant, A. Nickel Complexes Featuring Iminophosphorane-Phenoxide Ligands for Catalytic Ethylene Dimerization. *Organometallics* **2014**, *33*, 6193–6199.

(139) Haghverdi, M.; Tadjarodi, A.; Bahri-Laleh, N.; Nekoomanesh-Haghighi, M. Synthesis and Characterization of Ni(II) Complexes Bearing 2-(1 H -Benzimidazol-2-yl)-Phenol Derivatives as Highly Active Catalysts for Ethylene Oligomerization. *Appl. Organomet. Chem.* **2018**, *32*, e4015.

(140) Oliveira, L. L. de; da Silva, S. M.; Casagrande, A.C.A.; Stieler, R.; Casagrande, O. L. Synthesis and Characterization of Ni (II) Complexes Supported by Phenoxy/Naphthoxy-Imine Ligands with Pendant N - and O -Donor Groups and Their Use in Ethylene Oligomerization. *Appl. Organomet. Chem.* **2018**, *32*, e4414.

(141) Wang, J.; Wan, L.; Zhang, D.; Wang, Q.; Chen, Z. trans-1,2-Diphenylethylene Linked Isoindoline-Salicylaldiminato Nickel(II) Halide Complexes: Synthesis, Structure, Dehydrogenation, and Catalytic Activity toward Olefin Homopolymerization. *Eur. J. Inorg. Chem.* **2013**, 2093–2101.

(142) Ngcobo, M.; Ojwach, S. O. Structural and Ethylene Oligomerization Studies of Chelated N O(imino/amino)phenol Nickel(II) Complexes. *J. Organomet. Chem.* **2017**, *846*, 33–39.

(143) Zaidman, A. V.; Khasbiullin, I. I.; Belov, G. P.; Pervova, I. G.; Lipunov, I. N. Catalytic Activity of New Nickel(II) Formazanates in Ethylene Oligomerization. *Pet. Chem.* **2012**, *52*, 28–34.

(144) Zaidman, A. V.; Pervova, I. G.; Vilms, A. I.; Belov, G. P.; Kayumov, R. R.; Slepukhin, P. A.; Lipunov, I. N. Synthesis, Characterization and Ethylene Oligomerization Studies of Nickel(II) Based New Formazane Derivatives. *Inorg. Chim. Acta* **2011**, *367*, 29–34.

(145) Zuo, W.; Tourbillon, C.; Rosa, V.; Cheaib, K.; Andrade, M. M.; Dagorne, S.; Welter, R. Synthesis, Crystal Structures and Use in Ethylene Oligomerization Catalysis of Novel Mono- and Dinuclear Nickel Complexes Supported by (E)-N'-(1-(thiophene-2-yl)ethylidene)benzohydrazide Ligand. *Inorg. Chim. Acta* **2012**, *383*, 213–219.

(146) Pinheiro, A. C.; Virgili, A. H.; Roisnel, T.; Kirillov, E.; Carpentier, J.-F.; Casagrande, O. L., Jr. Ni(II) Complexes Bearing Pyrrolide-Imine Ligands with Pendant N-, O- and S-Donor Groups: Synthesis, Structural Characterization and Use in Ethylene Oligomerization. *RSC Adv.* **2015**, *5*, 91524–91531.

(147) Xu, C.; Shen, Q.; Sun, X.; Tang, Y. Synthesis, Characterization, and Highly Selective Ethylene Dimerization to 1-Butene of [O-NX]Ni(II) Complexes. *Chin. J. Chem.* **2012**, *30*, 1105–1113.

(148) Keim, W.; Vogt, M.; Wasserscheid, P.; Driessen-Holscher, B. Perfluorinated Polyethers for the Immobilization of Homogeneous Nickel Catalysts. *J. Mol. Catal. A: Chem.* **1999**, *139*, 171–175.

(149) Benvenuti, F.; Carlini, C.; Marchionna, M.; Galletti, Anna Maria Raspolli; Sbrana, G. Propylene Oligomerization by Nickel Catalysts in Biphasic Fluorinated Systems. *J. Mol. Catal. A: Chem.* **2002**, *178*, 9–20.

(150) Olivier, H. Recent Developments in the Use of Non-Aqueous Ionic Liquids for Two-Phase Catalysis. *J. Mol. Catal. A: Chem.* **1999**, *146*, 285–289.

(151) Fehér, C.; Kriván, E.; Eller, Z.; Hancsók, J.; Skoda Földes, R. The Use of Ionic Liquids in the Oligomerization of Alkenes. In *Oligomerization of Chemical and Biological Compounds*; Lesieur, C., Ed.; InTech, **2014.**

(152) Olivier-Bourbigou, H.; Lecocq, V. Ionic Liquids as New Solvents and Catalysts for Petrochemical and Refining Processes. *Stud. Surf. Sci. Catal.* **2003**, *145*, 55–60.

(153) Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic Liquids and Catalysis: Recent Progress from Knowledge to Applications. *Appl. Catal., A* **2010**, *373*, 1–56.

(154) Chauvin, Y.; Gilbert, B.; Guibard, I. Catalytic Dimerization of Alkenes by Nickel Complexes in Organochloroaluminate Molten Salts. *J. Chem. Soc., Chem. Commun.* **1990**, 1715.

(155) Chauvin, Y.; Gilbert, B.; Guibard, I. Catalytic Dimerization of Olefins by Nickel Complexes in Organochloroaluminate Molten Salts. *Proc. - Electrochem. Soc.* **1990**, *90-17*, 822–832.

(156) Chauvin, Y.; Einloft, S.; Olivier, H. Catalytic Dimerization of Propene by Nickel-Phosphine Complexes in 1-Butyl-3-Methylimidazolium Chloride/$AlEt_xCl_{3-x}$ (x = 0, 1) Ionic Liquids. *Ind. Eng. Chem. Res.* **1995**, *34*, 1149–1155.

(157) Chauvin, Y.; Di Marco-Van Tiggelen, F.; Olivier, H. Determination of Aluminium Electronegativity in New Ambient-temperature Acidic Molten Salts based on 3-Butyl-1-Methylimidazolium Chloride and $AlEt_{3-x}Cl_x$ (x = 0-3) by ^1H Nuclear Magnetic Resonance Spectroscopy. *J. Chem. Soc. Dalton Trans.* **1993**, 1009–1011.

(158) Gilbert, B.; Olivier-Bourbigou, H.; Favre, F. Chloroaluminate Ionic Liquids: from Their Structural Properties to Their Applications in Process Intensification. *Oil & Gas Science and Technology - Rev. IFP* **2007**, *62*, 745–759.

(159) Einloft, S.; Kietrich, F. K.; Souza, R. F. de; Dupont, J. Selective Two-Phase Catalytic Ethylene Dimerization by Ni(II) Complexes/$AlEtCl_2$ Dissolved in Organoaluminate Ionic Liquids. *Polyhedron* **1996**, *15*, 3257–3259.

(160) Chauvin, Y.; Olivier, H.; Wyrvalski, C. N.; Simon, L. C.; Souza, R. F. de. Oligomerization of n-Butenes Catalyzed by Nickel Complexes Dissolved in Organochloroaluminate Ionic Liquids. *J. Catal.* **1997**, *165*, 275–278.

(161) Souza, R. F. de; Thiele, D.; Monteiro, A. L. Effect of Phosphine–CS_2 Adducts on the Nickel-Catalyzed Butenes Oligomerization in Organochloroaluminate Imidazolium Ionic Liquids. *J. Catal.* **2006**, *241*, 232–234.

(162) Simon, L. C.; Dupont, J.; Souza, R. F. de. Two-Phase n-Butenes Dimerization by Nickel Complexes in Molten Salt Media. *Appl. Catal., A* **1998**, *175*, 215–220.

(163) Thiele D.; Souza, R. F. de. The Role of Aluminum Species in Biphasic Butene Dimerization Catalyzed by Nickel Complexes. *J. Mol. Catal. A: Chem.* **2007**, *264*, 293–298.

(164) Ellis, B.; Keim, W.; Wasserscheid, P. Linear Dimerization of But-1-ene in Biphasic Mode Using Buffered Chloroaluminate Ionic Liquid Solvents. *Chem. Commun.* **1999**, 337–338.

(165) Keim, W.; Hoffmann, B.; Lodewick, R.; Peuckert, M.; Schmitt, G.; Fleischhauer, J.; Meier, U. Linear Oligomerization of Olefins via Nickel Chelate Complexes and Mechanistic Considerations Based on Semiempirical Calculations. *J. Mol. Catal.* **1979**, *6*, 79–97.

(166) Wasserscheid, P.; Eichmann, M. Selective Dimerisation of 1-Butene in Biphasic Mode Using Buffered Chloroaluminate Ionic Liquid Solvents — Design and Application of a Continuous Loop Reactor. *Catal. Today* **2001**, *66*, 309–316.

(167) Eichmann, M.; Keim, W.; Haumann, M.; Melcher, B. U.; Wasserscheid, P. Nickel Catalyzed Dimerization of Propene in Chloroaluminate Ionic Liquids: Detailed Kinetic Studies in a Batch Reactor. *J. Mol. Catal. A: Chem.* **2009**, *314*, 42–48.

(168) Wasserscheid, P.; Hilgers, C.; Gordon, C. M.; Muldoon, M. J.; Dunkin, I. R. Ionic liquids: Polar, but Weakly Coordinating Solvents for the First Biphasic Oligomerisation of Ethene to Higher α-Olefins with Cationic Ni Complexes. *Chem. Commun.* **2001**, 1186–1187.

(169) Wasserscheid, P.; Hilgers, C.; Keim, W. Ionic Liquids-Weakly-Coordinating Solvents for the Biphasic Ethylene Oligomerization to α-Olefins Using Cationic Ni-Complexes. *J. Mol. Catal. A: Chem.* **2004**, *214*, 83–90.

(170) Lecocq, V.; Olivier-Bourbigou, H. Biphasic Ni-Catalyzed Ethylene Oligomerization in Ionic Liquids. *Oil & Gas Science and Technology - Rev. IFP* **2007**, *62*, 761–773.

(171) Song, K.-M.; Gao, H.-Y.; Liu, F.-S.; Pan, J.; Guo, L.-H.; Zai, S.-B.; Wu, Q. Ionic Liquid-Supported Bis-(salicylaldimine) Nickel Complexes: Robust and Recyclable Catalysts for Ethylene Oligomerization in Biphasic Solvent System. *Catal. Lett.* **2009**, *131*, 566–573.

(172) Bernardo-Gusmao, K.; Trevisan Queiroz, Luiz F.; Souza, R. F. de; Leca, F.; Loup, C.; Reau, R. Biphasic Oligomerization of Ethylene with Nickel-1,2-Diiminophosphorane Complexes Immobilized in 1-n-Butyl-3-Methylimidazolium Organochloroaluminate. *J. Catal.* **2003**, *219*, 59–62.
(173) Nikiforidis, I.; Görling, A.; Hieringer, W. A Computational Study on Possible Active Species in Nickel(II)-Catalyzed 1-Butene Dimerization in [BMIM]+[AlCl4]− Ionic Liquid Solution. *J. Coord. Chem.* **2015**, *68*, 3362–3373.
(174) Machado Nobre Borba, K.; Oberson de Souza, M.; DeSouza, R. F.; Bernardo-Gusmao, K. β-Diimine Nickel Complexes in BMI·AlCl4 Ionic Liquid: A Catalytic Biphasic System for Propylene Oligomerization. *Appl. Catal., A* **2017**, *538*, 51–58.
(175) Doetterl, M.; Alt, H. G. Heavy Metal with a Heavy Impact: Olefin Dimerization Reactions in Triphenylbismuth Buffered Chloroaluminate Ionic Liquids. *ChemCatChem* **2011**, *3*, 1799–1804.
(176) Doetterl, M.; Alt, H. G. Buffered Aluminum Chloride as a Highly Efficient Cocatalyst for Olefin Dimerization and Polymerization. *ChemCatChem* **2012**, *4*, 370–378.
(177) Behr, A.; Bayrak, Z.; Samli, G.; Yildiz, D.; Peitz, S.; Stochniol, G. Oligomerization of n-Butenes in a Two-Phase Reaction System with Homogeneous Ni/Al-Catalysts. *Chem. Eng. Technol.* **2016**, *39*, 263–270.
(178) Behr, A.; Bayrak, Z.; Samli, G.; Yildiz, D.; Korkmaz, V.; Peitz, S.; Stochniol, G. Recycling and Oligomerization Activity of Ni/Al Catalyst in a Biphasic System with Ionic Liquids. *Chem. Eng. Technol.* **2017**, *40*, 196–204.
(179) Mehnert, C. P. Supported Ionic Liquid Catalysis. *Chem. - Eur. J.* **2005**, *11*, 50–56.
(180) van Doorslaer, C.; Wahlen, J.; Mertens, P.; Binnemans, K.; de Vos, D. Immobilization of Molecular Catalysts in Supported Ionic Liquid Phases. *Dalton Trans.* **2010**, *39*, 8377–8390.
(181) Doetterl, M.; Alt, H. G. Silica Based Cocatalysts for Heterogeneous Olefin Dimerization and Ethene Polymerization Reactions with Nickel Complexes. *ChemCatChem* **2012**, *4*, 660–667.
(182) Scholz, J.; Hager, V.; Wang, X.; Kohler, F. T. U.; Sternberg, M.; Haumann, M.; Szesni, N.; Meyer, K.; Wasserscheid, P. Ethylene to 2-Butene in a Continuous Gas Phase Reaction using SILP-Type Cationic Nickel Catalysts. *ChemCatChem* **2014**, *6*, 162–169.
(183) Kohler, F. T. U.; Gaertner, K.; Hager, V.; Haumann, M.; Sternberg, M.; Wang, X.; Szesni, N.; Meyer, K.; Wasserscheid, P. Dimerization of Ethene in a Fluidized Bed Reactor Using Ni-Based Supported Ionic Liquid Phase (SILP) Catalysts. *Catal. Sci. Technol.* **2014**, *4*, 936–947.
(184) Wang, X.; Sobota, M.; Kohler, F. T. U.; Morain, B.; Melcher, B. U.; Laurin, M.; Wasserscheid, P.; Libuda, J.; Meyer, K. Functional Nickel Complexes of N-Heterocyclic Carbene Ligands in Pre-Organized and Supported Thin Film Materials. *J. Mater. Chem.* **2012**, *22*, 1893–1898.
(185) Pettinari, C.; Marchetti, F.; Mosca, N.; Tosi, G.; Drozdov, A. Application of Metal − Organic Frameworks. *Polym. Int* **2017**, *66*, 731–744.
(186) Hendon, C. H.; Rieth, A. J.; Korzyński, M. D.; Dinca, M. Grand Challenges and Future Opportunities for Metal-Organic Frameworks. *ACS Cent. Sci.* **2017**, *3*, 554–563.
(187) Chughtai, A. H.; Ahmad, N.; Younus, H. A.; Laypkov, A.; Verpoort, F. Metal-Organic Frameworks: Versatile Heterogeneous Catalysts for Efficient Catalytic Organic Transformations. *Chem. Soc. Rev.* **2015**, *44*, 6804–6849.
(188) Kyogoku, K.; Yamada, C.; Suzuki, Y.; Nishiyama, S.; Fukumoto, K.; Yamamoto, H.; Indo, S.; Sano, M.; Miyake, T. Syntheses of Metal-organic Framework Compounds Containing Ni-bipyridyl Complex for Oligomerization of Ethylene. *J. Jpn. Petrol. Inst.* **2010**, *53*, 308–312.
(189) Canivet, J.; Aguado, S.; Schuurman, Y.; Farrusseng, D. MOF-Supported Selective Ethylene Dimerization Single-Site Catalysts through One-Pot Postsynthetic Modification. *J. Am. Chem. Soc.* **2013**, *135*, 4195–4198.
(190) Liu, B.; Jie, S.; Bu, Z.; Li, B.-G. Postsynthetic Modification of Mixed-Linker Metal–Organic Frameworks for Ethylene Oligomerization. *RSC Adv* **2014**, *4*, 62343–62346.
(191) Liu, S.; Zhang, Y.; Huo, Q.; He, S.; Han, Y. Synthesis and Catalytic Performances of a Novel Zn-MOF Catalyst Bearing Nickel Chelating Diimine Carboxylate Ligands for Ethylene Oligomerization. *J. Spectrosc.* **2015**, *2015*, 1–8.

(192) Madrahimov, S. T.; Gallagher, J. R.; Zhang, G.; Meinhart, Z.; Garibay, S. J.; Delferro, M.; Miller, J. T.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. Gas-Phase Dimerization of Ethylene under Mild Conditions Catalyzed by MOF Materials Containing (bpy)NiII Complexes. *ACS Catal.* **2015**, *5*, 6713–6718.

(193) Li, Z.; Schweitzer, N. M.; League, A. B.; Bernales, V.; Peters, A. W.; Getsoian, A. B.; Wang, T. C.; Miller, J. T.; Vjunov, A.; Fulton, J. L. *et al.* Sintering-Resistant Single-Site Nickel Catalyst Supported by Metal-Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 1977–1982.

(194) Bernales, V.; League, A. B.; Li, Z.; Schweitzer, N. M.; Peters, A. W.; Carlson, R. K.; Hupp, J. T.; Cramer, C. J.; Farha, O. K.; Gagliardi, L. Computationally Guided Discovery of a Catalytic Cobalt-Decorated Metal–Organic Framework for Ethylene Dimerization - Correction. *J. Phys. Chem. C* **2016**, *120*, 23576–23583.

(195) Metzger, E. D.; Brozek, C. K.; Comito, R. J.; Dinca, M. Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst. *ACS Cent. Sci.* **2016**, *2*, 148–153.

(196) Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dinca, M. Mechanism of Single-Site Molecule-Like Catalytic Ethylene Dimerization in Ni-MFU-4l. *J. Am. Chem. Soc.* **2017**, *139*, 757–762.

(197) Comito, R. J.; Metzger, E. D.; Wu, Z.; Zhang, G.; Hendon, C. H.; Miller, J. T.; Dinca, M. Selective Dimerization of Propylene with Ni-MFU-4 l. *Organometallics* **2017**, *36*, 1681–1683.

(198) Mlinar, A. N.; Keitz, B. K.; Gygi, D.; Bloch, E. D.; Long, J. R.; Bell, A. T. Selective Propene Oligomerization with Nickel(II)-Based Metal-Organic Frameworks. *ACS Catal.* **2014**, *4*, 717–721.

(199) Rozhko, E.; Bavykina, A.; Osadchii, D.; Makkee, M.; Gascon, J. Covalent Organic Frameworks as Supports for a Molecular Ni Based Ethylene Oligomerization Catalyst for the Synthesis of Long Chain Olefins. *J. Catal.* **2017**, *345*, 270–280.

(200) Kabanov, V. A.; Smetanyuk, V. I. Catalytic Behavior of Metal Complexes Immobilized in Functional Polymeric Carriers. *Macromol. Chem. Phys., Suppl.* **1981**, *5*, 121–154.

(201) Potapov, G. P.; Shepelin, V. A. Gel-Immobilized Catalytic Systems for Propylene Dimerization Containing Organophosphorus Ligands. *React. Kinet. Catal. Lett.* **1985**, *28*, 287–293.

(202) Peuckert, M.; Keim, W. Heterogenization of Homogeneous Nickel-Based Ethylene Oligomerization Catalysts. *J. Mol. Catal.* **1984**, *22*, 289–295.

(203) Nesterov, G. A.; Fink, G.; Zakharov, V. A. Ethylene Oligomerization by Supported Nickel-Complexes. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 669–673.

(204) Nesterov, G. A.; Zakharov, V. A.; Fink, G.; Fenzl, W. Heterogenization of a Homogeneous Nickel Chelate Ethylene Oligomerization Catalyst. *J. Mol. Catal.* **1991**, *66*, 367–372.

(205) Nesterov, G. A.; Zakharov, V. A.; Fink, G.; Fenzl, W. Supported Nickel Catalysts for Ethylene Oligomerization. *J. Mol. Catal.* **1991**, *69*, 129–136.

(206) Pomogailo, A. D.; Uflyand, I. E. Heterogenization of Homogeneous Catalysts by Chelate Formation with Macroligands. *J. Mol. Catal.* **1989**, *55*, 429–440.

(207) Uflyand, I. E.; Pomogailo, A. D. Comparative Analysis of Homogeneous and Immobilized Catalysts for Ethylene Dimerization Based on Nickel(II) Chelates. *J. Mol. Catal.* **1989**, *55*, 302–310.

(208) Braca, G.; Raspolli Galletti, A. M.; Di Girolamo, M.; Sbrana, G.; Silla, R.; Ferrarini, P. Organometallic Nickel Catalysts Anchored on Polymeric Matrixes in the Oligomerization and/or Polymerization of Olefins. Part II. Effect and Role of the Components of the Catalytic System. *J. Mol. Catal. A: Chem.* **1995**, *96*, 203–213.

(209) Raspolli Galletti, A. M.; Geri, G.; Sbrana, G.; Marchionna, M.; Ferrarini, P. Striking Different Behavior in the Activation of α-Olefins by Homogeneous and Heterogenized Catalysts Based on η^5-Cyclopentadienyl Nickel Derivatives. *J. Mol. Catal. A: Chem.* **1996**, *111*, 273–280.

(210) Angelescu, E.; Che, M.; Andruh, M.; Zãvoianu, R.; Costentin, G.; Miricã, C.; Dumitru Pavel, O. Ethylene Selective Dimerization on Polymer Complex Catalyst of Ni(4,4′-bipyridine)Cl_2 Coactivated with $AlCl(C_2H_5)_2$. *J. Mol. Catal. A: Chem.* **2004**, *219*, 13–19.

(211) Souza, M. O. de; Rodrigues, L. R.; Pastore, H. O.; Ruiz, J. A.C.; Gengembre, L.; Gauvin, R. M.; Souza, R. F. de. A Nano-Organized Ethylene Oligomerization Catalyst: Characterization and Reactivity of the $Ni(MeCN)_6(BF_4)_2$/[Al]-MCM-41/$AlEt_3$ System. *Microporous and Mesoporous Materials* **2006**, *96*, 109–114.

(212) Souza, M. O. de; Rodrigues, L. R.; Gauvin, R. M.; Souza, R. F. de; Pastore, H. O.; Gengembre, L.; Ruiz, J. A.C.; Gallo, Jean Marcel R.; Milanesi, T. S.; Milani, M. A. Support Effect in Ethylene Oligomerization Mediated by Heterogenized Nickel Catalysts. *Catal. Commun.* **2010**, *11*, 597–600.

(213) Muraza, O. Maximizing Diesel Production through Oligomerization: A Landmark Opportunity for Zeolite Research. *Ind. Eng. Chem. Res.* **2015**, *54*, 781–789.

(214) Marcilly, C. *Catalyse Acido-basique Application au Raffinage*, Editions Technip: Paris, 2003.

(215) Corma, A.; Iborra, S. *Oligomerization of Alkenes*. Catal. Fine Chem. Synth 4; John Wiley & Sons Ltd, **2006**.

(216) Bellussi, G.; Mizia, F.; Calemma, V.; Pollesel, P.; Millini, R. Oligomerization of Olefins from Light Cracking Naphtha over Zeolite-Based Catalyst for the Production of High Quality Diesel Fuel. *Microporous and Mesoporous Materials* **2012**, *164*, 127–134.

(217) Forget, S.; Olivier-Bourbigou, H.; Delcroix, D. Homogeneous and Heterogeneous Nickel-Catalyzed Olefin Oligomerization: Experimental Investigation for a Common Mechanistic Proposition and Catalyst Optimization. *ChemCatChem* **2017**, *9*, 2408–2417.

(218) Finiels, A.; Fajula, F.; Hulea, V. Nickel-Based Solid Catalysts for Ethylene Oligomerization – A Review. *Catal. Sci. Technol.* **2014**, *4*, 2412–2426.

(219) Nicholas, C. P. Applications of Light Olefin Oligomerization to the Production of Fuels and Chemicals. *Appl. Catal., A* **2017**, *543*, 82–97.

(220) Hulea, V. Toward Platform Chemicals from Bio-Based Ethylene: Heterogeneous Catalysts and Processes. *ACS Catal.* **2018**, 3263–3279.

(221) Skupinska, J. Oligomerization of Alpha-Olefins to Higher Oligomers. *Chem. Rev.* **1991**, *91*, 613–648.

(222) Ghashghaee, M. Heterogeneous catalysts for gas-phase conversion of ethylene to higher olefins. *Reviews in Chemical Engineering* **2017**, *34*, 595–655.

(223) Ziegler, K. Linked Polymerization of Ethylene and its Homologs. *Brennst.-Chem.* **1954**, *35*, 321–325.

(224) Ziegler, K.; Gellert, H. G. U.S. Patent US2695327, 1954.

(225) Morikawa, H. Reactivity of Lower Hydrocarbons. VI. Activation of Specific Bonds in Ethylene on Catalytic Surface. *Kogyo Kagaku Zasshi* **1938**, *41*, 350–351.

(226) Shiba, T.; Ozaki, A. A Catalyst Consisting of Nickel Oxide and Silica. I. The Catalytic Activity of Ethylene Polymerization Caused by Vacuum Heating. *Nippon Kagaku Zasshi* **1953**, *74*, 295–297.

(227) Bailey, G. C.; Reid, J. A. US Patent US2581228, 1952.

(228) Eidus, Y. T.; Puzitskii, K. V.; Ershov, N. I.; Kazanskii, B. A. Catalytic Polymerization of Olefins. III. Activity of the Nickelous Oxide-Silica Gel Catalyst for Polymerization of Ethylene. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 111–114.

(229) Eidus, Y. T.; Puzitskii, K. V.; Kazanskii, B. A. Catalytic Polymerization of Olefins. IX. Activity of Nickel Silicate Deposited on Aluminosilicate in the Reaction of Ethylene Polymerization. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 926–930.

(230) Wendt, G.; Fritsch, E.; Schoellner, R.; Siegel, H. Studies on Nickel Oxide Mixed Catalysts. II. Catalytic Properties of Nickel Oxide (NiO)/Silicon Dioxide Catalysts. *Z. Anorg. Allg. Chem.* **1980**, *467*, 51–60.

(231) Wendt, G.; Moerke, W.; Schoellner, R.; Siegel, H. Studies on Nickel Oxide Mixed Catalysts. I. Structural Properties of Nickel Oxide (NiO)/Silicon Dioxide Catalysts. *Z. Anorg. Allg. Chem.* **1980**, *467*, 43–50.

(232) Sohn, J. R.; Ozaki, A. Structure of NiO-SiO_2 Catalyst for Ethylene Dimerization as Observed by Infrared Absorption. *J. Catal.* **1979**, *59*, 303–310.

(233) Wendt, G.; Finster, J.; Deininger, D. On the Catalytic Performance of Nickel Monoxide/Silicon Dioxide and Nickel Monoxide-Aluminum Oxide/Silicon Dioxide Catalysts in the Dimerization of Olefins. *Wiss. Z. - Karl-Marx-Univ. Leipzig, Math.-Naturwiss. Reihe* **1981**, *30*, 346–357.

(234) Sohn, J. R.; Park, W. C.; Shin, D. C. Characterization of Nickel Sulfate Supported on SiO_2 for Ethylene Dimerization and Promoting Effect of Al_2O_3 on Catalytic Activity. *J. Mol. Catal. A: Chem.* **2006**, *256*, 156–163.

(235) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. The Preparation of Alkyltrimethylammonium-Kanemite Complexes and their Conversion to Microporous Materials. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988–992.

(236) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. Trimethylsilyl Derivatives of Alkyltrimethylammonium-Kanemite Complexes and their Conversion to Microporous Silica Materials. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1535–1537.

(237) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et, a. A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates. *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

(238) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism. *Nature* **1992**, *359*, 710–712.

(239) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **1998**, *279*, 548–552.

(240) Hartmann, M.; Poppl, A.; Kevan, L. Ethylene Dimerization in Nickel Containing MCM-41 and AlMCM-41 Studied by Electron Spin Resonance and Gas Chromatography. *Stud. Surf. Sci. Catal.* **1996**, *101*, 801–809.

(241) Iwamoto, M.; Kosugi, Y. Highly Selective Conversion of Ethene to Propene and Butenes on Nickel Ion-Loaded Mesoporous Silica Catalysts. *J. Phys. Chem. C* **2007**, *111*, 13–15.

(242) Iwamoto, M. Conversion of Ethene to Propene on Nickel Ion-Loaded Mesoporous Silica Prepared by the Template Ion Exchange Method. *Catal. Surv. Asia* **2008**, *12*, 28–37.

(243) Ikeda, K.; Kawamura, Y.; Yamamoto, T.; Iwamoto, M. Effectiveness of the Template-Ion Exchange Method for Appearance of Catalytic Activity of Ni–MCM-41 for the Ethene to Propene Reaction. *Catal. Commun.* **2008**, *9*, 106–110.

(244) Iwamoto, M. One Step Formation of Propene from Ethene or Ethanol through Metathesis on Nickel Ion-Loaded Silica. *Molecules* **2011**, *16*, 7844–7863.

(245) Tanaka, M.; Itadani, A.; Kuroda, Y.; Iwamoto, M. Effect of Pore Size and Nickel Content of Ni-MCM-41 on Catalytic Activity for Ethene Dimerization and Local Structures of Nickel Ions. *J. Phys. Chem. C* **2012**, *116*, 5664–5672.

(246) Burattin, P.; Che, M.; Louis, C. Metal Particle Size in Ni/SiO_2 Materials Prepared by Deposition-Precipitation: Influence of the Nature of the Ni(II) Phase and of Its Interaction with the Support. *J. Phys. Chem. B* **1999**, *103*, 6171–6178.

(247) Witt, S.; Hinrichsen, O. Hochdisperse Nickelkatalysatoren für einen neuen Weg der Propensynthese. *Chemie Ingenieur Technik* **2008**, *80*, 1250.

(248) Frey, A. S.; Hinrichsen, O. Comparison of Differently Synthesized Ni(Al)MCM-48 Catalysts in the Ethene to Propene Reaction. *Microporous and Mesoporous Materials* **2012**, *164*, 164–171.

(249) Lehmann, T.; Wolff, T.; Zahn, V. M.; Veit, P.; Hamel, C.; Seidel-Morgenstern, A. Preparation of Ni-MCM-41 by Equilibrium Adsorption — Catalytic Evaluation for the Direct Conversion of Ethene to Propene. *Catal. Commun.* **2011**, *12*, 368–374.

(250) Lehmann, T.; Wolff, T.; Hamel, C.; Veit, P.; Garke, B.; Seidel-Morgenstern, A. Physico-Chemical Characterization of Ni/MCM-41 Synthesized by a Template Ion Exchange Approach. *Microporous and Mesoporous Materials* **2012**, *151*, 113–125.

(251) Alvarado Perea, L.; Wolff, T.; Veit, P.; Hilfert, L.; Edelmann, F. T.; Hamel, C.; Seidel-Morgenstern, A. Alumino-Mesostructured Ni Catalysts for the Direct Conversion of Ethene to Propene. *J. Catal.* **2013**, *305*, 154–168.

(252) Lehmann, T.; Seidel-Morgenstern, A. Comment on "Effect of Pore Size and Nickel Content of Ni-MCM-41 on Catalytic Activity for Ethene Dimerization and Local Structures of Nickel Ions". *J. Phys. Chem. C* **2012**, *116*, 22646–22648.

(253) Tanaka, M.; Itadani, A.; Kuroda, Y.; Iwamoto, M. Reply to "Comment on 'Effect of Pore Size and Nickel Content of Ni-MCM-41 on Catalytic Activity for Ethene Dimerization and Local Structures of Nickel Ions'". *J. Phys. Chem. C* **2012**, *116*, 22649–22651.

(254) Perea, L. A.; Felischak, M.; Wolff, T.; Hamel, C.; Seidel-Morgenstern, A. Experimental Investigation of the Reaction Network of Ethene to Propene over Ni/AlMCM-41 Catalysts. *Chemie Ingenieur Technik* **2017**, *89*, 903–914.

(255) Speight, J. G. *Handbook of Petroleum Refining*; Chemical Industries 143; CRC Press: Boca Raton, **2017**.

(256) Sohn, J. R.: Ozaki, A. Acidity of Nickel Silicate and Its Bearing on the Catalytic Activity for Ethylene Dimerization and Butene Isomerization. *J. Catal.* **1980**, *61*, 29–38.

(257) Hogan, J. P.; Banks, R. L.; Lanning, W. C.; Clark, A. Polymerization of Light Olefins over Nickel Oxide on Silica-Alumina. *Ind. Eng. Chem.* **1955**, *47*, 752–757.

(258) Allum, K. G. U.S. Patent 3,729,428, 1973.

(259) Eidus, Y. T.; Ershov, N. I.; Puzitskii, K. V.; Kazanskii, B. A. Catalytic Polymerization of Olefins. VII. Polymerization of Ethylene over Nickelous Oxide-Aluminosilicate Catalyst. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 703–708.

(260) Eidus, Y. T.; Puzitskii, K. V.; Aleksanyan, V. T.; Sterin, K. E.; Kazanskii, B. A. Catalytic Polymerization of Olefins. I. Liquid Polymerization Products of Ethylene over the Catalyst of Nickelous Oxide-Aluminosilicate. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1959**, 1787–1793.

(261) Eidus, Y. T.; Puzitskii, K. V.; Ershov, N. I.; Kazanskii, B. A. Catalytic Polymerization of Olefins. X. Effect of Temperature and Contact Time on Course of Polymerization Reaction of Ethylene over Nickel Catalysts. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 1114–1118.

(262) Eidus, Y. T.; Puzitskii, K. V.; Ershov, N. I.; Kazanskii, B. A. Catalytic Polymerization of Olefins. VIII. Polymerization of Ethylene over Nickelous Oxide-Aluminosilicate Catalyst. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 920–925.

(263) Eidus, Y. T.; Puzitskii, K. V.; Kazanskii, B. A. Catalytic Polymerization of Olefins. VI. Effect of Addition of some Metallic Oxides on Activity of NiO-Al2O3-Silica Gel Catalyst in the Reaction of Ethylene Polymerization. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 513–518.

(264) Eidus, Y. T.; Puzitskii, K. V.; Ershov, N. I.; Kazanskii, B. A. Catalytic Polymerization of Olefins. IV. Polymerization of Ethylene over Nickelous Oxide-Silica Gel Catalyst Promoted with Aluminum Oxide. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 115–119.

(265) Mertzweiler, J. K.; Tenney, H. M. US Patent 3,562,351, 1971.

(266) Sakaguchi, T.; Mita, S.; Matsui, E.; Takahashi, M.; Okazaki, N.; Tada, A. Oligomerization of Ethene over Several Catalyst Beds Consisting of Both Ni/$SiO_2 \cdot Al_2O_3$ and BPO_4. *Phosphorus Res. Bull.* **2002**, *14*, 129–134.

(267) Glockner, P. W.; Barnett, K. W. US Patent US3527839, 1970.

(268) Kiessling, D.; Wendt, G.; Schoellner, R.; Weber, M.; Becker, K. DD Patent 273054, 1989.

(269) Wendt, G.; Hentschel, D.; Finster, J.; Schoellner, R.; Hanafi, S.; Mikhail, R. S. Studies on Nickel Oxide Mixed Catalysts Part 12.-Characterization of NiO/Al2O3-SiO2. *J. Chem. Soc., Faraday Trans. I* **1983**, *79*, 2013–2025.

(270) Wendt, G.; Hentschel, D.; Schoellner, R.; Finster, J.; Becker, K.; Weber, M.; Welker, J. DD Patent 160037, 1983.

(271) Wendt, G.; Finster, J.; Schoellner, R.; Siegel, H. Structural and Catalytic Properties of Nickel(II) Oxide-Aluminum Oxide/Silicon Dioxide Catalysts for the Dimerization and Isomerization of Olefins. *Stud. Surf. Sci. Catal.* **1981**, *7*, 978–992.

(272) Fritsch, E.; Wendt, G.; Becker, K.; Deininger, D.; Hentschel, D.; Schoellner, R.; Weber, M. DD Patent 0152331, 1981.

(273) Wendt, G.; Fritsch, E.; Deininger, D.; Schoellner, R. Studies on Nickel Oxide Mixed Catalysts. V. Propene Dimerization on Nickel Oxide-Alumina/Silica Catalysts. *React. Kinet. Catal. Lett.* **1981**, *16*, 137–141.

(274) Hentschel, D.; Wendt, G.; Becker, K.; Finster, J.; Schoellner, R.; Petzold, E.; Weber, M.; Welker, J. DD Patent 0152330, 1981.

(275) Hentschel, D.; Petzold, E.; Welsch, T.; Wendt, G. Studies on Nickel Oxide Catalysts. VI. On the Dimerization of Propene and n-Butene Mixtures in an Integral Flow Microreactor Under Increased Pressure. *Wiss. Z. - Karl-Marx-Univ. Leipzig, Math.-Naturwiss. Reihe* **1981**, *30*, 358–364.

(276) Kiessling, D.; Wendt, G.; Hagenau, K.; Schoellner, R. Dimerization of n-Butenes on Amorphous NiO-Al_2O_3/SiO_2 Catalysts. *Appl. Catal.* **1991**, *71*, 69–78.

(277) Lapidus, A. L.; Slinkin, A. A.; Rudakova, L. N.; Myshenkova, T. N.; Loktev, M. I.; Papko, T. S.; Eidus, Y. T. Effect of the Composition of the Nickel(II) Oxide-Silicon Oxide-Aluminum Oxide Catalyst System on its Catalytic Properties in Ethylene and Isobutylene Oligomerization Reactions. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 1956–1961.

(278) Lapidus, A. L.; Mal'tsev, V. V.; Slinkin, A. A.; Loktev, M. I.; Eidus, Y. T. Effect of the Ratio of Components and the Acidity of Aluminosilicate Catalysts on the Oligomerization of Ethylene and Isobutylene. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 1080–1084.

(279) Lapidus, A. L.; Avetisyan, R. V.; Eidus, Y. T. Catalytic Polymerization of Olefins. XVII. Isomerization of n-Butenes in the Presence of Nickel Oxide-Aluminum Silicate Catalyst and its Components. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 343–350.

(280) Matsuda, T.; Miura, H.; Sugiyama K.; Ohno, N.; Keino, S.; Kaise, A. Selectivity in Ethylene Dimerization over Supported Nickel Oxide Catalysts. *J. Chem. Soc., Faraday Trans. I* **1979**, *75*, 1513–1520.

(281) Nicolaides, C. P.; Scurrell, M. S.; Semano, P. M. Nickel Silica-Alumina Catalysts for Ethene Oligomerization - Control of the Selectivity to 1-Alkene Products. *Appl. Catal., A* **2003**, *245*, 43–53.

(282) Nicolaides, C. P.; Scurrell, M. S. Unusual Regioselectivity Observed in the Oligomerization of Propene on Nickel(II) Ion-Exchanged Silica-Alumina Catalysts. *Spec. Publ. - R. Soc. Chem.* **2001**, *266*, 226–232.

(283) Eidus, Y. T.; Lapidus, A. L.; Avetisyan, R. V. Catalytic Polymerization of Olefins. XVI. Effect of Reaction Conditions on the Composition of the Products of Ethylene Dimerization in the Presence of Nickel Oxide-Aluminum Silicate Catalyst. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 336–342.

(284) Espinoza, R. L.; Nicolaides, C. P.; Korf, C. J.; Snel, R. Catalytic Oligomerization of Ethene over Nickel-Exchanged Amorphous Silica-Alumina; Effect of the Nickel Concentration. *Appl. Catal.* **1987**, *31*, 259–266.

(285) Espinoza, R. L.; Korf, C. J.; Nicolaides, C. P.; Snel, R. Catalytic Oligomerization of Ethene over Nickel-Exchanged Amorphous Silica-Alumina; Effect of the Reaction Conditions and Modeling of the Reaction. *Appl. Catal., A* **1987**, *29*, 175–184.

(286) Toch, K.; Thybaut, J. W.; Marin, G. B. Ethene Oligomerization on Ni-SiO_2-Al_2O_3: Experimental Investigation and Single-Event MicroKinetic Modeling. *Appl. Catal., A* **2015**, *489*, 292–304.

(287) Zhang, Q.; Wang, T.; Li, Y.; Xiao, R.; Vitidsant, T.; Reubroycharoen, P.; Wang, C.; Zhang, Q.; Ma, L. Olefin-Rich Gasoline-Range Hydrocarbons from Oligomerization of Bio-Syngas over Ni/ASA Catalyst. *Fuel Process. Technol.* **2017**, *167*, 702–710.

(288) Nicholas, C. P.; Bhattacharyya, A.; Mackowiak, D. E. US Patent 8,021,620, **2011**.

(289) Lee, M.; Yoon, J. W.; Kim, Y.; Yoon, J. S.; Chae, H.-J.; Han, Y.-H.; Hwang, D. W. Ni/SIRAL-30 as a Heterogeneous Catalyst for Ethylene Oligomerization. *Appl. Catal., A* **2018**, *562*, 87–93.

(290) Aid, A.; Andrei, R. D.; Amokrane, S.; Cammarano, C.; Nibou, D.; Hulea, V. Ni-Exchanged Cationic Clays as Novel Heterogeneous Catalysts for Selective Ethylene Oligomerization. *Applied Clay Science* **2017**, *146*, 432–438.

(291) Nierlich, F.; Neumeister, J.; Wildt, T.; Droste, W.; Obenaus, F. DD Patent 3,914,817, 1989.

(292 Klerk, A. de. Fischer–Tropsch Refining: Technology Selection to Match Molecules. *Green Chem.* **2008**, *10*, 1249.

(293) Bercik, P. G.; Metzger, K. J.; Swift, H. E. Oligomerization of C3-C4 Olefins using a Novel Nickel-Aluminosilicate Catalyst. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 214–219.

(294) Shin, M.; Suh, Y.-W. Ethylene Oligomerization over SiO_2–Al_2O_3 Supported Ni_2P Catalyst. *ChemCatChem* **2019**, *49*, 109.

(295) Heveling, J.; Nicolaides, C. P.; Scurrell, M. S. Catalysts and Conditions for the Highly Efficient, Selective and Stable Heterogeneous Oligomerization of Ethylene. *Appl. Catal., A* **1998**, *173*, 1–9.

(296) Choudary, N. V.; Newalkar, B. L. Use of Zeolites in Petroleum Refining and Petrochemical Processes: Recent Advances. *J Porous Mater* **2011**, *18*, 685–692.

(297) Eidus, Y. T.; Avetisyan, R. V.; Lapidus, A. L.; Isakov, Y. I.; Minachev, K. M. Ethylene Conversion in the Presence of Nickel-Zeolite Catalysis. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2596-502.

(298) Lapidus, A.; Krylova, A. Ethylene Oligomerization over Ni- and Pd-Zeolites. *DGMK Tagungsber.* **2001**, *2001-4*, 245–251.

(299) Bonneviot, L.; Olivier D.; Che, M. Dimerization of Olefins with Nickel-Surface Complexes in X-Type Zeolite or on Silica. *J. Mol. Catal.* **1983**, *21*, 415–430.

(300) Elev, I. V.; Shelimov, B. N.; Kazansky, V. B. The Role of Ni+ Ions in the Activity of NiCaY Zeolite Catalysts for Ethylene Dimerization. *J. Catal.* **1984**, *89*, 470–477.

(301) Yashima, T. Polymerization of Ethylene over Transition-Metal Exchanged Y Zeolites. *J. Catal.* **1975**, *36*, 320–326.

(302) Riekert, L. The Kinetics of Ethylene Polymerization in Nickel-Y Zeolite. *J. Catal.* **1970**, *19*, 8–14.

(303) Forni, L.; van Mao; Invernizzi, R. Propylene-1-Butene Codimerization over Nickel-Zeolite Catalyst. Kinetic and Mechanistic Study. *Chim. Ind.* **1975**, *57*, 669–675.

(304) Forni, L.; Invernizzi, R.; van Le, M. 1-Butene Dimerization over Nickel Zeolite Catalyst. Kinetic and Mechanistic Study. *Chim. Ind.* **1975**, *57*, 577–580.

(305) Heveling, J.; van der Beek, A.; Pender, M. de. Oligomerization of Ethene over Nickel-Exchanged Zeolite Y into a Diesel-Range Product. *Appl. Catal.* **1988**, *42*, 325–336.

(306) Ng, F.T.T.; Creaser, D. C. Ethylene Dimerization over Modified Nickel Exchanged Y-Zeolite. *Appl. Catal., A* **1994**, *119*, 327–339.

(307) Nkosi, B.; Ng, F. T. T.; Rempel, G. L. The Oligomerization of Butenes with Partially Alkali Exchanged NiNaY Zeolite Catalysts. *Appl. Catal., A* **1997**, *158*, 225–241.

(308) Mlinar, A. N.; Ho, O. C.; Bong, G. G.; Bell, A. T. The Effect of Noncatalytic Cations on the Activity and Selectivity of Nickel-Exchanged X Zeolites for Propene Oligomerization. *ChemCatChem* **2013**, *5*, 3139–3147.

(309) Sohn, J. R.; Park, J. H. Characterization of Dealuminated NiY Zeolite and Effect of Dealumination on Catalytic Activity for Ethylene Dimerization. *Appl. Catal., A* **2001**, *218*, 229–234.

(310) Lallemand, M.; Finiels, A.; Fajula, F.; Hulea, V. Catalytic Oligomerization of Ethylene over Ni-Containing Dealuminated Y Zeolites. *Appl. Catal., A* **2006**, *301*, 196–201.

(311) Lallemand, M.; Rusu, O. A.; Dumitriu, E.; Finiels, A.; Fajula, F.; Hulea, V. NiMCM-36 and NiMCM-22 Catalysts for the Ethylene Oligomerization: Effect of Zeolite Texture and Nickel Cations/Acid Sites ratio. *Appl. Catal., A* **2008**, *338*, 37–43.

(312) Lallemand, M.; Rusu, O. A.; Dumitriu, E.; Finiels, A.; Fajula, F.; Hulea, V. Ni-MCM-36 and Ni-MCM-22 Catalysts for the Ethylene Oligomerization. *Stud. Surf. Sci. Catal.* **2008**, *174*, 1139–1142.

(313) Martínez, A.; Arribas, M. A.; Concepción, P.; Moussa, S. New bifunctional Ni–H-Beta Catalysts for the Heterogeneous Oligomerization of Ethylene. *Appl. Catal., A* **2013**, *467*, 509–518.

(314) Moussa, S.; Arribas, M. A.; Concepcion, P.; Martinez, A. Heterogeneous Oligomerization of Ethylene to Liquids on Bifunctional Ni-Based Catalysts: The Influence of Support Properties on Nickel Speciation and Catalytic Performance. *Catal. Today* **2016**, *277*, 78–88.

(315) Jan, O.; Song, K.; Dichiara, A.; Resende, F. L. P. Ethylene Oligomerization over Ni–Hβ Heterogeneous Catalysts. *Ind. Eng. Chem. Res.* **2018**, *57*, 10241–10250.

(316) Jan, O.; Resende, F. L.P. Liquid Hydrocarbon Production via Ethylene Oligomerization over Ni-Hβ. *Fuel Processing Technology* **2018**, *179*, 269–276.

(317) Garwood, W. E.; Kushnerick, J. D.; Tabak, S. A. US Patent US4717782, 1988.

(318) Beltrame, P.; Forni, L.; Talamini, A.; Zuretti, G. Dimerization of 1-Butene over Nickel Zeolitic Catalysts: A Search for Linear Dimers. *Appl. Catal., A* **1994**, *110*, 39–48.

(319) Wendt, G.; Hagenau, K.; Dimitrova, R.; Popova, Z.; DImitrov, C. Dimerization of n-Butenes on Nickel Mordenite Catalysts. *React. Kinet. Catal. Lett.* **1986**, *31*, 383–388.

(320) Ganjkhanlou, Y.; Groppo, E.; Bordiga, S.; Volkova, M. A.; Berlier, G. Incorporation of Ni into HZSM-5 Zeolites: Effects of Zeolite Morphology and Incorporation Procedure. *Microporous and Mesoporous Materials* **2016**, *229*, 76–82.

(321) Ganjkhanlou, Y.; Berlier, G.; Groppo, E.; Borfecchia, E.; Bordiga, S. In Situ Investigation of the Deactivation Mechanism in Ni-ZSM5 During Ethylene Oligomerization. *Top. Catal.* **2017**, *60*, 1664–1672.
(322) Corma, A. From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chem. Rev.* **1997**, *97*, 2373–2420.
(323) Hartmann, M.; Kevan, L.; Pöppl, A. Ethylene Dimerization and Butene Isomerization in Nickel-Containing MCM-41 and AlMCM-41 Mesoporous Molecular Sieves: An Electron Spin Resonance and Gas Chromatography Study. *J. Phys. Chem. C* **1996**, *100*, 9906–9910.
(324) Hartmann, M.; Poppl, A.; Kevan, L. Formation and Stability of Ni(I) Ions in MCM-41 Mesoporous Molecular Sieves. *J. Phys. Chem.* **1995**, *99*, 17494–17496.
(325) Hulea, V.; Fajula, F. Ni-exchanged AlMCM-41 - An Efficient Bifunctional Catalyst for Ethylene Oligomerization. *J. Catal.* **2004**, *225*, 213–222.
(326) Lallemand, M.; Finiels, A.; Fajula, F.; Hulea, V. Continuous Stirred Tank Reactor for Ethylene Oligomerization Catalyzed by NiMCM-41. *Chem. Eng. J.* **2011**, *172*, 1078–1082.
(327) Agirrezabal-Telleria, I.; Iglesia, E. Stabilization of Active, Selective, and Regenerable Ni-Based Dimerization Catalysts by Condensation of Ethene within Ordered Mesopores. *J. Catal.* **2017**, *352*, 505–514.
(328) Mlinar, A. N.; Shylesh, S.; Ho, O. C.; Bell, A. T. Propene Oligomerization using Alkali Metal- and Nickel-Exchanged Mesoporous Aluminosilicate Catalysts. *ACS Catal.* **2014**, *4*, 337–343.
(329) Lallemand, M.; Finiels, A.; Fajula, F.; Hulea, V. Ethylene Oligomerization over Ni-Containing Mesostructured Catalysts with MCM-41, MCM-48 and SBA-15 Topologies. *Stud. Surf. Sci. Catal.* **2007**, *170*, 1863–1869.
(330) Ravikovitch, P. I.; Neimark, A. V. Relations Between Structural Parameters and Adsorption Characterization of Templated Nanoporous Materials with Cubic Symmetry. *Langmuir* **2000**, *16*, 2419–2423.
(331) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **1998**, *279*, 548–552.
(332) Andrei, R. D.; Murescanu, M.; Hulea, V. Synthesis of Well-Ordered Mesoporous Al-SBA-15 by the "pH-Adjusting" Method as Supports for Ethylene Oligomerization Catalysts. *An. Univ. Craiova, Ser. Chim.* **2012**, *41*, 40–45.
(333) Andrei, R. D.; Popa, M. I.; Fajula, F.; Hulea, V. Heterogeneous Oligomerization of Ethylene over Highly Active and Stable Ni-AlSBA-15 Mesoporous Catalysts. *J. Catal.* **2015**, *323*, 76–84.
(334) Andrei, R. D.; Mureseanu, M.; Popa, M. I.; Cammarano, C.; Fajula, F.; Hulea, V. Ni-Exchanged AlSBA-15 Mesoporous Materials as Outstanding Catalysts for Ethylene Oligomerization. *Eur. Phys. J.: Spec. Top.* **2015**, *224*, 1831–1841.
(335) Hwang, A.; Kim, S.; Kwak, G.; Kim, S. K.; Park, H.-G.; Kang, S. C.; Jun, K.-W.; Kim, Y. T. Low Temperature Oligomerization of Ethylene over Ni/Al-KIT-6 Catalysts. *Catal. Lett.* **2017**, *147*.
(336) Kleitz, F.; Hei Choi, S.; Ryoo, R. Cubic Ia3d Large Mesoporous Silica:Synthesis and Replication to Platinum Nanowires, Carbon Nanorods and Carbon Nanotubes. *Chem. Commun.* **2003**, 2136.
(337) Andrei, R. D.; Popa, M. I.; Fajula, F.; Cammarano, C.; Khudhair, A. A.; Bouchmella, K.; Mutin, P. H.; Hulea, V. Ethylene to Propylene by One-Pot Catalytic Cascade Reactions. *ACS Catal.* **2015**, *5*, 2774–2777.
(338) Andrei, R. D.; Popa, M. I.; Cammarano, C.; Hulea, V. Nickel and Molybdenum Containing Mesoporous Catalysts for Ethylene Oligomerization and Metathesis. *New J. Chem.* **2016**, *40*, 4146–4152.
(339) Beucher, R.; Andrei, R. D.; Cammarano, C.; Galarneau, A.; Fajula, F.; Hulea, V. Selective Production of Propylene and 1-Butene from Ethylene by Catalytic Cascade Reactions. *ACS Catal.* **2018**, 3636–3640.
(340) Lacarriere, A.; Robin, J.; Swierczyński, D.; Finiels, A.; Fajula, F.; Luck, F.; Hulea, V. Distillate-Range Products from Non-Oil-Based Sources by Catalytic Cascade Reactions. *ChemSusChem* **2012**, *5*, 1787–1792.

(341) Babu, B. H.; Lee, M.; Hwang, D. W.; Kim, Y.; Chae, H.-J. An Integrated Process for Production of Jet-Fuel Range Olefins from Ethylene using Ni-AlSBA-15 and Amberlyst-35 Catalysts. *Appl. Catal., A* **2017**, *530*, 48–55.
(342) Chauvin, Y.; Commereuc, D.; Hugues, F.; Saussine, L. French Patent 2,608,594, **1989**.
(343) Chauvin, Y.; Commereuc, D.; Hugues, F.; Saussine, L. European Patent 0,272,970, **1991**.
(344) Chauvin, Y.; Commereuc, D.; Hugues, F.; Saussine, L. French Patent 2,641,477, **1993**.
(345) Cai, T.; Zang, L.; Qi, A.; Wang, D.; Cao, D.; Li, L. Propene Oligomerization Catalyst Derived from Nickel Sulfate Supported on γ-Alumina. *Appl. Catal.* **1991**, *69*, 1–13.
(346) Cai, T.; Cao, D.; Song, Z.; Li, L. Catalytic Behavior of $NiSO_4/\gamma\text{-}Al_2O_3$ for Ethene Dimerization. *Appl. Catal., A* **1993**, *95*, L1-L7.
(347) Cai, T. Studies of a New Alkene Oligomerization Catalyst Derived from Nickel Sulfate. *Catal. Today* **1999**, *51*, 153–160.
(348) Sohn, J. R.; Park, W. C. Nickel Sulfate Supported on $\gamma\text{-}Al_2O_3$ for Ethylene Dimerization. *J. Mol. Catal. A: Chem.* **1998**, *133*, 297–301.
(349) Sohn, J. R.; Park, W. C.; Kim, H. W. Characterization of Nickel Sulfate Supported on $\gamma\text{-}Al_2O_3$ for Ethylene Dimerization and Its Relationship to Acidic Properties. *J. Catal.* **2002**, *209*, 69–74.
(350) Li, L.; Palcheva, R. D.; Jens, K.-J. Conversion of Ethene to Propene by a Dual Function $NiSO_4/Re_2O_7/\gamma\text{-}Al_2O_3$ Catalyst. *Top Catal* **2013**, *56*, 783–788.
(351) Lavrenov, A. V.; Mikhailova, M.S., Buluchevskii, E. A. Russian Patent 2,427,421, **2011**.
(352) Zhang, Q.; Kantcheva, M.; Dalla Lana, I. G. Oligomerization of Ethylene in a Slurry Reactor Using a Nickel/Sulfated Alumina Catalyst. *Ind. Eng. Chem. Res.* **1997**, *36*, 3433–3438.
(353) Zhang, Q.; Dalla Lana, I. G. An Analysis of Mass Transfer and Kinetics During Ethylene Oligomerization over Nickel/Sulfated Alumina Catalyst in a Slurry Reactor. *Chem. Eng. Sci.* **1997**, *52*, 4187–4195.
(354) Heydenrych, M. D.; Nicolaides, C. P.; Scurrell, M. S. Oligomerization of Ethene In a Slurry Reactor Using a Nickel(II)-Exchanged Silica-Alumina Catalyst. *J. Catal.* **2001**, *197*, 49–57.
(355) Chaung, K. U.S. Patent 7,847,140 B2, **2010**.
(356) Davydov, A. A.; Kantcheva, M.; Chepotko, M. L. FTIR Spectroscopic Study on Nickel(II)-Exchanged Sulfated Alumina: Nature of the Active Sites in the Catalytic Oligomerization of Ethene. *Catal. Lett.* **2002**, *83*, 97–108.
(357) Hartmann, M.; Kevan, L. Ethylene Dimerization in Nickel Containing SAPO Materials Studied by Electron Spin Resonance and Gas Chromatography: - Influence of the Channel Size. *Stud. Surf. Sci. Catal.* **1997**, *105*, 717–724.
(358) Aufdembrink, B. A.; Wu, M. M. U.S. Patent 5,321,190, **1994**.
(359) Glockner, P. W. US Patent 3,530,200, **1970**.
(360) Sohn, J. R.; Kim H. J. High Catalytic Activity of $NiO\text{-}TiO_2/SO_4^{2-}$ for Ethylene Dimerization. *J. Catal.* **1986**, *101*, 428–433.
(361) Sohn, J. R.; Park, W. C. New $NiSO_4/ZrO_2$ Catalyst for Ethylene Dimerization. *Bull. Korean Chem. Soc.* **1999**, *20*, 1261–1262.
(362) Sohn, J. R.; Park, W. C. Characterization and Catalytic Activity for Ethylene Dimerization of Nickel Sulfate Supported on Zirconia. *Appl. Catal., A* **2002**, *230*, 11–18.
(363) Sohn, J. R.; Shin, D. C. New Catalyst of $NiO–ZrO_2/WO_3$ for Ethylene Dimerization. *J. Catal.* **1996**, *160*, 314–316.
(364) Sohn, J. R.; Lee, S. Y. High Catalytic Activity of $NiO\text{-}ZrO_2$ Modified with WO_3 for Ethylene Dimerization. *Appl. Catal., A* **1997**, *164*, 127–140.
(365) Pae, Y. I.; Lee, S. H.; Sohn, J. R. Correlation Between Acidic Properties of Nickel Sulfate Supported on $TiO_2\text{-}ZrO_2$ and Catalytic Activity For Ethylene Dimerization. *Catal Lett* **2005**, *99*, 241–248.
(366) Sohn, J. R.; Kwon, S. H.; Shin, D. C. Spectroscopic studies on NiO Supported on ZrO_2 Modified with MoO_3 for Ethylene Dimerization. *Appl. Catal., A* **2007**, *317*, 216–225.
(367) Sohn, J. R.; Lim, J. S. Ethylene Dimerization over $NiSO_4$ Supported on Fe_2O_3-Promoted ZrO_2 Catalyst. *Catal. Today* **2006**, *111*, 403–411.

(368) Pae, Y. I.; Sohn, J. R. Characterization of $NiSO_4$ Supported on Fe_2O_3 and Catalytic Properties for Ethylene Dimerization. *Bull. Korean Chem. Soc.* **2007**, *28*, 1273–1279.

(369) Pae, Y. I.; Shin, D. C.; Sohn, J. R. CeO_2-Promoted Highly Active Catalyst, $NiSO_4/CeO_2$-ZrO_2 for Ethylene Dimerization. *Bull. Korean Chem. Soc.* **2006**, *27*, 1989–1996.

(370) Deimund, M. A.; Labinger, J.; Davis, M. E. Nickel-Exchanged Zincosilicate Catalysts for the Oligomerization of Propylene. *ACS Catal.* **2014**, *4*, 4189–4195.

(371) Bogdanovic B. Selectivity Control in Nickel-Catalyzed Olefin Oligomerization. *Adv. Organomet. Chem.* **1979**, *17*, 105–140.

(372) Keim, W. Nickel: An Element with Wide Application in Industrial Homogeneous Catalysis. *Angew. Chem. Int. Ed.* **1990**, *29*, 235–244.

(373) Birkenstock, U.; Bönnemann, H.; Bogdanovic, B.; Walter, D.; Wilke, G. *Homogeneous catalysis : pi-allylnickel compounds as homogeneous catalysts*; Advances in Chemical Series 70; B. J. Luberoff, **1968**.

(374) Muthukumaru Pillai, S.; Ravindranathan, M.; Sivaram, S. Dimerization of Ethylene and Propylene Catalyzed by Transition-Metal Complexes. *Chem. Rev.* **1985**, *86*, 353–399.

(375) Wilke, G. Contributions to Organo-Nickel Chemistry. *Angew. Chem. Int. Ed.* **1988**, *27*, 185–206.

(376) Olivier-Bourbigou, H.; Saussine, L. *Dimerization and Codimerization*, Cornils, Herrmann; Applied Homogeneous Catalysis with Organometalllic Compounds; Wiley-VCH Verlag GmbH, 2002.

(377) Britovsek, G. J. P.; Malinowski, R.; McGuinness, D. S.; Nobbs, J. D.; Tomov, A. K.; Wadsley, A. W.; Young, C. T. Ethylene Oligomerization Beyond Schulz–Flory Distributions. *ACS Catal.* **2015**, *5*, 6922–6925.

(378) McGuinness, D. S. Olefin Oligomerization via Metallacycles: Dimerization, Trimerization, Tetramerization, and Beyond. *Chem. Rev.* **2011**, *111*, 2321–2341.

(379) Feldblyum, V. S. *Analogy in the Mechanism of Homogeneous and Heterogeneous Catalysis. Nature of Activity of Complex Ziegler Catalysts and the Mechanism of Olefin Dimerization*. Proc. Int. Congr. Catal., 4th 1; Akad. Kiado, **1971**.

(380) Ghambarian M.; Ghashghaee M.; Azizi Z.; Balar M. Structural Diversity of Metallacycle Intermediates for Ethylene Dimerization on Heterogeneous NiMCM-41 Catalyst: a Quantum Chemical Perspective. *Structural Chemistry* **2019**, *30*, 137–150.

(381) Brogaard, R. Y.; Olsbye, U. Ethene Oligomerization in Ni-Containing Zeolites: Theoretical Discrimination of Reaction Mechanisms. *ACS Catal.* **2016**, *6*, 1205–1214.

(382) Lu, K.; Jin, F.; Wu, G.; Ding, Y. The Synergetic Effect of Acid and Nickel Sites on Bifunctional MWW Zeolite Catalysts for Ethylene Oligomerization and Aromatization. *Sustainable Energy & Fuels* **2019**, *3*, 3569–3581.

(383) Henry, R.; Komurcu, M.; Ganjkhanlou, Y.; Brogaard, R. Y.; Lu, L.; Jens, K.-J.; Berlier, G.; Olsbye, U. Ethene Oligomerization on Nickel Microporous and Mesoporous-Supported Catalysts: Investigation of the Active Sites. *Catal. Today* **2018**, *299*, 154–163.

(384) Joshi, R.; Zhang, G.; Miller Jeffrey T.; Gounder, R. Evidence for the Coordination–Insertion Mechanism of Ethene Dimerization at Nickel Cations Exchanged onto Beta Molecular Sieves. *ACS Catal.* **2018**, *8*, 11407–11422.

(385) Moussa, S.; Concepción, P.; Arribas, M. A.; Martínez, A. Nature of Active Nickel Sites and Initiation Mechanism for Ethylene Oligomerization on Heterogeneous Ni-beta Catalysts. *ACS Catal.* **2018**, 3903–3912.

(386) Garbarino, G.; Riani, P.; Infantes-Molina, A.; Rodriguez-Castellon, E.; Busca, G. On the Detectability Limits of Nickel Species on NiO/γ-Al_2O_3 Catalytic Materials. *Appl. Catal., A* **2016**, *525*, 180–189.

(387) Pozdeeva, A. A.; Dzhemilev, U. M.; Popod'ko, N. R.; Khusnutdinov, R. I.; Zhdanov, S. I.; Tolstikov, G. A. Electrochemical Studies of Nickel Complexes Containing Phosphorus(III) Ligands and their Related Ziegler Catalysts. *J. Organomet. Chem.* **1989**, *367*, 205–232.

(388) Corker, J. M.; Evans, J. EXAFS Studies of the Activation of Homogeneous Nickel Dimerisation by Aluminium Reagents. *J. Chem. Soc., Chem. Commun.* **1991**, 1104–1106.

(389) Corker, J. M.; Dent, A. J.; Evans, J.; Hagelstein, M.; Kambhampati, V. L. Scanning and Energy Dispersive EXAFS Studies of Nickel Alkene Oligomerization Catalysts. *J. Phys. IV* **1997**, *7*, 879–881.

(390) Bogg, D.; Conyngham, M.; Corker, J. M.; Dent, A. J.; Evans, J.; Farrow, R. C.; Kambhampati, V. L.; Masters, A. F.; McLeod, D. N.; et, a. Scanning and Energy Dispersive EXAFS Studies of Ethyl Transmetallation in an Alkene Oligomerization Catalyst. *Chem. Commun.* **1996**, 647–648.

(391) de Souza, Roberto F.; Simon, L. C.; Alves, Maria do Carmo M. XAS Study of the Nickel(α-Diimine) Catalyst for Olefin Polymerization. *J. Catal.* **2003**, *214*, 165–168.

(392) Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. Synthesis of Coordinatively Unsaturated Diphosphine Nickel(II) and Palladium(II) Beta-Agostic Ethyl Cations: X-Ray Crystal Structure of $[Ni\{tBu_2P(CH_2)_2PtBu_2\}(C_2H_5)][BF_4]$. *J. Chem. Soc., Chem. Commun.* **1991**, 1601–1603.

(393) de Souza, Roberto F.; Souza, M. O. de; Monteiro, A. L.; Almeida, L.; Seferin, M. Dicationic Nickel Complexes: New Catalyst Precursors for Selective Ethylene Dimerization to But-1-ene. *New J. Chem.* **1993**, *17*, 437–438.

(394) Bogdanovic, B. Selectivity Control in Nickel Catalyzed Olefin Oligomerization. *Adv. Organomet. Chem.* **1979**, *17*, 105–140.

(395) Andrews, P.; Corker, J. M.; Evans, J.; Webster, M. Highly Active Homogeneous Nickel Catalysts for Alkene Dimerization: Crystal Structure of $[Ni(\eta^3\text{-}C_3H_5)(PPh_3)Br]$ and In Situ Characterization of $AlEt_3$-Activated $[Ni(\eta^3\text{-}C_3H_3)(PPh_3)Br]$ by Nuclear Magnetic Resonance and Extended X-Ray Absorption Fine Structure Spectroscopy. *J. Chem. Soc., Dalton Trans.* **1994**, 1337–1347.

(396) Maruya, K.; Kuroki, T.; Mizoroki, T.; Ozaki, A. Dimerization of Ethylene-d4 Catalyzed by Bis(Triphenylphosphine)-σ-1-Naphthylnickel (II) Bromide. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2002.

(397) Albers, I.; Álvarez, E.; Cámpora, J.; Maya, C. M.; Palma, P.; Sánchez, L. J.; Passaglia, E. Cationic η3-Benzyl Nickel Compounds with Diphosphine Ligands as Catalyst Precursors for Ethylene Oligomerization/Polymerization: Influence of the Diphosphine Bite Angle. *J. Organomet. Chem.* **2004**, *689*, 833–839.

(398) Pardy, R. B. A.; Tkatchenko, I. Synthesis of $(\eta^3$-Allyl)$(\eta^4$-Cycloocta-1,5-Diene)Nickel Cations: Valuable Catalysts for the Oligomerization of Alkenes. *J. Chem. Soc., Chem. Commun.* **1981**, 49–50.

(399) Dubois, M.-A.; Wang, R.; Zargarian, D.; Tian, J.; Vollmerhaus, R.; Li, Z.; Collins, S. Nickel Indenyl Complexes as Catalysts for the Dimerization and Polymerization of Ethylene. *Organometallics* **2001**, *20*, 663–666.

(400) Groux, L. F.; Zargarian, D.; Simon, L. C.; Soares, J. B. P. Dimerization and Polymerization of Ethylene Catalyzed by Nickel Complexes Bearing Multidentate Amino-Functionalized Indenyl Ligands. *J. Mol. Catal. A: Chem.* **2003**, *193*, 51–58.

(401) Wang, R.; Groux, L. F.; Zargarian, D. Nickel-Triflate Complexes as Precursors to Reactive Cations: Preparation and Reactivities of (1-R-indenyl)$Ni(PPh_3)(OSO_2CF_3)$. *Organometallics* **2002**, *21*, 5531–5539.

(402) Brookhart, M. S.; Hauptman, E. M. U.S. Patent 5,892,101, **1999**.

(403) Malinoski, J. M.; Brookhart, M. Polymerization and Oligomerization of Ethylene by Cationic Nickel(II) and Palladium(II) Complexes Containing Bidentate Phenacyldiarylphosphine Ligands. *Organometallics* **2003**, *22*, 5324–5335.

(404) Killian, C. M.; Johnson, L. K.; Brookhart, M. Preparation of Linear α-Olefins Using Cationic Nickel(II) α-Diimine Catalysts. *Organometallics* **1997**, *16*, 2005–2007.

(405) Burcher, B.; Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H. Iron-Catalyzed Oligomerization and Polymerization Reactions. In *Iron Catalysis II*; Bauer, E., Ed.; Topics in Organometallic Chemistry; Springer International Publishing: Cham, 2015; pp 217–257.

(406) Ceder, R.; Muller, G.; Sales, J.; Vidal, J.; Neibecker, D.; Tkatchenko, I. Catalytic Dimerization of Ethylene to 1-Butene by Square-Planar Nickel Complexes. *J. Mol. Catal.* **1991**, *68*, 23–31.

(407) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. Mechanistic Studies of Nickel(II) Alkyl Agostic Cations and Alkyl Ethylene Complexes: Investigations of Chain Propagation and Isomerization in (α-Diimine)Ni(II)-Catalyzed Ethylene Polymerization. *J. Am. Chem. Soc.* **2003**, *125*, 3068–3081.

(408) Shultz, C. S.; DeSimone, J. M.; Brookhart, M. Cationic Four- and Five-Coordinate Nickel(II) Complexes: Insights into the Nickel(II)-Catalyzed Copolymerization of Ethylene and Carbon Monoxide. *Organometallics* **2001**, *20*, 16–18.
(409) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. Novel Coordination of (Benzoylmethylene)Triphenylphosphorane in a Nickel Oligomerization Catalyst. *Angew. Chem. Int. Ed.* **1978**, *17*, 466–467.
(410) Keim, W. Mechanistic Consideration for the C-C Bond Linkage in Monoolefins. *New J. Chem.* **1987**, *11*, 531–534.
(411) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kuerschner, U.; Limbaecker, B.; Sistig, F. P. Reactions of Chelate Ylides with Nickel(0) Complexes. *Organometallics* **1986**, *5*, 2356–2359.
(412) Andrews, P.; Evans, J. In situ NMR and EXAFS Studies of the Homogeneous Alkene Oligomerization Catalyst Ni(cod)$_2$-Ph$_2$PCH$_2$C(CF$_3$)$_2$OH. *J. Chem. Soc., Chem. Commun.* **1993**, 1246–1248.
(413) Keim, W. Organometallic Complexes as Catalyst Precursors : Advantages and Disadvantages. *J. Mol. Catal.* **1989**, *52*, 19–25.
(414) Müller, U.; Keim, W.; Krüger, C.; Betz P. [{Ph$_2$PCH$_2$C(CF$_3$)$_2$O}NiH(PCy$_3$)] Support for a Nickel Hydride Mechanism in Ethene Oligomerization. *Angew. Chem. Int. Ed.* **1989**, *28*, 1011–1013.
(415) Aakermark, B.; Martin, J.; Nystroem, J.-E.; Stroemberg, S.; Svensson, M.; Zetterberg, K.; Zuber, M. A Proton Directly Attacks 1,5-Cyclooctadiene in Bis(1,5-Cyclooctadiene)Nickel(0) in the Formation of a Keim Type Oligomerization Catalyst. *Organometallics* **1998**, *17*, 5367–5373.
(416) Heinicke, J.; He, M.; Dal, A.; Klein, H.-F.; Hetche, O.; Keim, W.; Florke, U.; Haupt, H.-J. Methyl(2-Phosphanylphenolato[P,O])Nickel(II) Complexes - Synthesis, Structure, and Activity as Ethene Oligomerization Catalysts. *Eur. J. Inorg. Chem.* **2000**, 431–440.
(417) Younkin, T. R. Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms. *Science* **2000**, *287*, 460–462.
(418) Desjardins, S. Y.; Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H. Insertion into the Nickel-Carbon Bond of N-O Chelated Arylnickel(II) Complexes. The Development of Single Component Catalysts for the Oligomerization Of Ethylene. *J. Organomet. Chem.* **1996**, *515*, 233–243.
(419) Berkefeld, A.; Mecking, S. Deactivation Pathways of Neutral Ni(II) Polymerization Catalysts. *J. Am. Chem. Soc.* **2009**, *131*, 1565–1574.
(420) Komon, Z. J. A.; Bu, X.; Bazan, G. C. Synthesis, Characterization, and Ethylene Oligomerization Action of [(C$_6$H$_5$)$_2$PC$_6$H$_4$C(O-B(C$_6$F$_5$)$_3$)O-κ^{2}P,O]Ni(η^3-CH$_2$C$_6$H$_5$). *J. Am. Chem. Soc.* **2000**, *122*, 12379–12380.
(421) Boardman, B. M.; Bazan, G. C. Alpha-Iminocarboxamidato Nickel Complexes. *Acc. Chem. Res.* **2009**, *42*, 1597–1606.
(422) Chen, Y.; Wu, G.; Bazan, G. C. Remote Activation of Nickel Catalysts for Ethylene Oligomerization. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108–1112.
(423) Haan, R. de; Dekker, J. Catalytic dimerization of propylene. I. New Zerovalent Nickel Catalyst. *J. Catal.* **1974**, *35*, 202–205.
(424) Kraikivskii, P. B.; Saraev, V. V.; Matveev, D. A.; Zelinskii, S. N.; Tkach, V. S. Reactions of Aluminium Tribromide with Tetrakis(triphenylphosphine)nickel(0) and Tetrakis(triethyl phosphite)nickel(0) Complexes. *Russ. J. Coord. Chem.* **2003**, *29*, 431–434.
(425) Saraev, V. V.; Kraikivskii, P. B.; Annenkov, V. V.; Zelinskiy, S. N.; Matveev, D. A.; Vilms, A. I.; Danilovtseva, E. N.; Lammertsma, K. Catalysis of Olefin Oligomerization by Ni(I) Complexes. *ARKIVOC* **2005**, 44–52.
(426) Saraev, V. V.; Kraikivskii, P. B.; Zelinskiy, S. N.; Matveev, D. A.; Vilms, A. I.; Rohin, A. V.; Lammertsma, K. Influence of Alcohols on the Formation of the Nickel Complexes Active in Ethene Oligomerization in the Catalytic System Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$. *J. Mol. Catal. A: Chem.* **2005**, *236*, 125–131.

(427) Saraev, V. V.; Kraikivskii, P. B.; Matveev, D. A.; Vil'ms, A. I.; Zelinskii, S. N.; Lammertsma, K. Influence of the Order of Introduction of Protonic Acids on the Formation of Active Complexes in the $Ni(PPh_3)_4/BF_3{\cdot}OEt_2$ Catalytic System. *Kinet. Catal.* **2006**, *47*, 699–703.
(428) Saraev, V. V.; Kraikivskii, P. B.; Matveev, D. A.; Vilms, A. I.; Gotsko, M. D.; Bocharova, V. V.; Zelinskii, S. N. Mechanism of Ethylene Oligomerization by the Catalytic System $Ni(COD)_2/BF_3{\cdot}OEt_2$ modified with tertiary phosphines. *Curr. Catal.* **2012**, *1*, 149–154.
(429) Schmidt, F. K.; Belykh, L. B.; Gomboogiin, M.; Titova, Y. Y. Formation and Nature of Catalysts Based on Nickel(0) Phosphine Complexes Active in Lower Alkene Dimerization and Oligomerization. *Kinet. Catal.* **2010**, *51*, 235–243.
(430) Lapidus, A. L.; Isakov, Y. I.; Slinkin, A. A.; Avetisyan, R. V.; Minachev, K. M.; Eidus, Y. T. Forms of Nickel Used as Components of Nickel Aluminosilicate Catalysts of Ethylene Dimerization. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1904–1910.
(431) Elev, I. V.; Shelimov, B. N.; Kazanskii, V. B. Study of Ethylene Oligomerization on a Nickel Oxide/Aluminum Oxide Catalyst Activated by Photoreduction and Thermal Reduction by Hydrogen. *Kinet. Katal.* **1984**, *25*, 1124–1128.
(432) Choo, H.; Hong, S. B.; Kevan, L. Comparative ESR Studies on the Reducibility and Adsorbate Interactions of Paramagnetic Ni(I) in Synthetic Ferrierite and Mordenite. *J. Phys. Chem. B* **2001**, *105*, 1995–2002.
(433) Choo, H.; Kevan, L. Catalytic Study of Ethylene Dimerization on Ni(II)-Exchanged Clinoptilolite. *J. Phys. Chem. B* **2001**, *105*, 6353–6360.
(434) Lallemand, M.; Finiels, A.; Fajula, F.; Hulea, V. Nature of the Active Sites in Ethylene Oligomerization Catalyzed by Ni-Containing Molecular Sieves: Chemical and IR Spectral Investigation. *J. Phys. Chem. C* **2009**, *113*, 20360–20364.
(435) Deininger, D.; Wendt, G. Carbon-13 NMR Study of Propene Dimerization on Nickel-Oxide/Silicon Dioxide Catalysts. *React. Kinet. Catal. Lett.* **1981**, *17*, 277–280.
(436) Brogaard, R. Y.; Kømurcu, M.; Dyballa, M. M.; Botan, A.; van Speybroeck, V.; Olsbye, U.; Wispelaere, K. de. Ethene Dimerization on Zeolite-Hosted Ni Ions: Reversible Mobilization of the Active Site. *ACS catalysis* **2019**, *9*, 5645–5650.
(437) Moussa, S.; Arribas, M. A.; Concepción, P.; Martínez, A. Heterogeneous Oligomerization of Ethylene to Liquids on Bifunctional Ni-Based Catalysts: The Influence of Support Properties on Nickel Speciation and Catalytic Performance. *Catal. Today* **2016**, *277*, 78–88.
(438) Roberts, S. T.; Renshaw, M. P.; Lutecki, M.; McGregor, J.; Sederman, A. J.; Mantle, M. D.; Gladden, L. F. Operando Magnetic Resonance: Monitoring the Evolution of Conversion and Product Distribution During the Heterogeneous Catalytic Ethene Oligomerisation Reaction. *Chem. Commun.* **2013**, *49*, 10519–10521.
(439) Rabeah, J.; Radnik, J.; Briois, V.; Maschmeyer, D.; Stochniol, G.; Peitz, S.; Reeker, H.; La Fontaine, C.; Brückner, A. Tracing Active Sites in Supported Ni Catalysts during Butene Oligomerization by Operando Spectroscopy under Pressure. *ACS Catal.* **2016**, *6*, 8224–8228.
(440) Hasanayn, F.; Achord, P.; Braunstein, P.; Magnier, H. J.; Krogh-Jespersen, K.; Goldman, A. S. Theoretical Structure-Reactivity Study of Ethylene Insertion into Nickel-Alkyl Bonds. A Kinetically Significant and Unanticipated Role of Trans Influence in Determining Agostic Bond Strengths. *Organometallics* **2012**, *31*, 4680–4692.
(441) Ceder, R. M.; Cubillo, J.; Muller, G.; Rocamora, M.; Sales, J. Reactions of neutral and ionic square-planar organometallic nickel compounds with ethylene. *J. Organomet. Chem.* **1992**, *429*, 391–401.
(442) Escobar, M. A.; Trofymchuk, O. S.; Rodriguez, B. E.; Lopez-Lira, C.; Tapia, R.; Daniliuc, C.; Berke, H.; Nachtigall, F. M.; Santos, L. S.; Rojas, R. S. Lewis Acid Enhanced Ethene Dimerization and Alkene Isomerization—ESI-MS Identification of the Catalytically Active Pyridyldimethoxybenzimidazole Nickel(II) Hydride Species. *ACS Catal.* **2015**, *5*, 7338–7342.
(443) Maruya, K.; Mizoroki, T.; Ozaki, A. Dimerization of Ethylene Catalyzed by σ-Aryl Nickel Compound in the Presence of Trifluoroboron Etherate. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2255–2259.

(444) Grubbs, R. H.; Miyashita, A. The Metallacyclopentane-Olefin Interchange Reaction. *Chem. Commun.* **1977**, 864–865.

(445) Grubbs, R. H.; Miyashita, A.; Liu, M.-I. L.; Burk, P. L. The Preparation and Reactions of Nickelocyclopentanes. *J. Am. Chem. Soc.* **1977**, *99*, 3863–3864.

(446) Grubbs, R. H.; Miyashita, A.; Liu, M.-I. L.; Burk, P. L. Preparation and Reactions of Phosphine Nickelocyclopentanes. *J. Am. Chem. Soc.* **1978**, *100*, 2418–2425.

(447) Grubbs, R. H.; Miyashita, A. Metallacyclopentanes as Catalysts for the Linear and Cyclodimerization of Olefins. *J. Am. Chem. Soc.* **1978**, *100*, 7416–7418.

(448) Grubbs, R. H.; Miyashita, A. The Relationship between Metallacyclopentanes and Bis(Olefin)-Metal Complexes. *J. Am. Chem. Soc.* **1978**, *100*, 1300–1302.

(449) Mohammed, A. A.; Fateen, S.-E. K.; Ahmed, T. S.; Moustafa, T. M. A Kinetic Model for Ethylene Oligomerization using Zirconium/Aluminum- and Nickel/Zinc-Based Catalyst Systems in a Batch Reactor. *Appl. Petrochem. Res.* **2014**, *4*, 287–295.

(450) Choe, S. B.; Kanai, H.; Klabunde, K. J. Catalytic Dimerization of Ethylene and Propylene by (η^6-Arene)NiR_2 and in Combination with Alkylaluminum Halides. Production of Highly Active Homogeneous Catalysts. *J. Am. Chem. Soc.* **1989**, *111*, 2875–2882.

(451) Sakakibara, Y.; Aiba, K.; Sakai, M.; Uchino, N. A study on the Oligomerization of Olefins by Nickel Complexes. VI. A Kinetic Study of Propylene Dimerization Catalyzed by Bis(Acetylacetonato)Nickel(II)-Triethyldialuminum Trichloride-Triphenylphosphine. *Bull. Inst. Chem. Res., Kyoto Univ.* **1979**, *57*, 240–244.

(452) Brown, S. J.; Clutterbuck, L. M.; Masters, A. F.; Sachinidis, J. I.; Tregloan, P. A. Kinetic and mechanistic studies of nickel-catalyzed olefin oligomerization. *Appl. Catal.* **1989**, *48*, 1–11.

(453) Brown, S. J.; Masters, A. F.; Vender, M.; Sachinidis, J. I.; Tregloan, P. A. The Oligomerization of Lower Olefins by Catalysts Derived from Chloro(Tri-N-Butylphosphine)(Pentane-2,4-Dithionato)Nickel(Ii). *Polyhedron* **1990**, *9*, 2809–2814.

(454) Fan, L.; Krzywicki, A.; Somogyvari, A.; Ziegler, T. Density Functional Study of Ethylene Dimerization by (Acetylacetonato)nickel Hydride. *Inorg. Chem.* **1994**, *33*, 5287–5294.

(455) Fan, L.; Krzywicki, A.; Somogyvari, A.; Ziegler, T. A Theoretical Study of Ethylene Oligomerization by Organometallic Nickel Catalysts. *Stud. Surf. Sci. Catal.* **1996**, *100*, 507–514.

(456) Fan, L.; Krzywicki, A.; Somogyvari, A.; Ziegler, T. Theoretical Study of Ethylene Oligomerization by an Organometallic Nickel Catalyst. *Inorg. Chem.* **1996**, *35*, 4003–4006.

(457) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. Theoretical Study of Substituent Effects in the Diimine-M(II) Catalyzed Ethylene Polymerization Reaction Using the IMOMM Method. *J. Am. Chem. Soc.* **1998**, *120*, 1581–1587.

(458) Stromberg, S.; Zetterberg, K.; Siegbahn, P. E. M. Trends within a Triad: Comparison Between Σ-Alkyl Complexes of Nickel, Palladium and Platinum with Respect to Association of Ethylene, Migratory Insertion and β-Hydride Elimination. A Theoretical Study. *J. Chem. Soc., Dalton Trans.* **1997**, 4147–4152.

(459) Roy, D.; Sunoj, R. B. Ni-, Pd-, or Pt-Catalyzed Ethylene Dimerization: a Mechanistic Description of the Catalytic Cycle and the Active Species. *Organic & biomolecular chemistry* **2010**, *8*, 1040–1051.

(460) Nikiforidis, I.; Goerling, A.; Hieringer, W. On the Regioselectivity of the Insertion Step in Nickel Complex Catalyzed Dimerization of Butene: A Density-Functional Study. *J. Mol. Catal. A: Chem.* **2011**, *341*, 63–70.

(461) Kissin, Y. V.; Beach, D. L. Oligomerization of Ethylene with a Homogeneous Sulfonated Nickel Ylide-Aluminum Alkoxide Catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 147–155.

(462) Svejda, S. A.; Brookhart, M. Ethylene Oligomerization and Propylene Dimerization Using Cationic (α-Diimine)Nickel(II) Catalysts. *Organometallics* **1999**, *18*, 65–74.

(463) D'Aniello Jr, M. J.; Barefield, E. K. Mechanistic Studies on the Catalysis of Isomerization of Olefins by $(Ph_3P)_3$NiX. *J. Am. Chem. Soc.* **1978**, *100*, 1474–1481.

(464) Heyndrickx, W.; Occhipinti, G.; Minenkov, Y.; Jensen, V. R. Neutral Nickel Oligo- and Polymerization Catalysts: The Importance of Alkyl Phosphine Intermediates in Chain Termination. *Chem. - Eur. J.* **2011**, *17*, 14628–14642.

(465) Heyndrickx, W.; Occhipinti, G.; Jensen, V. R. Neutral Nickel Ethylene Oligo- and Polymerization Catalysts: Towards Computational Catalyst Prediction and Design. *Chem. - Eur. J.* **2014**, *20*, 7962–7978.
(466) Ortega, D. E.; Cortes-Arriagada, D.; Trofymchuk, O. S.; Yepes, D.; Gutierrez-Oliva, S.; Rojas, R. S.; Toro-Labbe, A. The Role of Co-Activation and Ligand Functionalization in Neutral Methallyl Nickel(II) Catalysts for Ethylene Oligomerization and Polymerization. *Chem. - Eur. J.* **2017**, *23*, 10167–10176.
(467) Tognetti, V.; Le Floch, P.; Adamo, C. How The Choice of a Computational Model Could Rule the Chemical Interpretation: The Ni(II) Catalyzed Ethylene Dimerization as a Case Study. *J. Comput. Chem.* **2010**, *31*, 1053–1062.
(468) Tognetti, V.; Fayet, G.; Adamo, C. Can Molecular Quantum Descriptors Predict the Butene Selectivity in Nickel(II) Catalyzed Ethylene Dimerization? A QSPR Study. *Int. J. Quantum Chem.* **2010**, *110*, 540–548.
(469) Tognetti, V.; Buchard, A.; Auffrant, A.; Ciofini, I.; Floch, P.; Adamo, C. Ethylene Dimerization Catalyzed by Mixed Phosphine-Iminophosphorane Nickel(II) Complexes: a DFT Investigation. *J. Mol. Model.* **2013**, *19*, 2107–2118.
(470) Bernardi, F.; Bottoni, A.; Rossi, I. A DFT Investigation of Ethylene Dimerization Catalyzed by Ni(0) Complexes. *J. Am. Chem. Soc.* **1998**, *120*, 7770–7775.
(471) Behr, A.; Rentmeister, N.; Seidensticker, T.; Fassbach, T. A.; Peitz, S.; Maschmeyer, D. Nickel Catalyzed Dimerization Reactions of Vinylidene Compounds: Head-to-Head Couplings and Catalyst Stabilization. *J. Mol. Catal. A: Chem.* **2014**, *395*, 355–363.
(472) Berkefeld, A.; Moeller, H. M.; Mecking, S. Unusual Reactivity of N,N,N',N'-Tetramethylethylenediamine-Coordinated Neutral Nickel(II) Polymerization Catalysts. *Organometallics* **2009**, *28*, 4048–4055.
(473) Clutterbuck, L. M.; Field, L. D.; Humphries, G. B.; Masters, A. F.; Williams, M. A. Carbon Monoxide Poisoning as a Probe for the Active Site(s) of a Nickel-Based Olefin Oligomerization Catalyst. *Appl. Organomet. Chem.* **1990**, *4*, 507–512.
(474) Nomura, K.; Minamide, C.; Nagase, M.; Itagaki, M.; Suzukamo, G. Fluorinated Alcohol Modified Nickel-Phosphine Catalyst System for Efficient Dimerization of Propylene. *J. Mol. Catal. A: Chem.* **1999**, *137*, 1–14.

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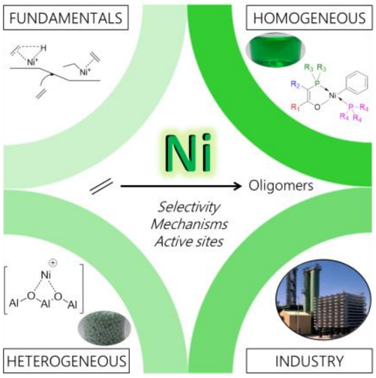
FUNDAMENTALS
HOMOGENEOUS
Ni
Oligomers
Selectivity
Mechanisms
Active sites
HETEROGENEOUS
INDUSTRY