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Pedro S.F. Mendes, João M Silva, M. Filipa Filipa Ribeiro, Antoine Daudin, Christophe Bouchy. Synergies, cooperation and other effects: a review for hydroconversion catalysts. *Catalysis Today*, 2020, 356, pp.260-270. 10.1016/j.cattod.2019.08.055 . hal-03103953

**HAL Id: hal-03103953**

**<https://ifp.hal.science/hal-03103953>**

Submitted on 8 Jan 2021

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## Synergies, cooperation and other effects: a review for hydroconversion catalysts

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This is the submitted, **non-peer reviewed** version of the following article: P. S. F. Mendes, J. M. Silva, M. F. Ribeiro, A. Daudin, C. Bouchy, Catal. Today 356 (2020) 260–270, which has been published in final form at <https://doi.org/10.1016/j.cattod.2019.08.055>.

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## **Abstract**

Mixing different components is the basis of chemistry. In heterogeneous catalysis, combinations of active phases are frequently used, but involved in a mystery similar to alchemy. The language employed to describe such systems is typically imprecise due to the lack of clear definitions and efforts to quantify the observed performances. In this review, focused in the particular case of bifunctional catalysis, a set of definitions is provided aiming at an analytical and coherent examination of the literature. The works on hybrid zeolite based catalysts for hydroconversion processes are reviewed, and an attempt to classify the various origin of potential cooperation effects is provided. By such means, we hope to provide not only a clear view on the current state-of-the-art on hydroconversion catalysts but also a common framework for a more rigorous investigation of possible synergies of hybrid catalysts all over catalysed reactions.

**Keywords:** hydroisomerization; hydroconversion; bifunctional catalysis; metal-acid balance; cooperative effect; synergies; hybrid catalyst; zeolite.

## 1 Bifunctional catalysts

Bifunctional catalysts, comprising metal and acid sites, were first developed for catalytic reforming of naphtha, being employed industrially since the 1950's [1, 2]. Nowadays, bifunctional catalysts are the heart of a panoply of processes, ranging from oil refining to bio-refining or in the field of fine chemicals synthesis. The main applications within the traditional oil & gas industry are catalytic reforming and hydrocracking, but other processes like hydroisomerization of C<sub>5</sub>-C<sub>6</sub> alkanes, hydroisomerization of C<sub>8</sub> aromatics, and hydroisomerization of long paraffins for catalytic dewaxing also employ bifunctional catalysts [3-5]. In the context of diversification of carbon sources for the production of jet fuel and diesel, an upgrading step involving a selective hydroisomerization process is frequently required to improve the cold flow properties of the renewable hydrocarbon fuel [6, 7]. Namely, in the production of synthetic diesel by the Low Temperature Fischer-Tropsch process [8, 9] and of biodiesel from vegetable oils [10-12]. In the case of biomass-based fuels, the goal of the catalytic upgrading of bio-oil is twofold: to achieve the adequate liquid fuel properties (e.g. carbon range, cold flow properties), and to decrease the level of oxygenates [13]. Finally, bifunctional catalysts will also have a role in the valorisation of waste plastics (to fuels) either in the direct conversion of plastics [14] or in the upgrading of plastic-derived pyrolysis oil [15].

In this review, we will focus on bifunctional catalysts for hydroconversion processes in which the main aim is the hydroisomerization and/or hydrocracking of alkanes. These types of reactions can also be performed by monofunctional acidic catalysts. However, bifunctional catalysts allow a much lower reaction temperature, due to the transformation over the metal sites of saturated hydrocarbons into unsaturated ones which are much more reactive [16]. In addition, wider product ranges can be achieved over a bifunctional catalyst [17] and the product distribution can be more easily tuned (e.g. via the operating conditions) [16].

### 1.1 Hydroconversion catalysts

Bifunctional catalysis applied to hydroconversion processes is based on the transformation of olefinic intermediates, taking place on metal hydro-dehydrogenating



Catalytic properties of such catalysts are then primarily dictated by the properties of the acidic phase.

Although the formulation of the catalyst will depend on the product aimed at and the feedstock to be processed, common features can be recognized amongst all bifunctional catalysts. The most active HD/DHD functions are granted by finely dispersed noble metals such as platinum or palladium [30]. However, those are quite sensitive to impurities (namely, sulphur-containing molecules present in heavy oil cuts) [31, 32]. Therefore, non-noble metal sulphide promoted with other metals (commonly, Mo or W promoted with Ni or Co) are typically employed when such impurities are present [30, 33].

Typical acidic supports for bifunctional catalysts are zeolites (usually USY, Beta, Mordenite, ZSM-5, ZSM-22), silicoaluminophosphates (typically SAPO-11, SAPO-31, SAPO-41), mesoporous materials (typically MCM-41, AlMCM-41) and amorphous oxides or mixtures of oxides (typically HF-treated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>) [30, 34-37]. Careful attention should be also paid to bifunctional catalysts based on realuminated SBA-15 [6], and on mesoporous silica-alumina (MSA) [34]. It is worth mentioning that all these materials are porous and based somehow on silicon and/or aluminium oxides (except for zirconium-based materials). Zeolites are frequently the preferred materials to perform the acidic function in hydroconversion catalysts due to their tunable acido-basic properties (via synthesis or post-synthesis treatments) and interconnected channel systems (which can be tuned by selecting the proper topology) [5, 6, 38-40]. In practice, zeolite based catalysts typically show a higher activity (owing to higher acid strength), higher thermal/hydrothermal stability, and better resistance to poisoning by sulphur and nitrogen impurities [6, 41]. We will now focus on strategies that can be used to improve bifunctional catalysts performances by tuning the properties of the acid function.

## *1.2 Strategies towards acidic function improvement*

Hydrocracking processes typically aim at processing heavy cuts (e.g. vacuum gas oil) into lighter ones like high-quality middle distillates fuels as diesel and jet fuel. During the last

few decades, the most widely employed zeolite framework type to perform that conversion has been the large-pore FAU (and namely the ultra-stabilized Y zeolite - USY) [30]. Literature reports have, on the other hand, highlighted promising results with BEA-based catalysts [22, 42-45]. Dewaxing processes, via hydroisomerization, aim at improving cold flow properties of the feedstock by isomerizing linear paraffins. To achieve high yields in isomers, *n*-paraffins should selectively react, reducing in that way the cracking of *i*-paraffins. In this case, molecular shape selectivity, exerted in the channel systems of zeolites, is extremely useful to develop suitable bifunctional catalysts [46-48]. High isomerization yields have been observed over non-interconnected medium-pore size zeolites, e.g. ZSM-22 [49] and, more recently, IZM-2 [50] and ZSM-23 [51]. These promising results are related to the predominance of pore-mouth catalysis. Conversely, this means that only a low fraction of the protonic sites contributes to the activity [47]. All in all, there is still room for improving bifunctional zeolitic catalysts performances.

In theory, the most suitable strategy consists of the design of the ideal zeolite for the foreseen application and the synthesis of corresponding new crystalline structure (so-called bottom-up) [50, 52, 53]. Zeolite crystals are formed by hydrothermal synthesis, i.e. by the action of heat upon low temperatures and low pressures [54, 55]. Albeit each zeolite structure presents a preferential range of synthesis conditions [56], composition and properties of the zeolite can be controlled to some extent for each framework type [57]. In addition, the use of structure directing agents (e.g. organic cations) has enabled the synthesis of a multiplicity of topologies (e.g. MFI and BEA zeolites) [58]. Unfortunately, this approach is quite time- and resource-consuming, being thus scarcely employed in industrial practice. Furthermore, using organic structure directing agent can be costly and/or intensify health/safety/environment (HSE) concerns.

The most common approaches to get hold of a suitable acidic function are the synthesis of existing structures with different procedures and the modification of synthesized zeolites by post-treatments. Dealumination methods enable to increase the Si/Al framework ratio by essentially removing the protonic sites, transforming along the way some of them into Lewis acid sites [59]. Aiming at hierarchical zeolites, mesopores can

be generated by either dealumination or desilication using steaming or acid or base leaching treatments [60-62]. It is worth mentioning that, as result of the removal of Al and/or Si, undesired impact on both the crystallinity and the acidity of the final solid can occur during post-synthesis treatments [60]. The later introduction of the so-called hard templates led to the direct synthesis of hierarchical zeolites [60, 63].

As the best suited acid function for a given application is obtained by tuning topology, hierarchical structure, and acid-basic properties, the combination of acid functions, namely zeolites, with different properties can be advantageous. Therefore, an alternative strategy is the combination of different acidic solids in a way that a cooperative effect or, most commonly named, synergy between them can occur. In fact, catalysts based on the coexistence of two different zeolites have been used in industry in the last decades [64]. Conversely, this topic has been less studied than the previous ones in open literature and there is particular lack of scientific contributions providing a global picture on the state-of-the-art. The aim of this article is to shed light into this undervalued field.

## **2 Setting up a well-framed picture: basic concepts and terminology**

One of the main issues faced when studying the topic of synergism in heterogeneous catalysis is the lack of common terminology throughout literature. As no clear guidelines exist on the key concepts, the ambiguity in their use is widespread. Hence, we will first define some concepts that are mandatory to have a clear discussion and understanding on the topic. Whereas the ultimate goal is to build up a common language in this scientific community, the terminology employed hereafter should not be applied when analysing preceding studies.

### *2.1 Hybrid catalysts*

IUPAC has coined two different expressions comprising the term *hybrid* that can be applied for catalysts. A *hybrid material* is “composed of an intimate mixture [typically on scales less than 1  $\mu\text{m}$ ] of inorganic components, organic components, or both types of component” [65]. This would look like a somewhat restrictive definition, but a

*chemically bonded hybrid material* has also been defined as a “hybrid material in which the different components are bonded to each other by covalent or partially covalent bonds” [66]. Therefore, the term *hybrid material* comprises both physical and chemical mixtures of different components being thus meaningful in the context of catalysis. Concerning the term *composite*, IUPAC distinguishes between *composite material* and *composite sample*. The former is defined as a “multicomponent material comprising multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase” [65]. The latter consists of “...a representative mixture of several different (usually bulk) samples...” [65]. The first term could be applicable for some catalysts but implies the existence of a matrix (i.e. a continuous phase) which would not hold, for instance, for 50:50 physical mixtures of two catalysts. The expression *composite sample* is more related to sampling, being hence counterintuitive when referring to on-purpose design of a mixture of components to yield a given catalytic action. Consequently, the expression *hybrid catalyst* is, in our opinion, preferred to designate a catalyst with two or more components.

In dedicated literature, the clearest definition of *hybrid catalyst* based on zeolites was given by Smirniotis *et al.* [64]: “it consist(s) of two distinct phases with entirely different properties and functionalities”. However, the expression *zeolite-based composite materials* was employed. Following the previous reasoning, we would rather define *zeolite-based hybrid materials* as consisting of two distinct components with entirely different properties and functionalities. This category comprises, for instance, combinations of two zeolites as well as combinations of a zeolite and a low acidic or even inert solid. Meanwhile, a *zeolite-based composite material* solid implies the presence of a matrix falling under the latter example: dilution of a zeolite in an inert or low acidic matrix. In short, according to our definitions the expression *hybrid catalyst* holds for a broader range of catalysts than *composite catalyst*. In the specific case of bifunctional catalysts, a *hybrid bifunctional catalyst* can be defined as a bifunctional catalyst comprising three or more distinct components with entirely different properties and functionalities.

## 2.2 *Cooperative and antagonistic effects*

In the context of heterogeneous catalysis, the use of a hybrid solid aims at enhancing the catalytic performance as compared to that of individual components. In Figure 2, that comparison of catalytic performance between hybrid-based catalyst and individual components catalyst is outlined for a two-component catalyst. The average performance of individual catalysts can be roughly represented by a straight line between the two individual catalysts. Therefore, whenever the catalytic performance of the hybrid catalyst lies on this line, a so-called additive effect is at stake. More specifically, the behaviour of the hybrid catalyst corresponds to the addition of the outlet flows of two parallel reactors, each running with one of the components, at similar operating conditions. This requires that the contact time in the parallel reactors must be the same as the one observed for each individual component in the hybrid catalyst. In other words, when testing the individual components separately, the feed flow rate must be split in proportion to the component weight fraction in the hybrid catalyst.

Conversely, a catalytic performance situated in any other place of the catalytic performance mapping than the “additive line” indicates an effect upon the combination of the two components. Upgraded catalytic behaviour compared to the average performance of the individual catalysts (upper right side in Figure 2) reflects cooperation (or a cooperative effect) between two individual components. Such effect is also commonly called in literature synergy or synergetic effect. Hereafter, we will keep the term cooperation. Meanwhile, downgraded performance of the hybrid catalyst as compared to individual components (lower left side on Figure 2) discloses an antagonistic effect.

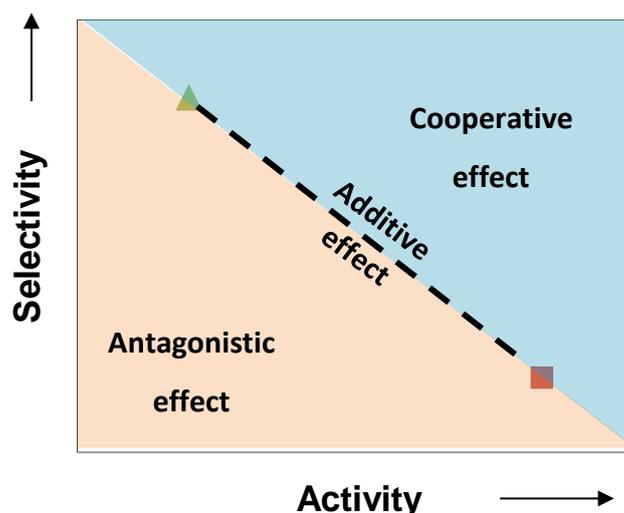


Figure 2: Representation of a performance mapping for hybrid catalytic systems. Symbols represent the individual performance of each component. The line stands for the average performance between the individuals.

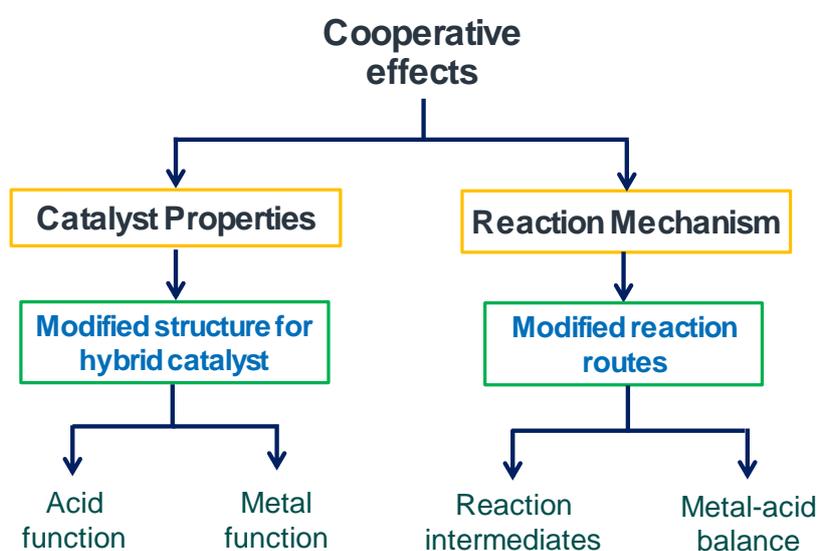
### 3 The origins for cooperative effects in hybrid bifunctional catalysts

Whereas recognizing cooperative effects is the first step, identifying the origin(s) of such effects is the crucial one to understand hybrid bifunctional catalysts. In that sense, we will start by reviewing the literature based on the origins of the cooperative effects (this section) and the tools to reveal those (section 4) to later discuss potential applications taking into account the insights grasped (section 5).

Figure 3 depicts a possible systematization of the causes for cooperation effects in hybrid bifunctional catalysts. Starting with the HDH function, the optimal operation of each metal phase (e.g. Pt, NiMoS, etc...) occurring at very different operating conditions, the interest in combining different metal phases is limited. For a given phase, the HDH properties tend to be relatively similar. Therefore, hybrid bifunctional catalysts can be treated in practice as comprising a single HDH function. Combining two components with different metal loadings can thus mainly lead to a change on the metal-acid balance (section 3.1). Consequently, to enhance the properties of the acid function, a combination of two acid functions or one acid function with one inert material is of utmost interest. These combinations can result in either changes in the reaction

intermediates, while the individual acid functions remain intact, (section 3.2) or modifications in the acid function itself (section 3.3).

Cooperation originated by modifications of the HDH function in hybrid catalysts have not yet been reported in literature. Therefore, potential cooperative effects will only be discussed in section 5 and not in this section. Finally, in some studies the origin of the cooperation could not be identified or remains dubious (section 3.4).

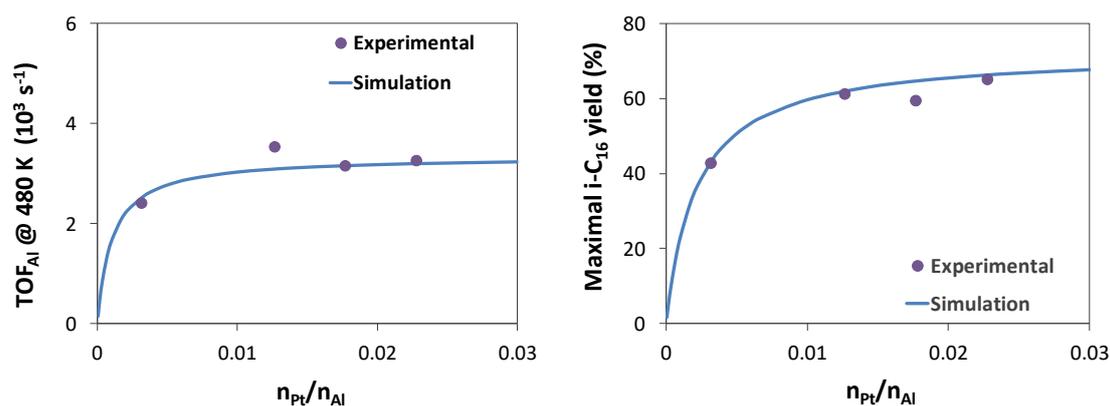


**Figure 3: Origins of cooperative effects in hydroconversion bifunctional catalysts.**

### 3.1 Impact of metal-acid balance

As abovementioned, the balance between metal and acid functions determines, for a given zeolite, the catalyst behaviour in hydroconversion reactions. As a result, comparisons between zeolites should always be carried out at similar metal/acid balances (the most practical way being hence to compare well-balanced catalysts). For the same reason, one should be aware of the role of the metal-acid balance in hybrids before dive into the effects directly related with the combination of different zeolite structures.

To date, a small number of studies covers this topic for hybrid catalysts. In our work, mixtures of Pt/H-USY and Pt/H-BEA covering a broad range of metal-acid balances, i.e. from poor-balanced up to well-balanced catalysts, were evaluated for *n*-hexadecane hydroconversion [67]. Strikingly, the performance of hybrid catalysts was observed to vary significantly with the metal to acid sites ratio (i.e. metal-acid balance) (Figure 4). In addition, an excellent agreement between the experimental performances and the performances simulated by a dual-function model for 2-populations of Brønsted sites coexisting in the same catalyst was obtained [67]. The parameters of the dual-function model, at the basis of the simulations, were obtained by regression of the individual performances of Pt/H-USY and Pt/H-BEA catalysts [22]. In other words, the performance of the hybrid catalysts matched that simulated purely based on the characteristic behavior of individual Pt/zeolite catalysts.



**Figure 4:** Experimental and simulation results for *n*-hexadecane hydroconversion: a) turnover frequency per protonic site at 480 K and b) maximal feed isomer yield as function  $n_{Pt}/n_{Al}$  ratio for mixtures of 75%Pt/H-USY with 25% of Pt/H-BEA. Adapted from [67] by permission of The Royal Society of Chemistry.

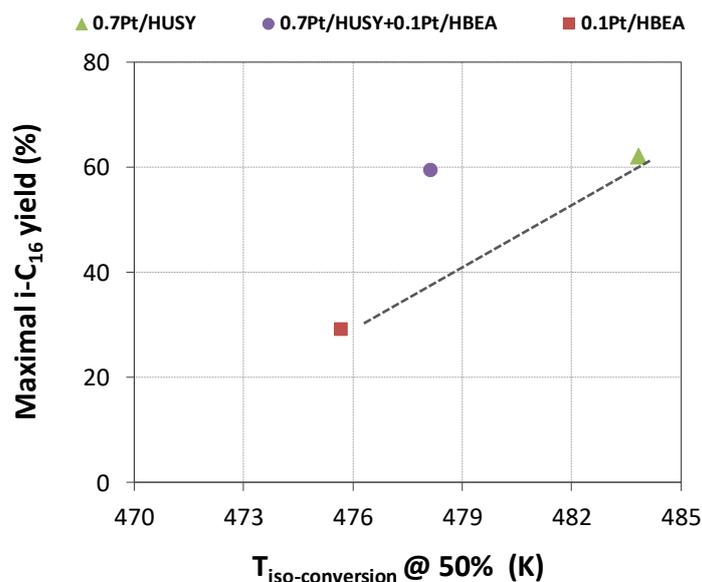
Thus, the hybrid catalysts behaved systematically as a bifunctional catalyst based on one single HDH and acid functions, with the intermediary characteristics between those of H-USY and H-BEA zeolites. There was, hence, no interference of one zeolite with the other. This implies that the catalytic behavior of hybrid catalysts, consisting of a given pair of zeolites, is governed solely by a global metal-acid balance.

These results also hint for the role of the distance between metal and acid sites in hybrid catalysts. As postulated by Weisz's intimacy criterion [25], the distance between sites should be below a critical value to obtain a well-balanced catalyst. The fact that the hybrids performances could be simulated considering one single metal function and one single acid function shows that the distance between the functionalities respected Weisz's criterion in this case study. Other studies have also pointed to the irrelevance of Pt location in hybrid catalysts [68]. Nevertheless, these findings should not be immediately extrapolated to all hybrid catalysts. Primarily, because the largest distance that ensures adequate intimacy between functionalities depends on the reactant and the operating conditions [25]. Secondly, the effective distance will depend on the preparation method of the hybrid catalyst. In the current examples in literature in which optimal intimacy was achieved, hybrid catalysts were obtained by grinding the individual solids together [67-69] (e.g. ball-milling, mortar). This can be expected to ensure an intimacy in the range of a few micrometres to hundreds of nanometres. In contrast, hundreds of micrometres to a few centimetres would be obtained upon conventional physical mixture of powders or extrudates, respectively.

In summary, the well-known metal-acid balance effect over single-zeolite bifunctional catalysts seems to hold as well for hybrid ones. However, this does not mean that no cooperative or antagonistic effects can arise when only the metal-acid balance plays a role in the performance of hybrid catalysts. In fact, out of the four catalysts shown to match the behaviour of the individual catalysts (Figure 4), a clear cooperation between a well-balanced Pt/HUSY and poorly-balanced Pt/H-BEA was observed (Figure 5)<sup>2</sup>. The remarkable improvement in terms of yield in feed isomers was attributed to the excess of HDH function in the Pt/HUSY catalyst [67]. This HDH capacity in excess is, when mixed with another zeolite, available to balance the acid function, improving its performance and so the overall performance of the hybrid catalyst as well.

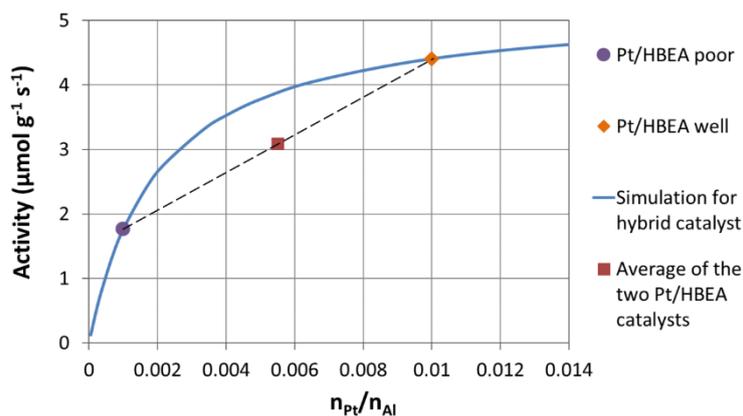
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<sup>2</sup> It is worth mentioning that in this case, the optimal catalyst is in the upper left corner of the charts (lowest temperature and greatest isomers yield).



**Figure 5:** Mapping of hybrid vs. individual catalysts according to the temperature at 50% feed conversion and maximal feed isomer yield. Adapted from [67] by permission of The Royal Society of Chemistry.

As a matter of fact, pure kinetic simulation results suggest that cooperation can arise upon mixing two catalysts featuring the same zeolite but different metal/acid ratios [70]. As in the previous case, this can be explained by a more efficient use of the excess of Pt in one catalyst to balance the acidic function of the second one. Mechanistically, this is explained by the effect of the metal to acid sites ratio in both activity and maximal yield in feed isomers [70] (Figure 6). This effect decreases with increasing ratios, and the activity and maximal isomerization yield are reaching a plateau for high metal to acid sites ratios. For low ratios, the variation in performance will be steeper than a linear relation, which is obtained for two reactors in parallel with the individual catalysts. In other words, in the hybrid catalyst, the increase in performance in the poorly-balanced catalyst is more significant than the lost in performance in the well-balanced one.



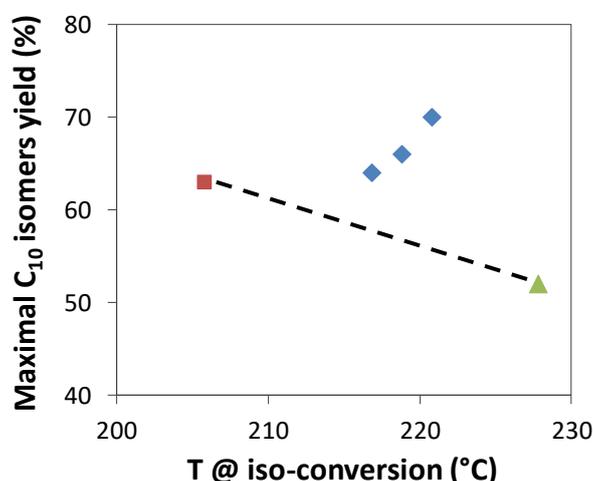
**Figure 6:** Simulation of catalytic activity for *n*-hexadecane hydroconversion at 480 K as function of  $n_{\text{Pt}}/n_{\text{Al}}$  over hybrid catalysts consisting of two Pt/HBEA catalysts, in a 50:50 (wt./wt.) mixture. Reproduced from [70].

Even though cooperation between two different bifunctional catalysts can be a sole consequence of their dissimilar degrees of metal-acid balances, the amplitude of this cooperation depends on the diversity of catalytic properties of the zeolites. Particularly, hybrid catalysts featuring performances superior to both individual catalysts can only be achieved for sufficiently different zeolites [70]. On the one hand, the more the intrinsic catalytic properties differ, the highest is the relative gain in performance with a hybrid catalyst. On the other hand, and at the same time, the narrower is the range of metal to acid sites ratio over which such gain can be obtained.

### 3.2 Impact of zeolite structures on reaction pathways

A number of reports by Martens and co-workers has focused on mixtures of zeolites or Pt/zeolite catalysts [68, 69, 71-73]. In particular, mixtures of low activity Y zeolite (i.e. either deep-bed steamed or partially  $\text{Na}^+$  exchanged) with ZSM-22 were intensively studied [68, 71-73]. For instance, a noticeable cooperative effect between the individual NaH-Y and ZSM-22 catalysts was revealed for *n*-decane hydroisomerization (Figure 7). The hydroisomerization patterns of individual Pt/zeolite catalysts have been proposed to be at the origin of the cooperative effects [68, 71, 72]. Indeed, the higher isomer yield obtained using a mixture was claimed to be the result from primary mono-branching on Pt/H-ZSM-22 and secondary multi-branching on Pt/NaH-Y. The increased concentration

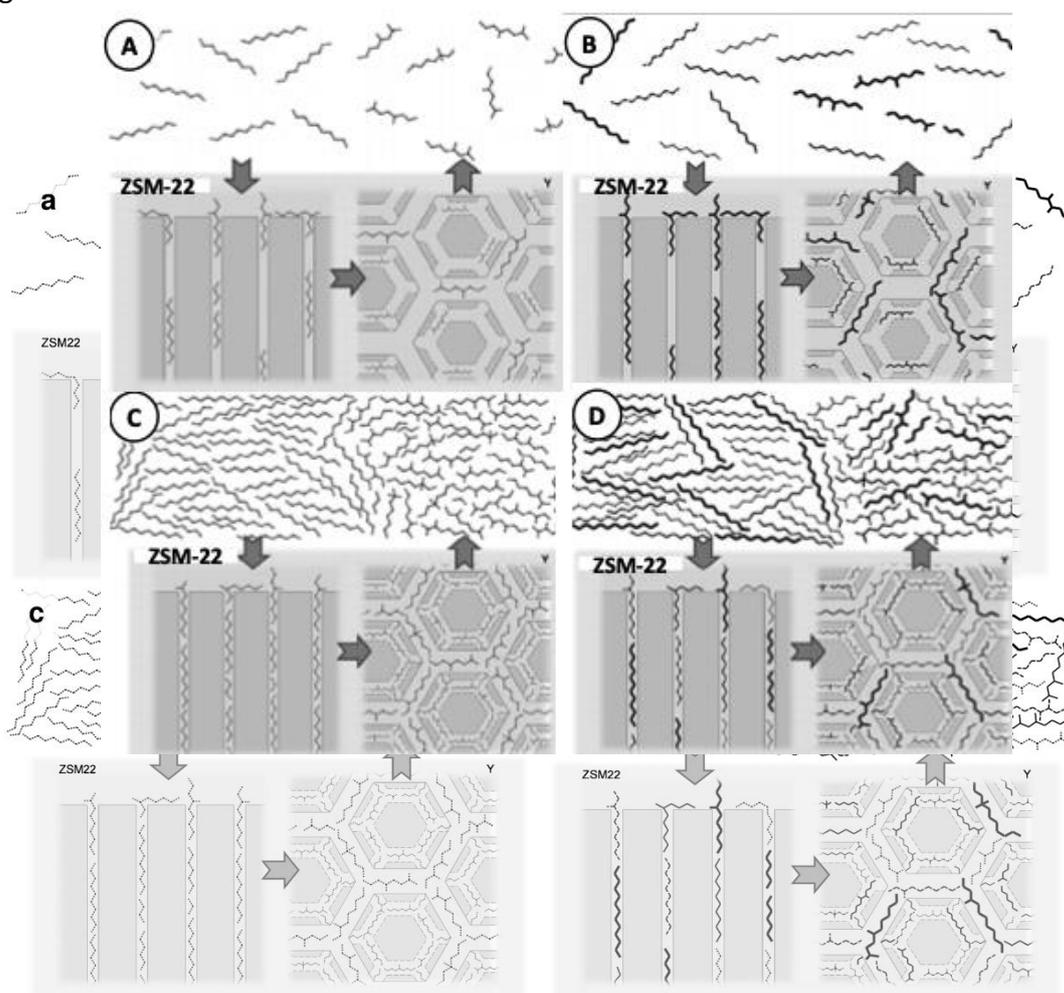
of monobranched olefins shortens the lifetime of the multi-branched species by competitive adsorption, with multi-branched isomers rather than cracked products being produced.



**Figure 7:** Mapping of hybrid vs. individual catalysts according to the temperature at 50% feed conversion and maximal feed isomer yield in the hydroconversion of *n*-decane (data from [72]). Catalysts: Pt/NaH-Y (▲), Pt/ZSM-22 (■), and Pt/NaH-Y+Pt/ZSM-22 (◆) with different individual proportions.

Single-Event MicroKinetic (SEMK) modelling data and results on 9-methylnonane hydroconversion further suggest that the aforementioned cooperation only occurs when important monobranched paraffins formation takes place on the TON architecture (ZSM-22) [68, 72]. As a matter of fact, in the hybrid catalyst tested, Pt/H-ZSM-22 was four times more active than Pt/NaH-Y catalyst [72]. In terms of SEMK simulations, the maximal feed isomer yield estimated was for a 60:40 mixture of those catalysts and so with an activity ratio (weight basis) of 6:1 between Pt/H-ZSM-22 and Pt/NaH-Y catalysts [72]. Accordingly, a protonation enthalpy for secondary carbenium formation at the H-ZSM-22 pore mouth sites 10 kJ/mol more negative than at the protonic sites of NaHY was claimed to be necessary for cooperation [72]. The formation of monobranched paraffins is thus required to be significantly superior to competitively force the desorption of the multibranched species from the protonic sites on the 12-MR zeolite.

More recently, the potential of these hybrid catalysts was shown to be enhanced for mixtures of longer *n*-alkanes under liquid-phase reaction conditions validating their applicability under industrial-like conditions [73]. In gas-phase, the adsorption of shorter molecules is preferred which hampers the cooperation between Pt/H-ZSM-22 and Pt/DB-Y<sup>3</sup>. However, for these hybrid catalysts only low activity levels could be achieved due to the extensive steaming of Y zeolite, and the low intrinsic activity of ZSM-22 based catalysts [68]. The entire findings revealed over this catalytic system are summarized in Figure 8.



**Figure 8:** Schematic representation of the different cooperation effects possible between ZSM-22 and NaHY. (a and c) *n*-decane and paraffin hydroconversion (b and d) under gas-phase (a and b) and liquid-phase conditions (c and d). Reproduced from Ref. [73] with permission from The Royal Society of Chemistry.

<sup>3</sup> DB-Y: deep-bed steamed Y zeolite (vide [68])

A mixture of two 10-MR zeolite-based catalysts, Pt/ZSM-48 and Pt/ZSM-22, also revealed a cooperative effect in the hydroconversion [69]. In this case, due to shape-selectivity intrinsic to each individual zeolite structure, the possible pathways for isomerization are limited and differ from one zeolite to another. The authors suggested hence that the higher number of available hydroisomerization pathways in the two zeolites mixtures compared with individual zeolites was at the origin of the cooperative effect. The fact that the distribution of multibranched isomers on the mixture is rather similar to that of Pt/ZSM-48 was explained by the higher catalytic activity of this catalyst.

Holding to the apparent importance of zeolites diversity to cooperation in hybrid catalysts, a strategy was developed to maximize the diversity in terms of catalytic behaviour of the individual catalysts [67, 74]. Each individual catalyst was well-balanced and contributed in equal proportions to the hybrid catalyst activity. From the thirty hybrid catalysts tested in *n*-hexadecane hydroconversion, only three catalytic systems exhibit cooperative effects, in particular enhanced isomerization yields. Two of those were Pt/EU-1+Pt/NU-10 and Pt/NU-10+Pt/ZSM-48 catalysts. All the individuals being 10-MR zeolites, the enhanced selectivity was explained by an increased contribution of multibranching reaction pathways upon combination of the individuals, in line with hypothesis made for Pt/ZSM-48+Pt/ZSM-22 hybrids catalysts [69]. In other catalytic system, Pt/NU-10 and Pt/silica-alumina, an improved isomerization yield was also claimed [75]. The underlying cooperative effect was justified by the different hydroisomerization patterns of individual catalysts as proposed formerly by Martens and co-workers. Briefly, it was suggested that isomerization would occur consecutively over the zeolites: *n*-hexadecane into monobranched feed isomers over Pt/NU-10 and these into multibranched feed isomers over Pt/silica-alumina. In presence of NU-10, the concentration of monobranched isomers increases which favours the desorption of multibranched isomers from silica-alumina.

Concerning the other mixtures, different selectivity degrees and reaction intermediates of both co-existing acid functions did not impact the reaction mechanism, irrespectively of how diverse the performances of individual catalysts were [67, 74]. The fact that no

cooperative effect was evidenced for the vast majority of hybrid catalysts tested in that study can be tentatively attributed to the similar contribution to activity from individual catalysts. As referred above, an activity ratio (weight basis) of ranging from 4:1 to 6:1 was determined to be required to achieve maximal cooperative effects [72].

### 3.3 *Impact of acid function modifications*

H-Y/H-BEA hybrid zeolites consisting of a core of Y zeolite and a shell of BEA zeolite with a thickness of about 80 nm have been also studied as an acidic function for VGO hydrocracking catalysts [76, 77]. The authors claim that superior middle distillates yields can be achieved over the core-shell catalysts, but the performance of individual catalysts is missing, and the comparisons between mechanical mixtures and core-shell catalysts were not carried out at iso-conversion. On the other hand, the results clearly show an increase in tall oil conversion for the core-shell catalysts. This improved activity was attributed to the higher amount of accessible Brønsted sites to bulky molecules in the core-shell hybrids, despite the lower total Brønsted acidity [77]. The higher accessibility to the acid sites was attributed to the hierarchical pore system created during the hybrid zeolites synthesis [77].

The combination of acid component with an inert material (as compared to the acid component at stake) also falls into the category of modifications to the acid function. Pt-loaded hybrids based on mixtures of an acid component (H-BEA or H-MCM-22) and an inert mesoporous or macroporous solid (MCM-41 or SiO<sub>2</sub>) have led to both higher activity and selectivity towards *n*-heptane isomerization compared to the individual catalysts [78]. This was attributed to the enhanced diffusion properties and so faster adsorption-desorption of the C<sub>7</sub> isomers. As no Pt was loaded on the inert, an effect related to improved metal-acid balance can be excluded. The hypothesis proposed is hence plausible.

Along the same lines, a Pt-loaded mechanical mixture was compared to an MCM-41 overgrown on zeolite Y, forming a layer in the outer surface of zeolite Y crystals [79]. Even though the samples featured a similar metal to acid sites ratio, the overgrown hybrid outperformed the mechanical mixture both in terms of activity and selectivity to

*n*-dodecane isomers. The authors attributed this cooperation to the shorter diffusion path of alkenes in the zeolite, due to the lower zeolite agglomeration promoted by the MCM-41 overgrown layer [79]. However, the location of the Pt particles in the hybrid sample was not clear which can also affect the metal-acid balance.

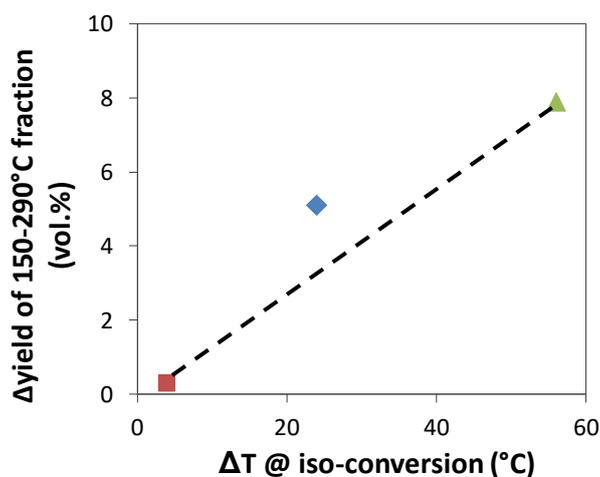
This aspect was further studied by changing the crystal size of the Y zeolite and depositing, according to the authors, in the MCM-41 layer [80]. The smallest Y zeolite size led to higher feed isomer yield, attributed to the shorter distance between metal and zeolite acid sites. Previously, a series of studies by some of us had revealed as well the importance of minimal aggregation among zeolite crystallites in order to improve the intimacy between metal and acid sites in hydroconversion [81, 82]. In that case, zeolite H-BEA was dispersed on the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles.

The combination of a zeolite with a binder upon shaping can also be considered an example of a hybrid solid, but a comprehensive review of this topic falls out of the scope of this article owing to its complexity [83]. In short, most of the existing reports point either to reduced [84-87] or enhanced acidity [88-90] upon shaping. On the other hand, from the point of view of hybrid catalysts based on combinations of zeolites, the possibility to retain the properties of the zeolites, as optimized in powder form, during catalyst scale-up is the most interesting one. For that reason, full preservation of the zeolites should be aimed at. Even if scarcely reported, full preservation is possible in practice [29, 91]. Finally, other studies on mixtures of a zeolite with inert materials also exist in literature but there the inert serves solely as a support for the HDH function [92-94].

#### *3.4 From unidentified origins to ill-defined effects*

A series of patents claims an improved performance when two large-pore zeolites (USY and BEA) are used as an acidic function for VGO hydrocracking catalysts. Figure 9 depicts the catalytic performance of one of the hybrid catalysts (50:50 in zeolite weight proportion) revealing a cooperative effect when the yield towards gas oil is considered [95, 96]. However, no justification for the cooperative effect is proposed in that case. Taking into account the previous discussions, it is tempting to attribute this behaviour

to an effect of global metal-acid balance, as no conventional shape-selectivity are at stake. On the other hand, the molecules in real feedstocks are far bulkier than the model ones. Therefore, shape selectivity might arise even for 12-MR zeolites. Furthermore, the difference in activity between the individual zeolites seems to fulfil the minimum criterion for cooperation discussed above<sup>4</sup>. Finally, these catalysts were obtained by extruding the zeolite together with alumina and the metal precursors. Thus, although conceptually unlikely, a possible influence of this step cannot be excluded.



**Figure 9:** Mapping of hybrid vs. individual catalysts according to the variation in the temperature at iso-conversion and variation in the yield of 150-290°C fraction for the hydrocracking of light VGO (data from Table II in [96]). Catalysts: NiMoS/USY (▲), NiMoS/BEA (■), and NiMoS/(USY+BEA) (◆). Zeolite mass ratio in the hybrid: 1:1.

A series of other patents claiming improved performances over hybrid H-USY+H-BEA catalysts were more recently issued [97-99]. In this case, the authors claim improved middle distillate selectivities of H-BEA+H-USY-based catalysts when compared to H-USY-based catalysts. However, no comparison to H-BEA-based catalysts is provided therein precluding the evaluation of potential cooperative effects.

A study on hybrid catalysts based on combinations of Pt/H-Y and Pt/H-MCM-41 revealed improved selectivity towards isomers of *n*-decane over the mechanical mixtures as compared to the individuals [79]. This cooperative effect was ascribed both to faster

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<sup>4</sup> Assuming an apparent activation energy of 180 kJ mol<sup>-1</sup> [20, 22] and reaction temperatures around 300 °C [30], both typical for hydrocracking, a difference of 55 °C reaction temperature at iso-conversion (as reported in Figure 9) corresponds to an activity ratio of 9.

diffusion of bulky molecules (similarly to the phenomenon arising upon acid function modifications) and improved metal-acid balance. As such, it is impossible to decouple the two phenomena, but it is worth noting that the metal to acid sites ratio in the mixture was more than twice the one in the Pt/H-Y catalyst. A study varying the metal to acid sites ratio of the latter catalyst would allow to settle this matter.

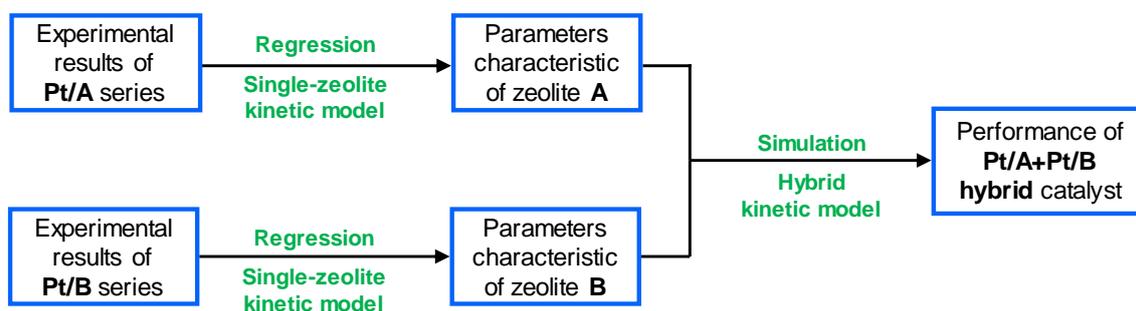
Additionally, a few reports disclosed remarkable improvement in catalytic activity with negligible loss of selectivity when a small amount of zeolite is added to a low acidic solid, as MCM-41 [100] or silica-alumina [101]. However, in none of the cases a comparison with the individual zeolite catalyst was established, precluding hence to recognize a possible cooperative effect. Likewise, improved activity was claimed on hybrid ZSM-5/SBA-15 bifunctional catalysts [102], but no benchmarking with individual ZSM-5 catalyst was carried out. Furthermore, the cracking selectivity of the hybrid catalyst was above 90 % throughout the whole range of conversions, precluding actually its industrial applicability.

#### **4 Simulation of hybrid catalysts via kinetic modelling**

Recurring hurdles in the evaluation of hybrid catalysts are the difficulties to predict and rationalize the catalytic performances. Comparison to individual catalysts enables the identification of a cooperative effect but remains insufficient in clarifying its origin. By employing kinetic models, simulation of the performance of hybrid catalysts based on those of individual components is a trustworthy approach, though seldom used, to disclose the origin of cooperative effects. In the review by Smirniotis and co-authors, a methodology to model hybrid FCC catalysts is described [64]. Herein, the focus will remain on bifunctional catalysts. The insights provided by these models have been already discussed in the previous section (section 3.2). Hereafter, the focus will be on the models themselves and their capabilities. Detailed discussions on general purpose kinetic models for hydroconversion processes can be found elsewhere [103, 104].

The two kinetic models used to date to study hybrid bifunctional catalysts differ in terms of the phenomena accounted for and the mechanistic detail, but follow a similar philosophy resulting in an identical modelling approach. These models for hybrid

catalysts are extensions of already existing models for typical (i.e. single-zeolite) bifunctional catalysts. During their development, the kinetic parameters of the individual zeolites were incorporated as much as possible in the model for hybrids. In both cases, the authors have succeeded in describing the reaction over hybrid catalysts without recurring to any parameters other than the ones for the individual catalysts. In practice, this means that modelling the behaviour of individual catalysts suffices to simulate that of the hybrid ones, as sketched in Figure 10, using two acid zeolites (A and B) with Pt as HDH function.



**Figure 10:** Simplified flowchart for the kinetic simulation of hybrid catalysts performance in the hydroconversion of *n*-paraffins. For simplicity, the metal function was herein represented by Pt.

Simulation of the performance of a hybrid catalyst with such a model enables the identification of cooperative or antagonistic effects. If the experimental performance matches the simulated one, the key phenomena occurring over the hybrid are the ones accounted by the model (vide examples in Section 3). On the contrary, if the experimental and simulated performances are not identical, those phenomena can be excluded as crucial to the behaviour of the hybrid catalyst. Moreover, extending the simulations for “extreme” individual performance might lead to a better understanding of the likelihood and magnitude of potential cooperative or antagonistic effects. Finally, by reversing the approach, hybrid catalysts featuring optimized performance can be looked-for and directly linked to promising catalyst formulations or zeolite properties.

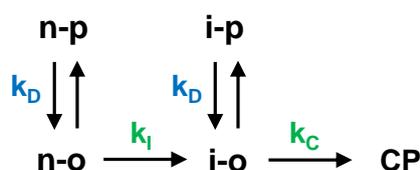
The features of the two models (dual function and Single-Event MicroKinetic model (SEMK)) are summarized in Table 1 and will be discussed briefly in the following sections.

**Table 1: Comparison of the available kinetic models to simulate cooperative effects.**

Model	Dual-function	SEMK
Original work	[22]	[72]
Subsequent reports	[67, 70]	[73]
Cooperative effects simulated	Metal-acid balance	Reaction intermediates
Requirements of the model	None. Regression against the experimental results can be done directly.	Single-event, thermodynamic and kinetic parameters have to be estimated <i>a priori</i>
Reactor	Plug-flow reactor	Plug-flow reactor (but easily interchangeable to others)
Reaction medium	Gas-phase	Gas-phase Gas-liquid-phase
Additional features	Mixtures of more than two solids	Mixtures of more than two solids Extrapolation for other operating conditions

#### 4.1 Two-population dual-function model

The two-population dual-function model is an extension of a dual function model aiming at adequately describe the effect of metal-acid balance on the performance of a given bifunctional catalyst [22]. The main catalytic steps, i.e. hydrogenation-dehydrogenation and acid-catalysed reactions, are accounted without any assumption on the rate-determining step and according to the classical bifunctional mechanism [16, 17]. To minimize number of model parameters, a simplified reaction scheme, based on lumped products: *n*-paraffins (*n*-p), *i*-paraffins (*i*-p) and cracked products (CP), was employed (Scheme 1).



**Scheme 1:** Simplified bifunctional mechanism for *n*-paraffin hydroconversion.  $k_D$ ,  $k_I$  and  $k_C$  are the apparent rate constants for dehydrogenation, isomerization, and cracking steps, respectively (reproduced from [22]).

Contrarily to a typical kinetic model, in which product flowrates are calculated based on more or less complex reaction rate laws, the dual-function model was built to directly calculate performance indicators. Once again, this aimed at keeping the number of parameters to be estimated as low as possible. The performance indicators chosen are the catalytic activity (in mol of reactant per catalyst mass per unit of time) and the maximal yield of feed isomers ( $Y_{i-feed}$ ). In this model, both indicators are a function of the ratio of the number of accessible metal sites ( $n_{Pt}$ , in mol of surface sites per catalyst mass) to the number of acid sites ( $n_{Al}$ , in mol of Brønsted sites per catalyst mass), through two parameters (Equation 1 and 2). More details on those parameters and the validity of the model can be found elsewhere [22]. In practice, such parameters are regressed for a catalyst series based on the same zeolite but with different number of metal sites and/or number of Brønsted sites.

$$Activity = \frac{n_{Al}\alpha}{1 + \beta(n_{Al}/n_{Pt})} \quad \text{Equation 1}$$

$$Y_{i-feed} = \frac{\gamma}{1 + \varepsilon(n_{Al}/n_{Pt})} \quad \text{Equation 2}$$

When extending the model for hybrid catalysts, a single metal function (corresponding to the sum of those of the individual catalysts) and *n* populations of acid sites were considered. Such approach yields expressions for the performance of a hybrid catalyst (Equations 3 to 6, for two populations) which are mathematically similar to the ones for individuals. The parameters of these expressions combine the characteristic parameters of each individual population of acid sites pondered by the weight fraction of each population ( $y_A$  and  $y_B$ ) [22]. In such a way and as generically described above, the performance of the hybrid catalyst may be directly related to the performances of the individual solids.

$$Activity^{A+B} = \frac{y_A n_{Al,A} \alpha_A + y_B n_{Al,B} \alpha_B}{1 + (y_A \beta_A + y_B \beta_B) (n_{Al}/n_{Pt})} \quad \text{Equation 3}$$

$$Y_{i-feed}^{A+B} = \frac{\Lambda^{\Lambda/(1-\Lambda)}}{1 + (y_A \varepsilon_A + y_B \varepsilon_B) (n_{Al}/n_{Pt})} \quad \text{Equation 4}$$

$$\Lambda = \frac{y_A \alpha_A \lambda_A + y_B \alpha_B \lambda_B}{y_A \alpha_A + y_B \alpha_B} \quad \text{Equation 5}$$

$$\gamma = \lambda^{\frac{\lambda}{1-\lambda}} \quad \text{Equation 6}$$

The model was first validated for single-zeolite catalysts [22], subsequently applied to hybrid ones [67] and, finally, employed in exploratory simulations [70].

#### 4.2 Single-Event MicroKinetic model

The SEMK model applied for mixtures of hydroconversion catalysts relies on two individual SEMK models. These models account explicitly for physisorption, dehydrogenation and protonation, but assume quasi-equilibrium for all three reaction families. The rate-determining step is, thus, an acid-catalysed one, restraining the application of these models to well-balanced catalysts. Conversely, in addition to the mechanistic detail, all components involved in the reaction network are accounted for via reaction families, according to the SEMK methodology [105].

To simulate the hybrid catalysts, the alkane net production rates as calculated from the individual SEMK models are summed up, at every axial point in the plug-flow reactor, proportionally to their concentration in the catalyst mixture [72]. As in that work the focus was on the cooperation between Pt/NaH-Y and Pt/H-ZSM-22, the authors selected SEMK models that had been validated for these catalysts individually. For Pt/NaH-Y, the model considers all the possible hydroconversion reactions, according to the referred assumptions [19, 106]. In contrast, the model for Pt/H-ZSM-22 accounted for the shape-selective effects via a contribution method developed to account for physisorption,

protonation, and reaction exclusively at the pore mouth and bridge sites [107, 108] (see Figure 8).

The SEMK model for hybrids was validated against experimental data [72], reproducing the results and corroborating the hypotheses formulated in the original experiments [68]. By incorporating liquid-phase fugacities, the original SEMK models were further extended to liquid-phase operation and used to simulate hybrid catalysts under such conditions [73]. It should be noted that the dual-function model is only valid for gas-phase experiments.

## 5 Systematizing cooperative effects and their applications in hydroconversion

Table 2 summarizes the main findings related to those origins reported in section 3. Most of the well-documented cooperative effects have been attributed to the diverse hydroisomerization patterns of individual Pt/zeolite catalysts. This type of cooperation has been observed over different catalytic systems and feeds resulting in improved selectivity to isomers. Such catalysts are thus promising for processes based on hydroisomerization, as catalytic dewaxing. Conversely, this type of cooperation seems to be hence intrinsically restrained to low catalytic activities. In all examples, pore-mouth catalysis predominated in the most active individual catalyst. As a consequence, only a small part of the acid sites effectively catalysed hydroconversion, limiting the catalytic activity. Nevertheless, taking into account the consolidated knowledge on these catalysts and the kinetic modelling tools available, the optimization of such catalysts to industrial application seems, at the least, feasible.

**Table 2: Causes, requirements and expected outcomes for cooperative effects.**

Origin	Acid function	Metal function	Reaction intermediates	Metal-acid balance
Reports	[77-79, 81, 82]	[109]	[68, 69, 71, 72]	[67, 70]
Hybrid system	Core-shell Y-BEA zeolites	Pt-impregnated	12-MR + 10-MR zeolites	Pt/HUSY + Pt/HBEA

	Mixtures of zeolites with mesoporous	mixtures of zeolites	10-MR + 10-MR zeolites	
	Zeolite Y with outer layer of MCM-41			
	Zeolite BEA dispersed on alumina surface			
<b>Cooperative effect confirmed</b>	Yes	No	Yes	Yes
<b>Feed</b>	VGO	-	<i>n</i> -alkanes	<i>n</i> -hexadecane
<b>Requirements</b>	Properties of acid function improved on hybrid catalyst	Metal location improved on hybrid catalyst	Distinct hydroisomerization pathways of individual catalysts Adequate activity ratio	Different degree of metal-acid balance of individual catalysts
<b>Expected outcome</b>	Enhanced activity and/or selectivity	Enhanced metal-acid site intimacy	Enhanced isomerization selectivity	Enhanced isomerization selectivity

More recently, we have observed and studied the cooperation between Pt/zeolite catalysts with remarkably different metal-acid balance. Such cooperation was attributed to an improved global metal-acid balance on the hybrid catalyst, reflecting an excess of Pt to adequately balance the acid functionality of one of the individual catalysts in the mixture. Furthermore, the simulation studies carried out revealed that those cooperative effects are likely to arise for many combinations of different individual catalysts but the range of metal-acid balances in which they occur as well as the gain in catalytic performance depend strongly on the properties of individual catalysts. While more studies are still necessary, this type of cooperative effects can be of interest for catalytic systems in which the metal-acid balance is limited [67], as it is most likely the case in industrial hydrocracking catalysts featuring transition metal sulphides HDH functions [110].

Another cause for cooperative effects can be generically designated as the modification of acid function properties in the hybrid catalyst as compared to the parent zeolites. This is rather unlikely in mechanical mixtures (only one example has been reported in literature [78]) but can occur via the modification (or even synthesis) of the zeolite during the synthesis of the hybrid acid function. One of the possible outcomes is the lower agglomeration between the zeolite crystals in the hybrids, shortening then the diffusion path of alkene intermediates and/or the distance between metal and acid sites under hydroconversion conditions. Achieving low agglomeration levels for nano-sized crystals of zeolites is challenging [111]. Consequently, commercial zeolites typically feature high agglomeration levels [109] which can lead to insufficient metal-acid site intimacy, as discussed in section 3.4. Another possible outcome is the modification of the intrinsic zeolite properties (i.e. porosity and acidity) during the synthesis of the hybrid acid function. Such modifications can also be achieved via the methods referred in section 1.2, but the hybrid route presents an opportunity to get hold of the same properties, potentially in a more controlled/tuneable way as the starting materials can be chosen as function of the desired properties.

Although no report still exists in literature, cooperative effects may also arise from enhanced HDH functions in hybrid catalysts. Particularly, in the case of a lack of intimacy between HDH and acid sites as reported in section 3.3, a preferential deposition on the “hardest to balance” zeolite is expected to enhance the performance of hybrid catalysts. As a matter of fact, the preferential location of Pt in HBEA zeolite when Pt was deposited on mixtures of HUSY and HBEA zeolites suggests that possibility [109].

As initially stated, the goal of this review was to recognize and identify the causes of cooperative effects. To do so, individual and hybrid catalysts should be compared at equivalent operating conditions, taking particular attention to adjusting the space velocity to the proportion of individual component in the hybrid (see section 2.2). However, when commercialized, catalysts are typically compared under similar industrial conditions, i.e. at identical space velocities. Moreover, several patents claiming the improved performances over hybrid catalysts report tests at a single space velocity [97-99]. Under the same operating conditions, the activity depends also on the

percentage of each zeolite in the hybrid and selectivity depends also on the conversion level over each catalyst. In short, the catalytic performances are circumstantial to the particular operating conditions (e.g. a given contact time). Therefore, the hybrid catalyst, as any other catalyst, might outrank the corresponding individuals. Under given operating conditions, the properties of the hybrid catalyst can be thus the golden mean between those of the individual catalysts. This behaviour unveils a fifth category of cooperative effects in which the in-between properties of the hybrid give rise to an optimal combination of the properties of the individuals. However, in contrast to the cooperation discussed so far, this cooperative effect is not intrinsic to the hybrid catalyst and it is restricted to the chosen operating conditions.

## **6 Conclusions**

In the search for superior hydroconversion catalysts, several strategies have been developed to get hold of suitable acidic functions. The less explored approach is the combination of different acidic solids, in particular zeolites, in a way that a cooperative effect between them can occur. The combination of different zeolites is, hence, a promising route to develop improved acidic functions for hydroconversion catalysts. The interest on mixing catalysts with different selectivities or metal-acid balances has been demonstrated and rationalized through experiments and kinetic simulations in literature. Conversely, it still exists a number of revealed cooperative effects which are not understood, particularly in patents literature. In addition to the cooperative effects already reported, two other plausible origins for cooperatives effects are also suggested: specific metal location on the hybrid catalyst and improved performance due to operating conditions effects.

## **Acknowledgments**

Authors would like to thank G. Pirngruber and E. Guillon for the fruitful discussions and Fundação para a Ciência e Tecnologia for financial support, through CQE (Project UID/QUI/00100/2013) and PhD grant (SFRH/BD/87927/2012).

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