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Aurélien Bonnin, Jean-Dominique Comparot, Yannick Pouilloux, Vincent Coupard, Denis Uzio, et al..
Mechanisms of aromatization of dilute ethylene on HZSM-5 and on Zn/HZSM-5 catalysts. Applied
Catalysis A : General, 2021, 611, pp.117974. 10.1016/j.apcata.2020.117974 . hal-03159920

HAL Id: hal-03159920

<https://ifp.hal.science/hal-03159920>

Submitted on 3 Feb 2023

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Mechanisms of aromatization of dilute ethylene on HZSM-5 and on Zn/HZSM-5 catalysts

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Abstract

Catalysts with a Zn/H⁺ molar ratio ranging from 0 (H-ZSM5) to 1.8 (Zn/H-ZSM5), were prepared by wet impregnation from three commercial zeolites with Si/Al ratio of 15, 40 and 75. The texture, acidity and reactivity of the bifunctional catalysts were characterized by: N₂, IR followed by adsorption of pyridine and NH₃-TPD, and tested at 500 °C with low partial pressure of ethylene (P_{C₂H₄} = 0.005 MPa) and a high GHSV (ca 13300 h⁻¹).

The intrinsic activity of protonic acid sites in ethylene transformation depends on their density or rather on the concentration of next nearest neighbours pairs of Al atoms. Brønsted acid pair sites converts ethylene into aromatics while isolated protonic site are almost inactive. Two apparent primary products were distinguished: iso-butene and propene, resulting from the oligomerization-cracking catalytic pool, followed at high conversion by the concomitant formation of alkanes and aromatics through hydrogen transfer.

The deposition of Zn was achieved by wet impregnation of the nitrate precursor. The thermal decomposition of the ZnOH⁺ cation by calcination is a function of the fraction of Al atoms in the nearest neighbours. Three main species of Zn could be identified: i) oxo-binuclear Zn²⁺ cations (O⁻-Zn²⁺-O-Zn²⁺-O⁻), ii) mononuclear Zn²⁺ cations (O⁻-Zn²⁺-O⁻ and iii) ZnO particles located on the external surface. These species were quantified from the residual Brønsted acid sites probed by pyridine. A correlation has been established: one neutralized protonic site generates one Zn Lewis acid sites which coordinates two pyridine molecules. The ethylene conversion is proportional to the concentration of oxo-binuclear Zn cations and mononuclear Zn cations only correlate with hydrogenation and hydrogenolysis of olefins, while bulk ZnO is inactive.

A metallacyclic mechanism of ethylene aromatization involving cyclo-butyl-zinc species has been proposed accordingly.

Key words: Zn/H-ZSM-5, dilute ethylene, reaction mechanisms, aromatization, active sites.

Introduction

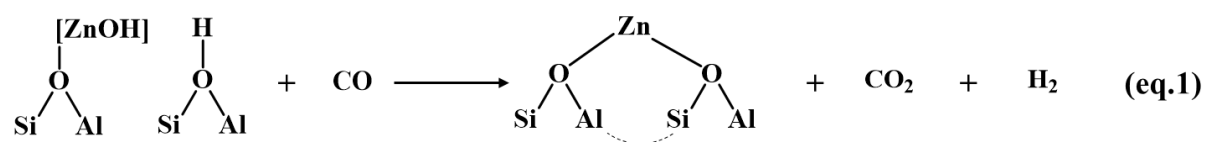
Pervasive in our daily lives as plastics, packaging, clothing, digital devices, medical equipment, tyres etc., petrochemicals provide substantial benefits to society, including a growing number of applications in various cutting-edge, clean technologies critical for sustainable energy economy. They are set to account for more than a third of the growth in oil demand to 2030, and nearly half in 2050. [1] Meanwhile, oil demand for the production of transportation fuel is expected to decrease due to the combined effects of improved fuel economy, alternatives fuels and electrification. As a result, the landscape for the petrochemical, oil and gas industries is shifting toward “High-Value Chemicals” (HVCs) such as light olefins (ethylene and propylene) and aromatics (benzene, toluene and mixed xylenes, (BTX) which are the building blocks for many value-added chains.

Some “by-products” from oil refining are now considered more like “co-products” or even “primary products”. For instance, the FCC dry gas containing ethylene (5 to 50% by weight) and ethane is currently used as refinery fuel. [2] Since 50,000 barrels per day for a FCC unit burn approximately 200 tons of dry gas per day, 10-100 tons of ethylene are burned each day. A diligent option would be to transform ethylene into value-added products such as propylene or aromatics. Over the past decade, several companies developed technologies for the oligomerization and aromatization of concentrated ethylene from dry gas: $3\text{C}_2\text{H}_4 \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$. The Beijing Huiersanji Green Chem DTL process licensed by Invista Performance Technologies is the most mature, with 12 operating units in China in 2018. [3] Wood and Siluria Technologies launched Modus TM, the first treatment technology to convert FCC gases into refinery products, and UOP LLC developed a process that converts more than 40% of ethylene into fuels in a single pass.

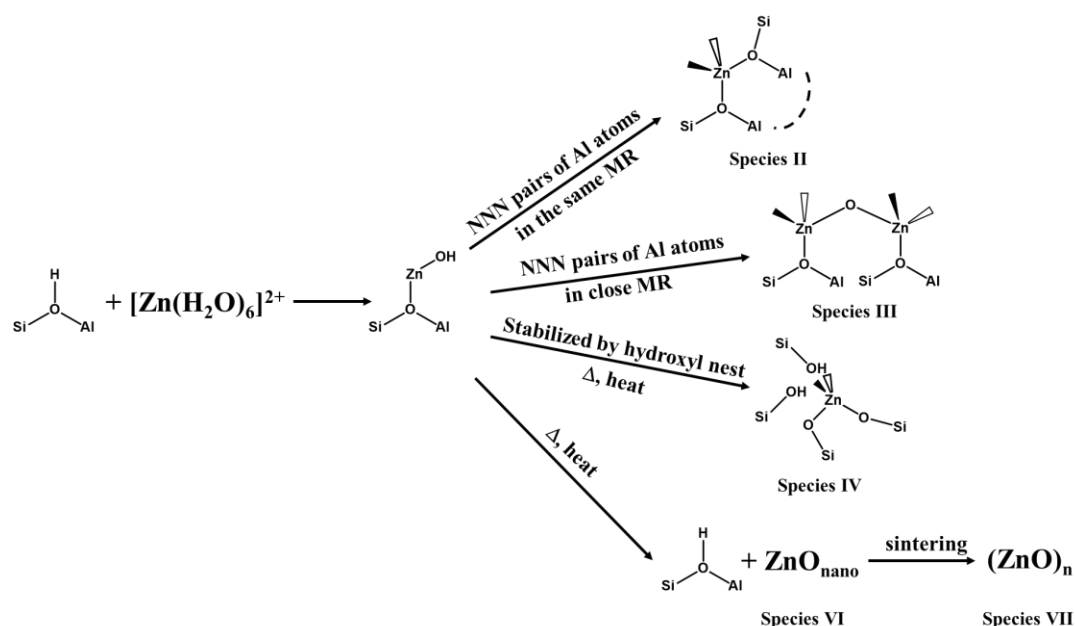
Zn-loaded H-ZSM-5 is a promising catalyst for the aromatization of ethylene due to the specific dehydrogenation/hydrogenation performances of the metal cation [4-6] and the

high selectivity towards aromatics related to the size and shape of the zeolite micropores. However, the role of Zn metallic site is still unclear. The oxidation states of Zn species are limited to 0, +1 and +2. Considering that the total reduction of (ZnO)_n is hardly achieved even by hydrogen treatment at 600 °C [7] and Zn (+1) has never been observed in zeolites, the formal oxidation state of Zn in zeolite is expected to be +2.

Ion exchange and wetness impregnation are typical preparation methods. The hexaaquo Zn complex ion acts as an acid by giving a hydrogen ion to water molecule in the aqueous solution ($[Zn(H_2O)_6]^{2+} + H_2O \rightleftharpoons [ZnOH(H_2O)_5]^+ + H_3O^+$). The monovalent cation can be exchanged with all the zeolite protons. Water from the aqua complex is stepwise removed during calcination resulting in the formation of [ZnOH]O_z species (**species I**) [8], which was described as the active site for the formation of aromatics from ethylene [9], *n*-pentane [10], and methanol [11-13]. Bernt et al. identified this species using a temperature-programmed surface reaction with CO (TPSR / CO). [14] Since the CO reaction on protonic ZSM-5 (Si/Al=23) zeolite gives equimolar amounts of CO₂ and H₂, the authors proposed the following reaction equation:



CO inserts in the OH group of Zn species, giving a formate species that reacts with a neighbouring H⁺ and decomposes into CO₂ and H₂. Yet, Biscardi et al. showed by X-ray adsorption experiments that the [ZnOH]O_z species was not thermally stable. [15] Their decomposition paths depends on the Al atom fraction in the next nearest neighbours (NNN) position (**Scheme 1**).

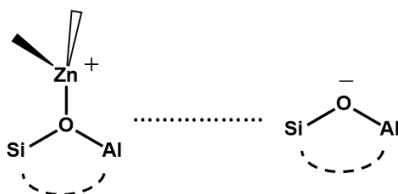


Scheme 1: Different possible species of Zn cations on zeolite H-ZSM-5 after ion exchange and wet impregnation followed by calcination.

Rice et al. [16] calculated by stochastic simulations the probability in ZSM-5 zeolite of NNN pairs of Al atoms able to stabilize a divalent cation (M^{2+} , **Species II**) and form an oxo-binuclear cation, i.e. two M^{2+} bridged by an oxygen atom ($(-\text{M}-\text{O}-\text{M}-)^{2+}$ (**Species III**). The assessment of the maximum probability to form bridged M^{2+} cations is 0.12 for $\text{Si}/\text{Al} = 12$ and decreases to 0.07 with half of the framework aluminium ($\text{Si}/\text{Al} = 24$) (**Figure SI.1**). Relative to the binuclear oxo metal cation, the probabilities are higher: 0.30 and 0.19 for $\text{Si}/\text{Al} = 12$ and 24, respectively. The distribution of the Zn cation species therefore depends on the zeolite Si/Al ratio (**Figure SI.1**). It is worth mentioning that the divalent cation can also be stabilized by being linked by an Al centred tetrahedron and an internal silanol group in its vicinity (**Species IV**). [17]

In the case of the catalyst prepared through ion exchange or wetness impregnation, the exchange is commonly 60%. [18] Thus, the isolated cationic $(\text{ZnOH})^+$ species cannot be stabilized during calcination and decomposes into ZnO nanoclusters (**Species VI**) regenerating the initial Brønsted acid site.

Complete substitution of framework aluminium is only possible through the chemical deposition method [17,19]. This preparation method also allows an unusual location of Zn^{2+} cations [18,20], which is stabilized at an ionic site of the zeolite with a distantly located second charge-compensating (AlO_2^-) framework unit (**Species V**, **Scheme 2**).



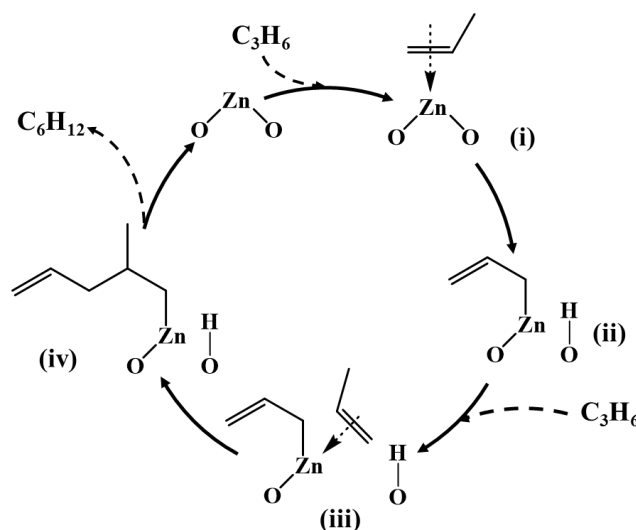
Scheme 2: Zn cation species (Species V) with alternating positive and negative electric charges.

Hence, Zn/H-ZSM-5 catalyst prepared using conventional techniques leads to $(\text{ZnOH})^+$ which decomposes into a bridging Zn^{2+} cation by two framework aluminium (**Species II**), or by a framework aluminium (FAL) and an internal silanol (**Species IV**), a binuclear oxo Zn cation (**Species III**), and nanoclusters of zinc oxide (**Species IV**).

UV-Vis diffuse reflectance spectroscopy can distinguish subnanometric ZnO clusters within the zeolite micropores (275 nm, [21-22]) from large $(\text{ZnO})_n$ particles on the external surface (375 nm, [23-24] **Species VII**). Temperature programmed reduction allows the detection of zinc oxide, since its reduction starts around 580 °C. In contrast, Zn^{2+} is stable even at 880 °C. [15] Large $(\text{ZnO})_n$ crystals can be considered as spectator species, due to their inactivity in the aromatization of ethane [25], propane [15] and CO activation [14]. Nanocrystals $(\text{ZnO})_n$ catalyse dehydrogenation reaction but impede the diffusion of products, thus deteriorating the stability of the catalyst. [11]

Zn cation species are involved in the dehydrogenation step but mainly catalyze the recombination-desorption of H atoms into H_2 , which is considered to be the rate limiting step in alkane aromatization. [26-28] The mechanism here is bifunctional because the Brønsted acid sites allows the di/trimerization of the olefins, which are then cyclized: $2 \text{C}_3\text{H}_8$

127 $\xrightarrow{\text{Zn}} 2 \text{C}_3\text{H}_6 + 2\text{H}_2 \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12} \xrightarrow{\text{Zn}} \text{C}_6\text{H}_6 + 3\text{H}_2$. This bifunctional mechanism of olefins to
 128 aromatics is commonly accepted by the scientific community. [29] However, Lobo et al
 129 suggested that Zn in the form of Lewis acid sites can lead to the oligomerization of ethylene.
 130 [25] Indeed, Stepanov et al. [30-31] have shown by ^{13}C MAS NMR and FTIR spectroscopic
 131 studies that Zn cation species on ZSM-5 zeolite oligomerize propylene. The stages of the
 132 proposed mechanism follow a Cosse-Arlman mechanism and can be summarized as follows
 133 **(Scheme 3)**: i) propylene adsorption on a Zn^{2+} site ii) dissociation of propylene resulting in a σ
 134 allylzinc species and a Si-O(H)-Al group, iii) adsorption of a second propylene molecule on
 135 the Zn sites forming a new π -complex, iv) recombination of the π -complex and of the
 136 allylzinc species, and v) desorption of C_6H_{12} and regeneration of active site.



137
 138 **Scheme 3:** Mechanism of propylene oligomerization on $\text{Zn}^{2+}/\text{H-ZSM-5}$ cation, adapted from
 139 [30].
 140

141 Hence, the possibility that oligomerization of olefins may occur on Zn cation species
 142 raises the question of the bifunctional mechanism of ethylene aromatization on Zn/ZSM-5
 143 zeolite. The goal of this study is to identify the mechanisms and the active sites of the
 144 ethylene aromatization over H-ZSM-5 and Zn/H- ZSM-5 catalysts. We will demonstrate that

the intrinsic activity of the protonic acid sites depends on the concentration of the nearest neighbours Al atom pairs and that on the bifunctional catalyst, ethylene aromatization occurs by monofunctional catalysis via a metallacyclic mechanism on oxo-binuclear Zn^{2+} cations. For this purpose, more than 15 catalysts with a molar balance between the two functions (Zn/Al) ranging from 0 (H-ZSM5) to 1.8 (Zn/H-ZSM5), were prepared, characterised by different probe molecules (N_2 , pyridine and NH_3), and tested with dilute ethylene at 500 °C. This paper focuses only on the initial conversion and does not take into account the deactivation that occurs during the ethylene aromatization, this point is discussed in another publication.

Experimental

Materials: Three series of Zn-containing catalysts were prepared from three commercial zeolites (Zeolyst) with global Si/Al molar ratios of 15 (CBV 3042E), 40 (CBV 8014) and 75 (CBV 1502) zeolites. The CBV 3042E and CBV 8014 under ammonium form were calcined in air at 500 °C. Another commercial protonic zeolite with a Si/Al molar ratio of 25 (CBV 5020) was also used.

Zn-containing zeolites were prepared by wet impregnation by stirring protonic zeolite with an aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 60 °C for 30 minutes, in the proportion of 1 g of zeolite per 10 mL of solution. Then, the samples were dried at 120 °C for 12 h and calcined at 500 °C under air (60 mL min^{-1}) for 12 h.

$0.8\text{Zn}40^{\text{IE}}$ was prepared by ion exchange by stirring HZ40 under ammonium form in an aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($m/V = 0.02 \text{ g l}^{-1}$) at 80 °C for 2h. In contrast to wet impregnation, the sample is rinsed with water. Ion exchange was carried out successively three times before drying and calcination. $0.8\text{Zn}40^{\text{DI}}$ was prepared by dry impregnation, with a volume of the metal solution equivalent to the micropore volume of the zeolite i.e. 0.18 cm^3

169 $\text{g}^{-1}_{\text{zeolite}}$. All zeolites under protonic form and bifunctional catalysts are calcined at 500 °C
170 before catalytic test.

171 **Characterizations:** The elemental composition of the bifunctional catalysts (Si, Al,
172 Zn) was determined using an inductively coupled plasma-atomic emission spectroscopy (ICP-
173 AES) on an Optima 2000 DV (Perkin-Elmer). The samples (30-40 mg) were mineralized by
174 three successive acid attacks by HNO_3 (69 vol. %), HCl (37 vol. %) and HF (40 vol. %) in the
175 proportion of 4/2/2 mL, respectively. Mineralization was carried out in sealed vessels at 180
176 °C under an autogenous pressure of 2.0 MPa for 45 min using a microwave oven (Anton-Parr
177 Multiwave Pro). Finally, 12 mL of a saturated solution of H_3BO_4 was added to the sample.

178 Samples were characterized by transmission electronic microscopy (TEM) using a
179 JEOL 2100 microscope equipped with a LaB_6 filament operating at 200 kV. The samples
180 were first prepared by ultrasonic dispersion in ethanol and then dropped onto a copper grid,
181 previously covered with a carbon film.

182 Nitrogen adsorption and desorption measurements were carried out at -196 °C on a
183 Micromeritics ASAP 2420 apparatus. Before analysis, the samples were pre-treated at 350 °C
184 under vacuum for 15h. The micropore volumes (V_{micro}) were calculated according to the t -plot
185 method and the total pore volume was calculated at $p/p_0 = 0.98$.

186 ^{27}Al magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) spectra were
187 recorded at 104.28 MHz on a Bruker advance II 400 MHz spectrometer using a spinning rate
188 of 12 kHz, a pulse length of 0.42 μs and a recycle time of 0.5 s.

189 The nature, concentration of acidity were studied using adsorption of pyridine
190 followed by infrared spectroscopy (FTIR) with a Nicolet 5700 apparatus with 2 cm^{-1} optical
191 resolution. Prior to analysis, the catalyst was pressed (0.5 ton) into a self-supporting wafer (2
192 cm^2) and pretreated from 20 °C to 500 °C under nitrogen flow (100 $\text{cm}^3\text{min}^{-1}$). The sample
193 was then degassed (10^{-5} bar) during 1h at 200 °C, after which an IR spectrum was taken. The

sample was then cooled to 150 °C and exposed to a pyridine pressure of 1.5 mbar for 5 min and then degassed (10^{-5} bar) to remove the physisorbed pyridine. The Beer-Lambert-Bouguer law was applied in the form $[PyH^+] \text{ or } [PyL] = \left(\frac{S}{m}\right) \frac{A}{\varepsilon}$ where $[PyH^+]$ and $[PyL]$ is the concentration of Brønsted and Lewis acid sites ($\mu\text{mol g}^{-1}$), A denotes the integrated absorbance of the corresponding IR bands (1545 and 1455 cm^{-1}), which is normalized to zeolite wafer density (ratio of the wafer weight (mg) to wafer surface (cm^2), and ε is the integrated molar adsorption coefficient: $\varepsilon_{1545} = 1.13$ and $\varepsilon_{1454} = 1.28 \text{ cm mol}^{-1}$. [32] The calibration curves were obtained on a MFI (Si/Al=27) and a $\gamma\text{-Al}_2\text{O}_3$ by adding to the IR cell a known amount of pyridine vapour from gas inlet compartment (0.9122 cm^3) (**Figure. SI.2**). All the reported FTIR spectra are normalized to a wafer density (mg cm^{-2}).

The temperature-programmed desorption of ammonia (NH_3 -TPD) profiles were measured using a flow-through micro-reactor system connected to a thermal conductivity detector (TCD). The samples (0.4 g) were activated under helium at 500 °C for 1 hour then cooled to 100 °C, prior to adsorption of ammonia (5 vol. % in He) for 45 minutes. The physisorbed ammonia was removed by purging with helium at 100 °C for 3 hours. Ammonia desorption was achieved in the temperature range of 100 to 550°C with a heating rate of 5 °C min^{-1} under He.

Catalytic test: A typical catalytic test for the ethylene conversion (Air Liquid, > 99%) was carried out at atmospheric pressure in a fixed-bed continuous flow quartz reactor at 500 °C with a N_2 /reactant molar ratio of 19, which correspond to an ethylene partial pressure of 0.005 MPa. Under standard conditions, the weight gas hourly space velocity WHSV (g of injected C_2H_4 per hour and per g of catalyst) was 2 h^{-1} , and the gas hourly space velocity was $13\,300 \text{ h}^{-1}$ which corresponds to a short contact time of $7.5 \times 10^{-5} \text{ h}$. For the kinetic study, the GHSV varied from 13 300 to 213 400 h^{-1} . Prior to testing, catalysts were compacted, crushed and sieved to obtain homogeneous particles (0.2-0.4 mm). Samples were pre-treated at 500 °C

under nitrogen flow (100 mL min^{-1}) for 1 h. The gaseous products and hydrogen were analysed on-line by a Varian CP-3800 gas chromatograph equipped with a FID detector connected to a fused silica J&W GS-Gaspro capillary column ($60 \text{ m} \times 0.32 \text{ mm} \times 4 \text{ }\mu\text{m}$) and a TCD connected to a J&W PoraPLOT Q-HT capillary column ($25 \text{ m} \times 0.53 \text{ mm} \times 20 \text{ }\mu\text{m}$).

The catalytic results in this study relate only to the conversions and yields measured after 10 minutes of reaction.

Results and discussion

1. Textural and acidic properties of the four commercial H-ZSM-5 zeolites.

The protonic zeolites are named HZ followed by their Si/Al molar ratio. The textural properties of commercial zeolites are given in the supporting information (**Table SI.1**). Microporous volumes between $0.15\text{-}0.18 \text{ cm}^3 \text{ g}^{-1}$ were inferred for these samples, which is a typical value for ZSM-5 zeolites. [33] In addition, mesopore volumes between $0.11\text{-}0.14 \text{ cm}^3 \text{ g}^{-1}$ were deduced. Mesopores on HZ15 result from the aggregation of the small crystals as indicated by the strong nitrogen uptake at high relative pressure (**Figure SI.3 and Figure SI.4**), while on HZ40 and HZ75 the mesopore volume is rather intraparticular (**Figure SI.4**) as shown by the presence of a hysteresis loop of type IV (**Figure SI.3**). The intraparticular mesopores are probably generated during the steaming process applied during the preparation of the sample by the supplier.

Figure 1a compares the infrared spectra in the OH stretching region of the three zeolites. HZ75 has two IR bands: an intense band at $3610 \text{ cm}^{-1} (\pm 2)$ attributed to the bridged hydroxyl groups (Si-O(H)-Al) and an asymmetric band at 3740 cm^{-1} ascribed to the terminal silanol groups on the external surface. On HZ40, the shoulder at 3726 cm^{-1} corresponds to Si-OH located on the intraparticular defects and is correlated with the broad band centred at 3470 cm^{-1} , which is assigned to the hydroxyl nests. These internal defects are microcavities saturated with neighbouring OH groups close enough to interact through hydrogen bonds. [34] ^{27}Al

MAS NMR on HZ40, confirms that almost all of the Al ($\geq 95\%$) are of tetrahedral coordinated and thus within the zeolite framework (**Figure SI.5**).

HZ25 and HZ15 exhibit an intense band at 3665 cm^{-1} which corresponds to OH linked to extraframework aluminium species (e.g. AlOH^+). Chemisorption of pyridine at $150\text{ }^{\circ}\text{C}$ leads to a total disappearance of the bridged hydroxyl groups on the four zeolites, while the intensity of the silanol bands remains unchanged. The concentrations of the Brønsted acid sites able to retain pyridine at this temperature on H-ZSM-5 zeolites with Si/Al of 15, 25, 40, and 75 are of 515, 307, 286, and $148\text{ }\mu\text{mol g}^{-1}$, respectively (**Table 1**). The number of bridging acid sites in typical commercial MFI zeolites is significantly lower with respect to their Al content (i.e. 1041, 640, 386 and $219\text{ }\mu\text{mol g}^{-1}$, respectively). However, the quantification of the BAS is in agreement with these of White et al. obtained from ^1H MAS NMR spin counting (4.2 ppm peak). [35] For instance, on Si/Al = 15 they found a concentration of BAS of $560 \pm 18\text{ }\mu\text{mol g}^{-1}$, which is about the same as that measured by pyridine adsorption followed by FTIR, i.e. $515\text{ }\mu\text{mol g}^{-1}$. This means that 60-70% of the theoretical protons exists as BAS, with the other distributed among the other distorted framework sites or other nonframework sites. [35] Gabrienko et al. also found that on the commercial zeolite with Si/Al of 40 (CBV-8014), the concentration of BAS measured by ^1H MAS NMR is $312 \pm 28\text{ }\mu\text{mol g}^{-1}$, which is close to the concentration measured in this study, i.e. $286\text{ }\mu\text{mol g}^{-1}$. [36]

In addition, on HZ15 and HZ25 zeolites, one part of EFAL species chemisorbs pyridine (**Figure SI.6**) resulting in a slight increase in the concentration of Lewis acid sites (ca $15\text{ }\mu\text{mol g}^{-1}$). The presence of the iminium ion, indicated by the band centred at 1462 cm^{-1} [37] (**Figure 1b**), suggests a close proximity of the bridged OH groups with the EFAL species (**Figure SI.7**).

2. Textural and acidic properties of the three series of bifunctional catalyst: 15, 40 and 75.

Zn-based catalysts are referred to as $x\text{Zn}_y$ where x is the zinc content and y the Si/Al molar ratio. Three series of bifunctional catalysts were prepared by wetness impregnation from HZ15, HZ40 and HZ75 zeolites with a Zn loading ranging from 0.3 to 8.1 wt. % (**Table 1**). Zn loading on HZ40 was also prepared by ion exchange and dry impregnation: $0.8\text{Zn40}^{\text{IE}}$ and $0.8\text{Zn40}^{\text{DI}}$

2.1 Zn40 and 3.6 Zn40 exhibit similar characteristic of MFI structure, as shown in **Fig. SI.7**, suggesting that the introduction of Zn species by wet impregnation has no impact in the zeolite framework. Only very weak diffraction peaks of ZnO at 36.3° and 31.8° are observed.

Figure 2 shows the micropore volume (V_{micro}) as a function of the Zn content. For the HZ15 and HZ75 catalyst series, the micropore volume is only slightly affected by the high Zn loading, probably due to the deposition of a small amount of subnanometric $(\text{ZnO})_n$ particles (**Species IV**) in the micropores. On the other hand, for the series HZ40, V_{micro} decreases with increasing Zn content, suggesting that on this zeolite, which has internal defects, the Zn oxide species may be located in the microcavities formed by the hydroxyl nests.

The TPR study on 2.1Zn40 shows no reduction. Indeed, Biscardi and al have shown that Zn^{2+} cations in ion-exchanged 1.07Z14.5 do not reduce even at 877°C and ZnO crystals begin to reduce to Zn metal and sublime around 480°C in flowing hydrogen. [15] Moreover, the absence of metal Zn is confirmed by the fact that after 5 hours of reaction, the Zn content remains stable on all catalysts. It should be noted that a pretreatment of 2.1Zn40 under H_2 at 500°C has no impact on activity and selectivity, suggesting that the oxidation state of Zn is +2. (**Table SI.1**)

The intensities of the bridged OH-band of the three catalysts series (**Figure 3**) decrease partially, even with a Zn content in solution two to three times higher than their exchange

capacity, which is calculated assuming a Zn/Al molar ratio of 0.5 (1/2), i.e. 0.7, 1.4 and 3.4 wt. % on HZ75, HZ40 and HZ15, respectively (**Table 1**). Therefore, only a limited fraction of the proton can be substituted by Zn^{2+} cations. Most theoretical research has shown that the exchange of the cationic position corresponds to two aluminium atoms in the same four or six-membered ring in which Zn^{2+} coordinates four zeolite oxygens. [38-40] Yet the fraction of aluminum at the sites in the next-nearest position is rather limited. For the high-silica zeolite (HZ75), the consumption of bridged OH groups is limited due to the low probability of finding two Al ions in the same ring. [16] It is worth mentioning that complete substitution of proton by zinc ions even with a high-silica zeolite, can be achieved by chemical reaction with zinc vapour. [18,20]

Regardless of the Zn loading mode (wet and dry impregnation, and ion exchange), the IR spectra of OH region are similar. (**Figure SI.8**). For all three zeolites, the consumption of Si-O(H)-Al groups is concomitant with the increase of the band at 3665 cm^{-1} . This latter is not related to EFAL species since the ^{27}Al NMR spectra of 1.8Zn40 and 5.6Zn40 show only one peak centred at 50 ppm characteristic of framework aluminium (**Figure SI.5**). Some authors attribute the band at 3665 cm^{-1} on the Zn based catalyst to the cationic species ZnOH^+ (**Species I**) [41], but this latter is not stable and undergoes dehydration during calcination [15]. This band cannot be ascribed to hydroxylated zinc oxide, because the adsorption of hydrogen on $(\text{ZnO})_n$ gives an intense band at 3483 cm^{-1} [42]. The intensity of external silanols remains almost unchanged with the Zn loading, in contrast to those located in silanol nests (3470 cm^{-1}), which disappear completely. This suggests that Zn^{2+} cations are stabilized by their interaction with hydroxyl in silanol nests (**species IV**), which is consistent with the previously observed decrease in micropore volume (**Figure 2**). The incorporation of the metal into the framework of HZ40 is confirmed by UV-vis adsorption spectroscopy (**Figure SI.9**), which shows an adsorption band at about 265 nm. This was attributed by Zhang et al. to Zn in

the zeolite framework [43] (**Species IV**). An adsorption band at about 370 nm which corresponds to the band gap width of macrocrystalline ZnO (**Species VII**) [8] appears when the Zn loading exceeds 1.4 wt.%. Incorporation of Zn into the MFI framework can be done by isomorphic substitution by healing silanol nests. [44-45] The formation of **species IV** is directly related to the presence of internal defects in the zeolite crystal, therefore the incorporation of Zn into the zeolite framework is only possible in the 40 series.

TEM images (**Figure SI.10**) clearly show that some $(\text{ZnO})_n$ particles cover the external surface of the HZ40 zeolite. On the 3.6Zn40 catalyst, their size (9.1 nm, **Table 1**) is twelve times larger than the diameter of the larger void volume within the MFI framework, i.e. 0.70 nm in the channel intersections. [32] It appears that Zn cations, which do not exchange with zeolite protons, precipitates as $(\text{ZnO})_n$ species and grow on the outer surface during the solvent evaporation step. Their size therefore depends in part on the exchange capacity of the zeolite. The $(\text{ZnO})_n$ particles in 4.1Zn15 and 2.7Zn75 (**Table 1**) were measured 6.8 and 14.8 nm, respectively.

Figure 4 shows the NH_3 -TPD profiles obtained for all catalyst series. It should be noted that the shape and location of the peaks depend on the experimental conditions, i.e., heating rate or gas flow rate, making this technique rather inadequate for quantifying acid sites [46] However, under identical experimental conditions, the position of the peak provides information on the relative acid strength and the width of the peak on the strength distribution. The NH_3 -TPD profiles of acidic ZSM-5 zeolite exhibit two distinct peaks at low (L.T.P.) and high temperatures (H.T.P.), ca $215\text{ }^\circ\text{C} \pm 15$ and $460\text{ }^\circ\text{C} \pm 25$, respectively. The higher the Si/Al ratio, the higher the desorption temperature and the higher the intensity ratio between the high and low temperature peaks. The strength of the acid sites is higher on HZ15 due to the presence of EFAL species. Regardless of the Si/Al ratio, the L.T.P intensities remain

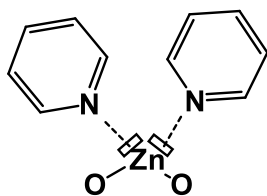
almost constant after Zn impregnation. On the other hand, H.T.P. decreases partially on HZ75, even with a high Zn loading, which excludes pore-blocking by ZnO species. [12] On HZ15 and HZ40 zeolites, the high temperature peaks disappear completely after addition of a low Zn content. The disappearance of HTP is concomitant with the appearance at ca 280 °C of shoulders to low temperature peak. Niu et al. attributed the shoulder peak to the medium acid sites of Lewis type derived from the zinc species. [13]

Pyridine adsorbed on zeolites leads to characteristic bands at 1546 and 1454 cm^{-1} which reflect pyridine protonated at Brønsted acid (BAS) and ring stretching vibration of pyridine coordinated to Lewis acid (LAS) sites, respectively. The intensity of these two bands decreases and increases concomitantly with Zn impregnation (**Table 1, Figure SI.11**). This indicates a neutralization of the protonic sites by the creation of Zn Lewis acid sites and that pyridine adsorbs in a similar way on Zn^{2+} as on Al^{3+} Lewis acid sites. [47] The concentration of pyridinium ions neutralized increases initially with the addition of Zn and then very slightly incorporation of additional metals (**Figure 5a**).

The disappearance of the bridging OH groups (Si-O(H)-Al) remains partial, (comprised, between 40 to 70%), despite impregnation of a Zn content much higher than that required for exchange capacity (**Table 1, Figure 3**). The decrease of the intensity of the bridging OH band is proportional to the decrease of the concentration of Brønsted acid sites (**Figure SI.12**). Therefore, we can evaluate the integrated molar adsorption coefficient ϵ_{OH} for IR band of the bridged Si-O(H)-Al through the ratio of the integrated intensity of this band to the concentration of BAS measured by pyridine. ϵ_{OH} for the band at 3610 cm^{-1} is 2.7 $\text{cm} \mu\text{mol}^{-1}$, which is close to that determined by Gabrienko (3.06 $\text{cm} \mu\text{mol}^{-1}$). [36]

The exchange capacity of zeolites with respect to a divalent cation depend not only on the concentration of aluminium in the zeolite framework, but also on their distribution, i.e. the fraction of Al in next nearest neighbours. In other words, during calcination, the NNN Al

exchange sites convert $[\text{ZnOH}]\text{O}_z$ (**Species I**) to Lewis acid sites (**Species II and/or III and/or IV**), while isolated Al exchange sites yield $(\text{ZnO})_n$ (**Species V and VII**) which thus regenerates the Brønsted acid sites. The concentration of the Zn-based Lewis acid sites follows the same trend as the neutralization of the Brønsted acid sites (**Figure 5b**). The ratio between the neutralized BAS and created LAS is two, regardless of the mode of Zn loading (**Figure 5c**). Moreover, this is consistent with the results obtained on Zn-based catalysts prepared by ion exchange (**Figure 5c**, [9]). Yet, it is inconsistent with the stoichiometry of exchange between two protonic sites located in the same 4-5- and 6- membered rings and one Zn^{2+} cation (2/1). The formation of the **Species II** ($\text{O}^--\text{Zn}^{2+}-\text{O}^-$) should give a $[\text{LAS}]_{\text{created}}/[\text{BAS}]_{\text{neutralized}}$ ratio of 0.5. This excludes the presence of Zn^{2+} cation stabilized by two vicinal lattice Al atoms. Assuming that the main species formed are oxo-binuclear cations: $\text{O}^--\text{Zn}^{2+}-\text{O}-\text{Zn}^{2+}-\text{O}^-$ (**Species III**) linked to NNN pairs of Al atoms, the ratio between the neutralized BAS and created LAS is 2/2. The difference between the theoretical values and measured values could simply be due to a problem of the quantification of the LAS. Indeed, the electronic configuration of the Zn^{2+} cation ($[\text{Ar}] 3d^{10}$) allows the coordination of two nitrogen-containing molecules (such as pyridine or ammonia). Berndt et al. concluded that the exchange of zinc ions generates Lewis-acidic sites, adsorbing two ammonia molecules. [48] The pyridine adsorption on Zn cation leads to the formation of bis(pyridine) ZnII complex (**Scheme 4**).



Scheme 4: Bis(pyridine)ZnII complex.

The $[\text{LAS}]_{\text{created}}/[\text{BAS}]_{\text{neutralized}}$ ratio corresponds to the measured ratio of 2 (4/2). In all the catalysts series, at least two main zinc species persist: oxo- binuclear cations ($\text{O}^--\text{Zn}^{2+}-\text{O}-$

$\text{Zn}^{2+}\text{-O}^-$) and oxide. The Zn cation can be quantified by pyridine and the amount of $(\text{ZnO})_n$ from the metal balance. However, it should be noted that on series 40, a slightly higher amount of Lewis acid sites were measured than would be expected in taking account the $[\text{LAS}]_{\text{created}}/[\text{BAS}]_{\text{neutralized}}$ of 2 (**Figure 5c**). On HZ40, some Zn^{2+} cation can be stabilized by internal silanols ($\text{Al-O-Zn}^{2+}\text{-O-Si}$). The stoichiometry here is 1/1, i.e. the neutralization of one Brønsted acid site yields one new Lewis acid site able to chemisorbed two pyridine molecules (**Species IV**). The concentration of mononuclear Zn cation stabilized by internal silanol is calculated from the difference between that of the oxo-binuclear cations drawn from the neutralization of Brønsted acid sites and that of measured LAS. It should be noted that it is more accurate to quantify the oxo-binuclear Zn cation (**Species III**) by the loss deficit of Brønsted acid sites than by the creation of Lewis acid sites (**Table 1**). The latter may underestimate their total amount due to (partially) hindered accessibility of the pyridine probe. Indeed, a distortion appears for high Zn content (> 4 wt. % (**Figure 5a and 5c**)).

The bar chart in **Figure 6** shows, for all catalyst series, the evolution of the distribution of the zinc species (**III**, **IV** and **VI-VII**) as a function of metal content. The impregnation of $\text{Zn}(\text{NO}_3)_2$, followed by a calcination, begins with the formation of an oxo-binuclear Zn cation, and in presence of internal silanols mononuclear species also appear (**Species IV**) appear. Their concentrations increase with the zinc content up to a plateau, which is reached at the zeolite exchange capacity. The maximum content on species **III** is 2.8, 1.3 and 0.4 wt. % for series 15, 40 and 75, respectively, that for species **IV** is 0.17 wt.%. The further addition of metal results in the deposition and accumulation of zinc oxide on the zeolite external surface.

3. Catalytic performances

3.1. Catalytic performances of the acidic zeolites: HZ 15, 24, 40, and 75:

The transformation of ethylene is carried out at 500 °C under atmospheric pressure with a high GHSV (13 300 h⁻¹) and diluted ethylene (0.005 MPa). **Figure 7a** shows the performance of the four protonic zeolites as a function of their concentration of Brønsted acid sites. On HZ40 and HZ75, less than 2% of ethylene is converted, which is apparently in direct contradiction with the results of many studies [Table SI.3, 9, 49-55]. Indeed, generally accepted mechanism of ethylene oligomerization on H-zeolites involves the olefin molecules protonation by BAS and further reactions through carbenium ions (conjunct polymerization, protolytic cracking). The low activity can be ascribed to the severe operating conditions that were employed. Indeed, the high temperature [5, 51], low olefin partial pressure [5, 51, 53-55] and short contact times limit the oligomerization reaction. For instance, on ZSM-5 (Si/Al = 103) at 475 °C with dilute ethylene (0.013 MPa), the conversion is only to 2% [53], whereas at 350 °C and P_{C₂H₄} of 0.1 MPa, over 83% conversion was reported. [50] The performance of HZ25 is consistent with what has been reported by Rosynek et al. also over a commercial H-ZSM-5 zeolite (PQ corporation) with the same Si/Al ratio.[50] They obtained a conversion of 40% at 520 °C with diluted ethylene (0.003 MPa) and a higher contact time. However, using a same contact time as used in this study (i.e., 0.27 s), the extrapolated is expected to be only 7.7%, which is in agreement with our results.

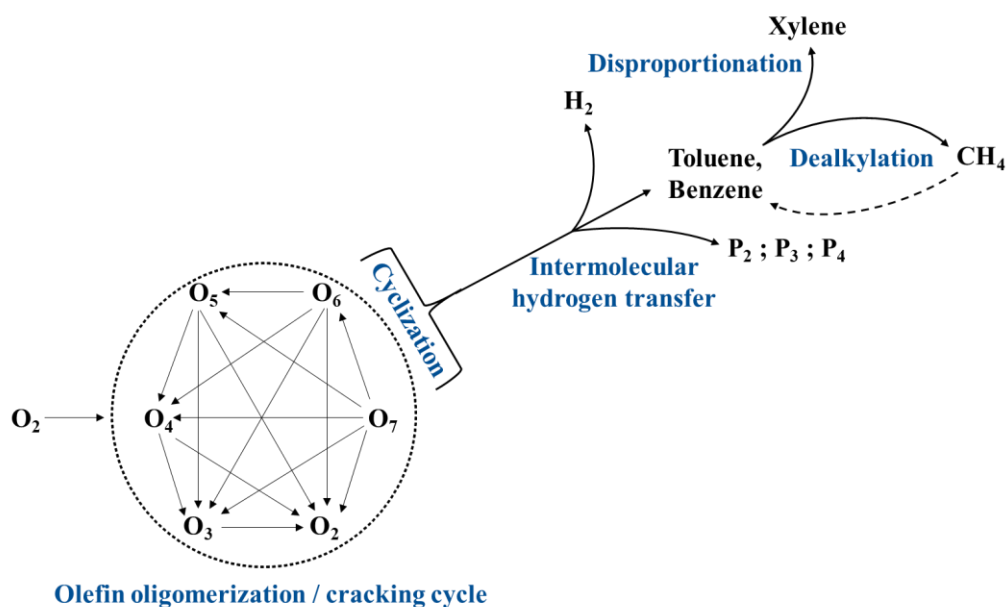
The conversion of ethylene is not proportional to the concentration of BAS, but increases exponentially as the Si/Al ratio decreases (**Figure 7a**). The increase only appears surprisingly from a large amount of BAS (~150 μmol g⁻¹). This means that the turnover frequency of protonic sites changes with the Si/Al ratio. The activity enhancement, in particular on HZ15, could be due to an exaltation of the strength of acid sites by the extraframework aluminum species (**Figure 4**), and/or be related to a higher local concentration of reactant that is adsorbed on EFAL species with Lewis acidity. [56] But, all studied samples demonstrate the presence of FTIR signature at 3665 cm⁻¹ from EFAL (**Figure 1** and **Figure 3**), but the

catalysts performance is different. HZ25 contains more Lewis sites than HZ15 (**Table 1**), but its activity in oligomerization reaction is lower (**Figure 7a**). Note, the BAS concentration is higher for HZ15 and its activity is higher too. Thus, the possible involvement of EFAL species in the reaction seems unlikely.

The results show that the intrinsic activity of protonic acid sites is not only determined by their strength but also by their density or rather on the concentration of next nearest neighbours pairs of Al atoms. The bimolecularity of ethylene transformation (dimerization) suggests that two protonic acid sites are implied in this catalysis. As the conversion is less than 1% on HZ75 despite the large quantity of BAS, the activity of the isolated protonic acid sites in the transformation of ethylene is almost negligible. Thus, the conversion of ethylene has been plotted as a function of the concentration of NNN pairs of Al atoms calculated from the Price simulation [16]: $[PyH^+] \times \text{fraction of NNN Al}$. (**Figure 7a**). Catalyst activity is proportional to the square of the concentration of NNN protonic sites. This proportionality was found in various bimolecular reaction over zeolite catalysts: bimolecular butane isomerization [57], alkane cracking through the carbenium ion chain mechanism [58], toluene disproportionation [59], etc.

On HZ15, the ethylene conversion is proportional to the contact time (**Figure 7b**) even at high conversion, indicating a pseudo-zero order reaction with a kinetic constant of $1.1 \cdot 10^6 \text{ mol h}^{-1}$. As a result, only a small fraction of reactant are in contact with active site in which they are able to react, and this fraction is continually replenished.

Figure 8 compares the initial molar yields of H_2 , CH_4 , paraffins (P_2 - P_4), olefins (O_3 - O_4) and aromatics (BTX) as a function of the ethylene conversion. **Scheme 3** presents a reaction scheme based on products selectivity obtained on HZ15 catalyst.



Scheme 5: Reactions of ethylene on H-ZSM-5 zeolite.

Propylene is the main product and *iso* and *n*-butene, are "apparent" primary products. Linear and branched hexene and pentene are also produced, but in low yields (<1%). These olefins are obtained by an oligomerization-cracking mechanism (**Scheme 5**) which appears instantaneously due to the higher reactivity of the sole primary product (i.e. *n*-butene) than for the reactant.

Methane, benzene and toluene, appear simultaneously as secondary products from a conversion of 7% (extrapolated value), indicating that dealkylation of toluene occurs at 500 °C. CH₄ could also be produced by α -scission of olefins. Yet, such monomolecular cracking, which requires very strong acid sites [59], is expected to lead concomitantly to the formation of methane and olefins, and hence CH₄ should appear as an apparent primary product. As this is not the case, CH₄ is mainly produced by dealkylation of toluene (**Scheme 5**).

Xylenes are ternary products appearing at ca 50% conversion, probably produced by the toluene disproportionation. This bimolecular reaction, which is catalysed by strong Brønsted acid sites associated with extra-framework aluminium species, requires a relatively high partial pressure of toluene. [60-61] It is noteworthy, that no particular para-selectivity is observed, despite of the use of the ZSM-5 zeolite. The concomitant formation of aromatics,

hydrogen and paraffins indicates that involvement of two mechanisms: intra-molecular dehydrogenation (DH) and inter-molecular hydrogen transfer (HT) (**Scheme 5**). Selectivity to HT has been correlated with the fraction of pair Al sites estimated by a statistical calculation [48], and is favoured by a high density acid sites. The dehydrogenation of cycloalkanes leads to a molar ratio of H_2 to aromatics of 3: $C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$, and the intermolecular hydrogen transfer with olefins to a molar ratio of paraffins to aromatics of 3: $C_6H_{12} + C_3H_6 \rightleftharpoons C_6H_6 + 3C_3H_{12}$. The proportion of the two mechanisms (molar ratio of paraffins to hydrogen) depends on the yield into aromatics due to the molecularity of the hydrogen transfer; HT and HD occur in the same proportion for a low BTX yield (3.4%), passing from 2.4 to double the yield.

Recently, Uslamin et al. are proposed, based on isotope labelling experiments, that mechanism of ethylene conversion on H-ZSM-5 shares similarities with the dual-cycle hydrocarbon pool mechanisms.[5] They shown that the intermediate species retained can contribute to the activation of ethylene *via* their alkylation, but in our case the data are analysed after only 10 min. of reaction and the quantity of coke retained is extremely low, below the detection limit (0.5wt%).

3.2. Catalytic performances of the bifunctional catalysts: series 15, 40 and 75

ZnO, HZ40 and HZ75 are inactive at 500 °C in the transformation of dilute ethylene. However, the wet impregnation of zinc on zeolite results in an increase of the conversion (**Figure 9a**). This suggests that under severe operating conditions of low ethylene partial pressure, high temperature and high GHSV, the oxo-binuclear Zn cation species are active at least in the dimerization of ethylene. Conversion increases with Zn content, despite the loss of BAS concentration (**Figure 9b**), until a plateau is reached that depends on the acidity of the protonic zeolite (**Figure 9a**). The higher the Si/Al, the lower the maximum conversion. But for the HZ15 zeolite, already active in the transformation of ethylene, the zinc deposit causes

a significant decrease in conversion, then increases with the Zn content until it reaches a plateau.

The gain in activity does not correlate with the concentration of Brønsted acid sites, but with that of the oxo-binuclear Zn species (**Species III**). A low content of Zn is sufficient to switch from the acid-catalyzed mechanism to the metal-catalyzed pathway. The conversion on series 15 and 75 is proportional to the concentration of **species II** and follows the same slope (**Figure 9c**). However, the conversion in series 40 is higher, meaning that the mononuclear Zn cations stabilized by the internal silanol (**Species IV**) are also active in the transformation of ethylene.

2.1Zn40 catalyst appears to be less active in the transformation of ethylene than HZ15 zeolite, for which the active site are the pair of Brønsted acid sites (**Figure 7c**). Hence, the initial decline in activity of HZ15 after the addition of Zn is consistent with the neutralization of the very active pair aluminium atoms. In addition, the apparent kinetic order is different on the two catalysts (**Figure 7b**). Indeed, on 2.1Zn40 the plot of $\ln(1-X)$ as a function of contact time gives a straight line through the origin, indicating a pseudo first-order reaction with a kinetic constant of $5.7 \times 10^3 \text{ h}^{-1}$ (**Figure SI.14**).

Regardless of the method used for Zn loading, its presence completely changes the selectivity of acid catalyst. C_4H_8 clearly is a primary product, while CH_4 , C_3H_6 , H_2 and aromatics composed of benzene (B), toluene (T) and also xylene (X) and ethylbenzene (EB), are secondary products. These products could be considered practically as primary products (**Figure 8**) because they are produced simultaneously from a very low conversion, ca 2% (extrapolated value).

.Hydrogen resulting from the dehydrogenation of naphthenes or olefinic naphthenes is also consumed at high conversion through the hydrogenation of olefins into light alkanes (mainly ethylene into ethane). The hydrogenating activity of Zn-based catalysts was studied

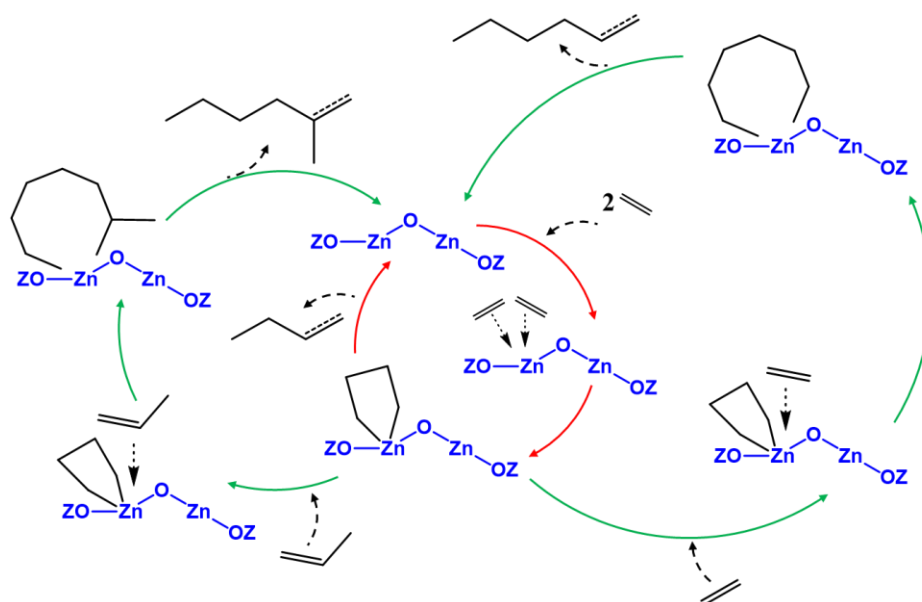
by conducting experiments with an equimolar mixture of C_2H_4/H_2 (5.3 kPa/5.3 kPa) on catalysts having the species: i) **II** and **III** (0.8 Zn₄₀ and 2.0 Zn₁₅) and ii) **II**, **III**, **VI** and **VII** (2.1 Zn₄₀ and 8.1 Zn₁₅). (**Figure 6**). All catalysts are active in ethylene hydrogenation, suggesting that the hydrogenating activity of ZnO is significantly lower than this of Zn cation. Higher metallic/Lewis acid site sites results to higher hydrogenation rates (**Figure SI. 13**), which is consistent with Mehdad et al. [25]. Functional density theory has shown that recombinant hydrogen desorption is easier on the Zn site stabilized by two framework Al atoms (species **II**) than on oxygen-bridged zinc sites (**species III**) [40], suggesting different hydrogenating activity on these two sites

The presence of hydrogen in the feed gas causes both an increase of the ethane yield and a decrease in aromatics formation (**Figure SI.13**). The hydrogenation of ethylene has a direct impact on aromatics yield, which is limited or even decreased when a large portion of ethylene is hydrogenated. The lower the partial pressure of the olefins, the lower the aromatics yield. Therefore, hydrogen should be removed from the reactor, which might be achieved through the use of catalytic membrane, in order to improve the performance of the dilute dry gas aromatization process. Toluene (T) and benzene (B) are the main aromatics products and are formed in the same proportions regardless of the conversion, contrary to what is observed with acid catalysts (**Figure 8**). The benzene formation is not the result of the dealkylation of toluene, as the very “strong” acid sites necessary for this reaction have disappeared after zinc impregnation (**Figure 4**). A T/B molar ratio of one has already been obtained by Biscardi et al. in the conversion of propane on Zn/H-ZSM-5 at 500 °C. [28] The authors assume that benzene and toluene are formed from a common pool of alkene intermediates [27] and the T/B molar ratios was an accurate measure of the average size of the alkenes in this pool. However, the toluene/benzene molar ratios are different on the acid catalysts than on the bifunctional catalysts. This would imply that the oligomerization-

cracking acid mechanism is influenced by the presence of the Zn-LAS, or that the olefins oligomerization occurred more rapidly on the metal cation. A further argument for the oligomerization of olefins over Zn cations, is the concomitant formation of aromatics at 6, 7 and 8 carbon atoms (A₆-A₈). The neutralization of the strongest acid sites by the Zn cation combined with a low partial pressure of toluene (especially at low conversion) is a strong argument that xylene do not result from the disproportionation of toluene. Xylenes are likely to be produced by the isomerization of ethylbenzene (EB), which requires weaker acid sites than the disproportionation [60-61], and is therefore rapid at 500 °C. Consequently, the yield into EB is low (~0.4 mol. %). Styrene, present in lower amount, appears at a higher conversion (**10%, Figure 8**), and is produced by dehydrogenation of the ethyl group. There are two potential pathways for the formation of EB, either by alkylation of benzene with ethyl carbenium ions (unfavourable at high temperature), or by a cyclization-dehydrogenation of octane/octadiene. The latter route suggests a new mode of olefin formation, different from the conventional oligomerization-cracking mechanism. The greater the length of the carbon chain, the higher the sensitivity to cracking by β -scission. The high reactivity of octene to cracking does not therefore make it possible to obtain a relatively high yield into A₈ (**Figure 8**) by conventional bifunctional catalysis (oligo-cracking-cyclization on acid sites and dehydrogenation on metal sites). As proposed by Lobo et al., Zn in the form of Lewis acid sites can oligomerize ethylene successively *via* the Cossee-Arman mechanism. [25] This mechanism involves an intermediate coordination complex that contains both the growing oligomer chain and ethylene. These ligands combine within the coordination sphere of the metal to form a polymer chain which is elongated by two carbon atoms (**Scheme SI.1**). Ethylene is also most likely oligomerized *by* a metallacyclic mechanism such as on a Philips polymerization catalyst (Cr/SiO₂). [63] Indeed, two molecules of ethylene are able to coordinate to the vacant coordination sphere of the Zn active site and form a zinco-

cyclopentane ring (**Scheme 6**). Two routes are possible, either via β -H transfer and release of but-1-ene, or through the coordination and insertion of another ethylene (or propylene which results from the hydrogenolysis of n-butene) to form a zinco-cycloheptane (or -cyclooctane) ring. Steric constraints lead to desorption of C_6H_{12} as well as, the regeneration of active site. A highly reactive olefin molecule diffuses to the BAS to cycle into naphthenes which dehydrogenate into aromatic molecules on a cationic Zn site.

The hydrogenation rate increases with the partial pressure of hydrogen, and seems to be favoured by the presence of the monomolecular Zn-LAS species. Hydrogenation could also be due the presence of nanoclusters of ZnO as proposed by Mehdad et al. [25]



Scheme 6: Metallacyclic mechanism for ethylene di and trimerization.

Figure 10 shows the molar yields of all products as a function of the content of oxo-binuclear Zn cation ($O^-Zn^{2+}-O-Zn^{2+}-O^-$, **Species III**). The formations of methane, ethane and hydrogen occur at a lower conversion on the series 40, while the yields of olefins (O_3 - O_4) and aromatics (BTX, EB, S) are similar on all three catalyst series. Consequently, selectivity depends on the nature of the Zn Lewis acid site. The mononuclear Zn cations stabilized by the internal silanol (**species IV**) catalyse only hydrogenolysis and hydrogenation reactions and the

oxobinuclear Zn cations catalyze the dimerization of ethylene. The higher activity on the series 40 is only due to the presence of hydrogenolysis and hydrogenation reactions.

Conclusion

The aromatization mechanism of light alkanes on Zn/H-MFI is accepted by the scientific community as bifunctional, which is initiated on the Zn species by dehydrogenation reaction of the alkanes (rate limiting-step), followed by oligomerization-cyclization of the desorbed olefin on acid sites, and terminated on the Zn species by dehydrogenation of the naphthenes. This bifunctional mechanism seems possible using propane/propene, as secondary intermediate carbenium ion are involved. However, as far as ethylene is concerned, the corresponding carbenium ions are primary and therefore the classical bifunctional mechanism becomes unlikely, especially under harsh operating conditions. The intrinsic activity of protonic acid sites in ethylene transformation depends on their density or rather on the concentration of next nearest neighbours pairs of Al atoms. The isolated Al atoms can be considered almost inactive in the dimerisation of ethylene. Butenes are rapidly converted on Brønsted acid pairs sites, resulting in a well-balanced oligomerization-cracking pool. Aromatics are obtained through a hydrogen transfer with olefins, or by dehydrogenation of cycloalkanes made possible by the EFAL species.

A small amount of Zn Lewis acid sites is sufficient to completely alter the kinetic and selectivity. The particular selectivity with the formation of styrene, ethylbenzene and toluene and benzene with a molar ratio of 1, indicates that the transformation of ethylene takes place by a new mechanism. The dimerization occurs *via* a metallacyclic mechanism by the formation of cyclobutyl-zinc intermediate and the growth of the carbon chain occurs, through the opening of cyclo-organozinc species. The desorbed products are olefins which cyclize easily into naphthenes on Brønsted acid sites. But this dual sites can also absorb hydrogen, leading to hydrogenolysis and mainly hydrogenation reactions. Therefore, the management of

hydrogen production appears to be a crucial issue for the development of the process of the aromatization of dilute ethylene using Zn/H-ZSM-5 catalysts.

This structure-reactivity study allowed to identify the active sites responsible of the formation of observed products. Spectroscopic studies should be carried out to support the mechanism proposal and further studies also should focus on the optimisation of catalytic site and the understanding of the deactivation mechanism(s).

Acknowledgment

The authors gratefully acknowledge IFPEN for the financial support. The authors acknowledge financial support from the European Union (ERDF) and "Région Nouvelle Aquitaine". Aurelien Bonnin thanks "Ministère de l'enseignement supérieur, de la recherche et de l'innovation" for Ph.D. grant.

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Table and figure Captions

- Table 1: Zn content and concentration of Brønsted and Lewis acid sites on the three catalyst series.
- Figure 1: IR spectra of (a) OH region and (b) pyridine coordinated to Lewis acid sites on the protonic zeolites with molar Si/Al ratio of 15, 25, 40, and 75. In the presented spectra, the adsorbance was normalized to sample wafer density (g cm^{-2}).
- Figure 2: Micropore volume as a function of zinc content on catalyst series 15 (\square), 40 (Δ) and 75 (\circ). (Full and open symbols = HZ and Zn based catalysts, respectively).
- Figure 3: FT-IR spectra of OH region as a function of zinc content on catalyst series 15, 40 and 75 (dashed line = HZ catalysts). In the presented spectra, the adsorbance was normalized to sample wafer density (g cm^{-2}).
- Figure 4: NH_3 -TPD profiles as a function of zinc content on catalyst series 15, 40 and 75 (dashed line = HZ zeolites).
- Figure 5: Concentrations of neutralized Brønsted acid sites (a) and formed Lewis acid sites (b) as a function of Zn content. (c) Stoichiometry of the transformation of BAS into LAS by Zn impregnation. (blue symbol: $.8\text{Zn}40^{\text{IE}}$ green symbol : $0.8\text{Zn}40^{\text{DI}}$, and full symbol data from [8]).
- Figure 6: Bar chart of the molar distribution of the Zn species on catalyst series 15, 40 and 75.

- Figure 7: Light olefins conversion on protonic zeolites:
 (a) Ethylene conversion as a function of concentration of BAS (black symbol) and pair of BAS (red symbol).
 (b) Ethylene conversion as a function of contact time on HZ15 (blue symbol) and 2.1Zn40 (red symbol).
- Figure 8: Molar yields of H₂, CH₄, paraffins: C₂-C₄ olefins: O₃-O₄ and aromatics: BTX, EB and styrene as a function of the conversion.
- Figure 9: Ethylene conversion as a function of impregnated zinc content (a), concentration of Brønsted acid sites (b) and content of oxo-binuclear Zn cation. (Operating condition: 500 °C, P= 1 atm, τ = 0.27 s).
- Figure 10: Molar yields of the products of ethylene transformation as a function of the content of oxo-binuclear Zn cation.

Supporting Information

- Table SI.1: Properties of commercial zeolites HZSM-5: 15, 25, 40 and 75.
- Table SI.2: Impact of pretreatment on conversion and products selectivity obtained at 500 °C on 2.1Zn40.
- Table SI.3: Operating conditions used in the open literature for ethene oligomerization on HZSM-5 catalyst.
- Figure SI.1: Probability of NNN pairs of Al atoms able to stabilize a divalent cation, and to form an oxo-binuclear cation drawn from stochastic simulation of Rice et al. [14].
- Figure SI. 2: Integrated adsorbance determined for pyridine adsorption on MFI (Si/Al =27) and α -Al₂O₃.
- Figure SI.3: Nitrogen sorption at -196 °C of the protonic zeolites with molar Si/Al ratio of 15, 25, 40, and 75.
- Figure SI.4: TEM images of commercial zeolites.
- Figure SI.5: ²⁷Al NMR spectrum of HZ40, 2.1Zn15 and 5.6Zn15 catalysts.
- Figure SI.6: FT-IR spectra of OH region HZ15 zeolite before (full line) and after (dashed line) pyridine adsorption at 150 °C.
- Figure SI.7: XRD spectra of HZ40 (green), 2.1Zn40 (blue) and 3.6Zn40 (black).

788 Figure SI.8: FT-IR spectra of OH region of Zn based catalysts prepared by wet (WI) and
 789 dry impregnation (DI) and ion exchange (IE). In the presented spectra, the
 790 adsorbance was normalized to sample wafer density (g cm^{-2}).

791 Figure SI. 9: UV-visible DRS spectra of catalysts series 40.

792 Figure SI. 10: TEM images of bifunctional catalysts with a lower and higher metal content
 793 than the Zn exchange capacity.

794 Figure SI. 11: FT-IR spectra of pyridine adsorption on 15, 40 and 75 catalyst series. In the
 795 presented spectra, the adsorbance was normalized to sample wafer density (g
 796 cm^{-2}).

797 Figure SI.12: Integrated intensity of Si-O(H)-Al band vs the concentration of Brønsted acid
 798 sites probed by pyridine at 150 °C.

799 Figure SI.13: Molar yields into (a) ethane and (b) aromatics as a function of the conversion,
 800 and (c) molar yield into ethane as a function of the content of oxo-binuclear Zn
 801 cation with (in red) and without (in black) of hydrogen (5 vol. %) in the feed
 802 gas.

803 Figure SI.14: Test for the first-order rate equation: $-\ln(1 - X_A) = k\tau$ on 2.1Zn40.

804 Scheme SI.1: Reaction scheme of the ethylene transformation at 500 °C on bifunctional Zn-
 805 HZSM-5 catalyst through a Cossee-Arlman mechanism.

Table 1: Zn content and concentration of Brønsted and Lewis acid sites on the three catalyst series.

Series	Catalyst ^a wt. %	Zn/Al ^a mol/mol	[PyH ⁺] ^b μmol g ⁻¹	[PyL] ^c	ZnO ^d nm
15	HZ15	-	515 (1041)	44	0.0
	0.7Zn15	0.3	364	346	
	2.0Zn15	0.3	201	671	
	3.4Zn15	0.5	144	792	
	4.1Zn15	0.6	121	688	
	8.1Zn15	1.2	84	655	6.8
40	HZ25	-	307 (640)	54	0.0
	HZ40	-	286 (386)	28	
	0.5Zn40	0.2	229	176	
	0.8Zn40	0.3	217	253	
	0.8Zn40 ^{IE}	0.2	198	189	
	0.8Zn40 ^{DI}	0.3	175	212	
	1.4Zn40	0.5	199	329	
	2.1Zn40	0.7	163	367	
	3.6Zn40	1.3	77	399	
	5.6Zn40	1.8	100	443	
75	HZ75	-	148 (219)	21	0.0
	0.3Zn75	0.2	111	67	
	0.7Zn75	0.4	92	98	
	2.7Zn75	1.6	84	102	14.8

^a = Zn content measured by ICP analysis, ^{b,c} = concentrations of Brønsted and Lewis acid sites probed by thermodesorption of pyridine at 150 °C.

^d = measured on MET images. In bracket theoretical acidity calculated from Al content.

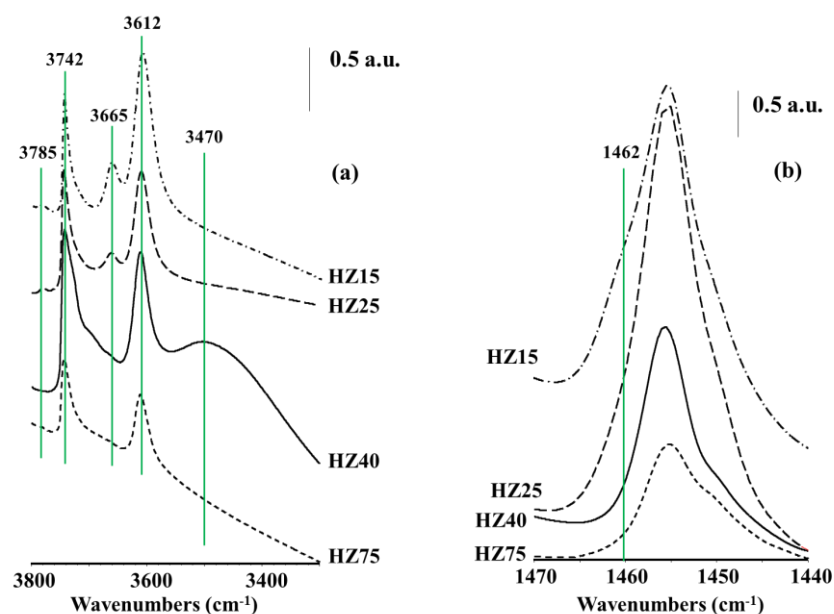


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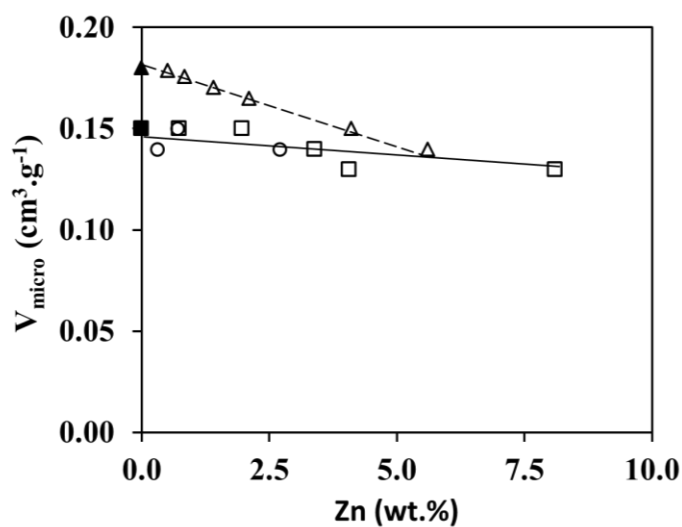


Figure 2: Microporous volume as a function of zinc content on 15 (\square), 40 (Δ) and 75 (\circ) catalyst series. (Full and open symbols = HZ and Zn based catalysts, respectively).

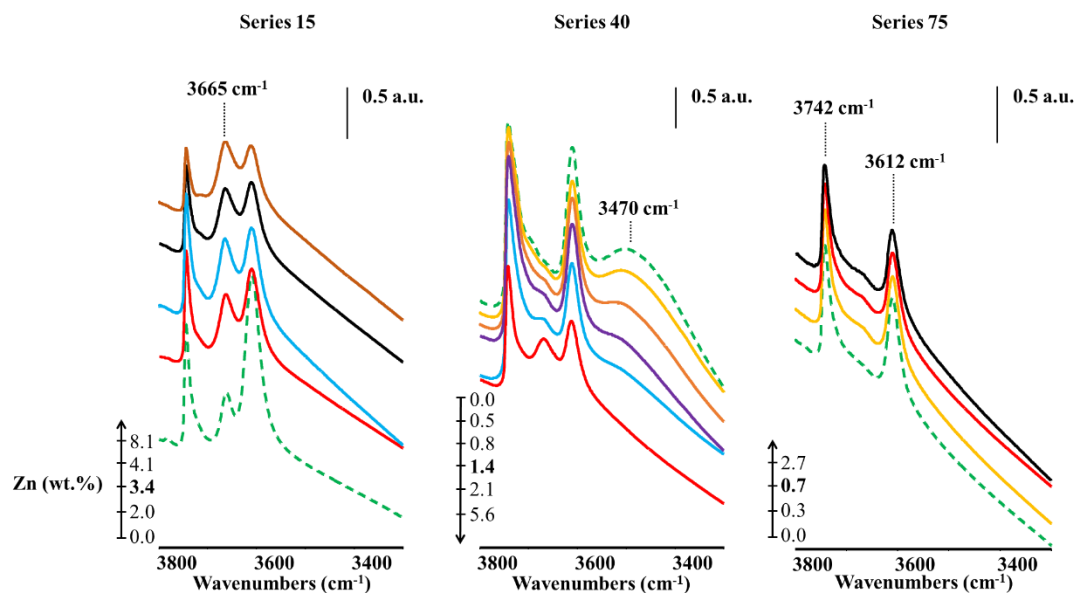


Figure 3: IR spectra of OH region as a function of zinc content on 15, 40 and 75 catalyst series (dashed line = HZ catalysts). In the presented spectra, the adsorbance was normalized to sample wafer density (g cm^{-2}).

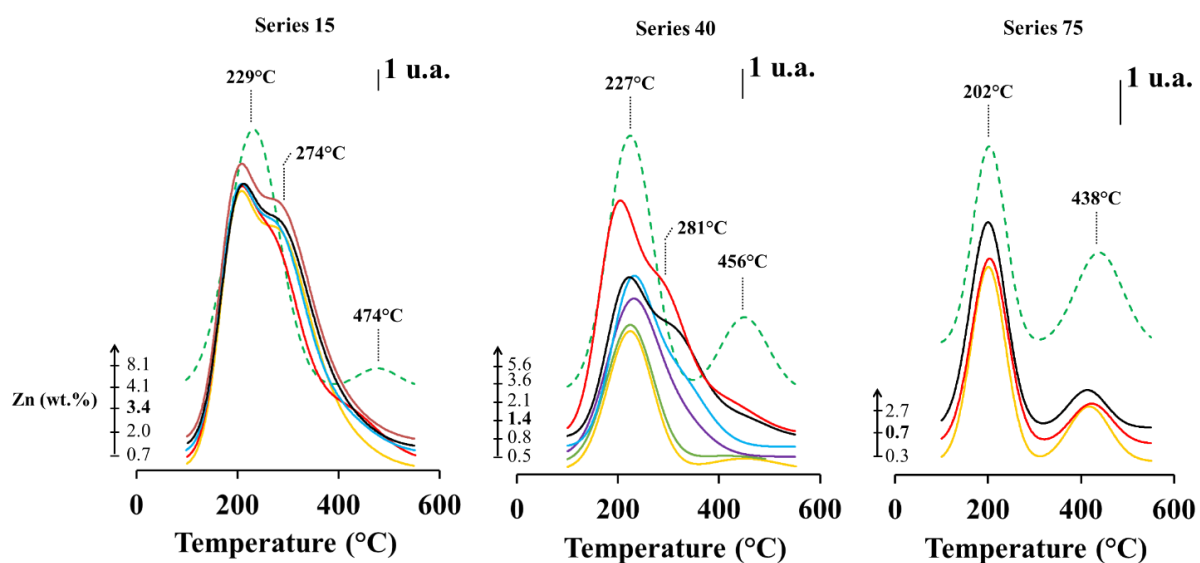


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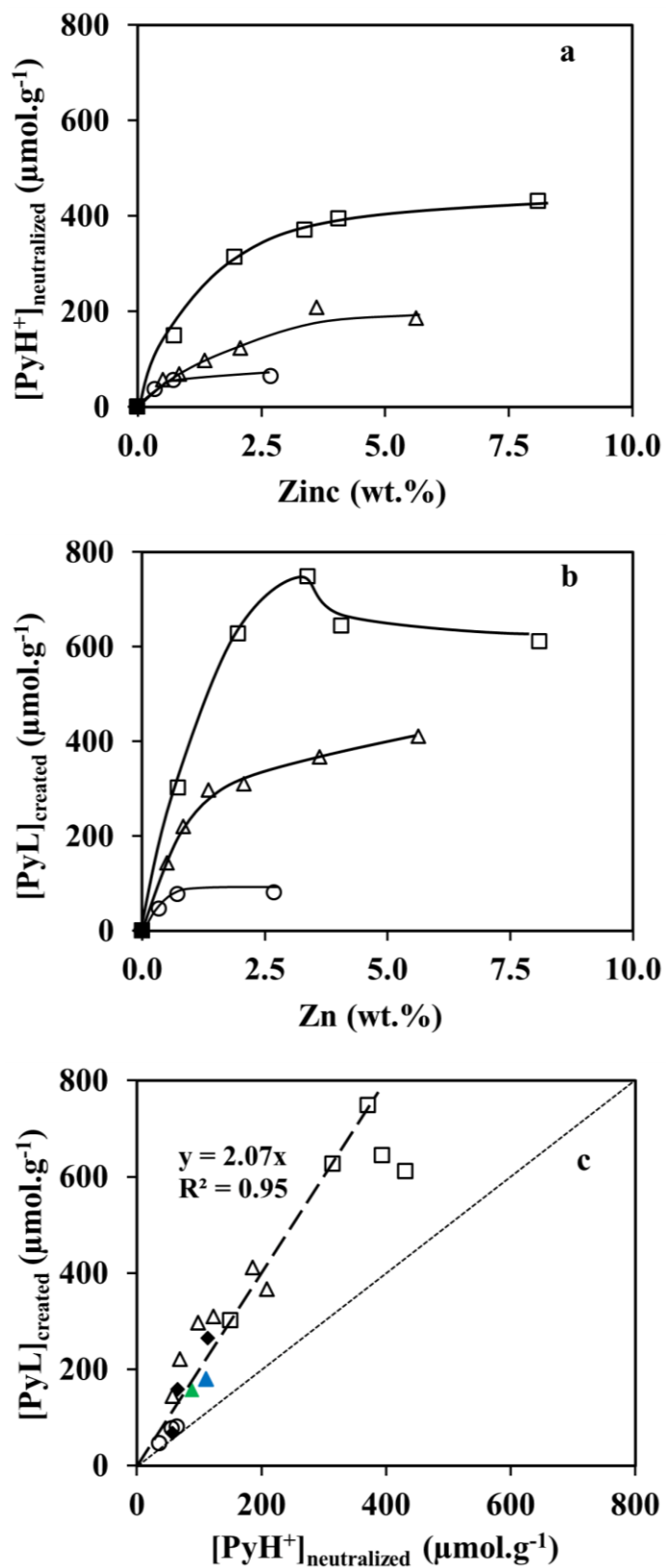


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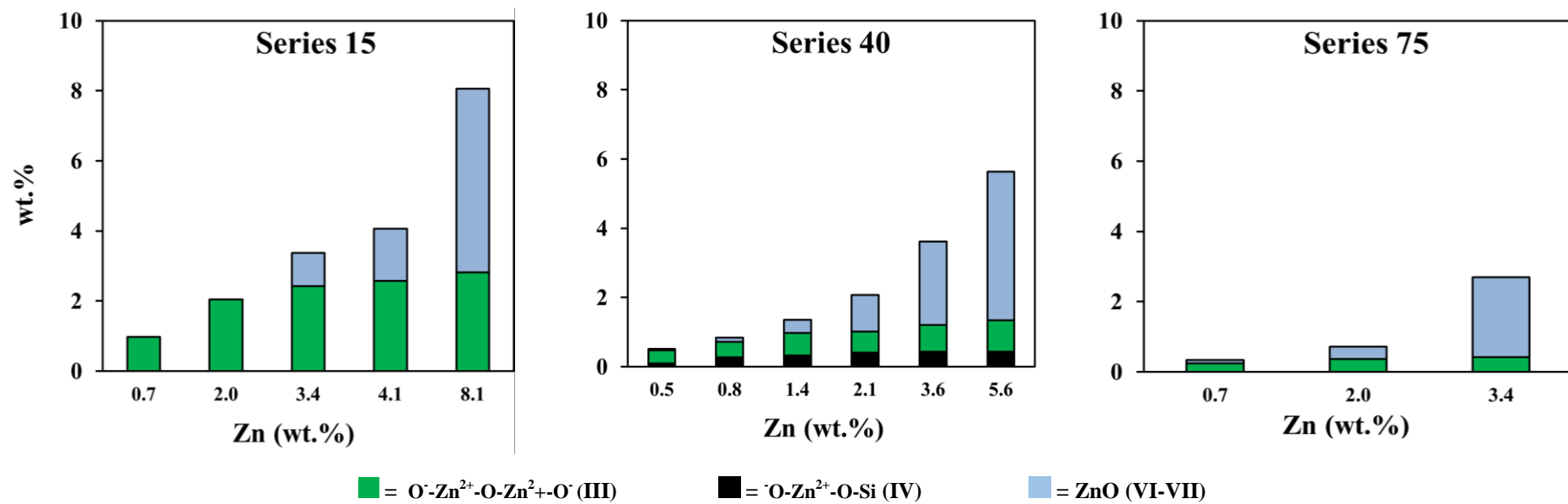


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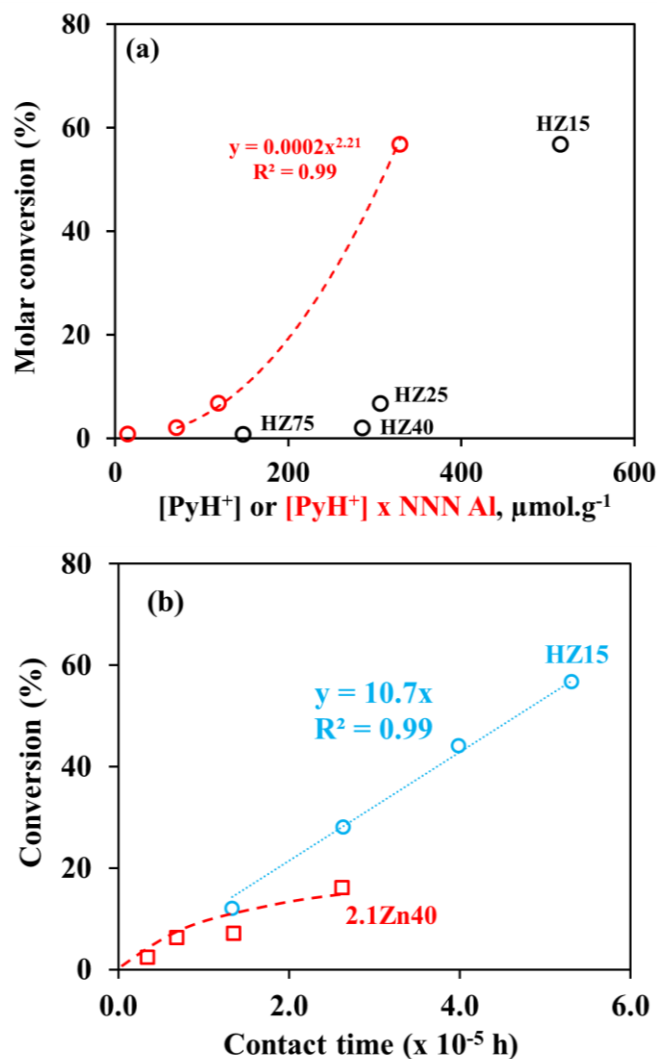
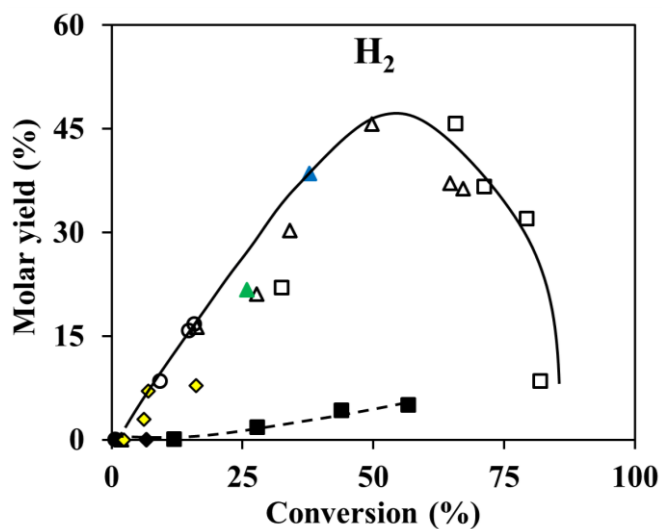
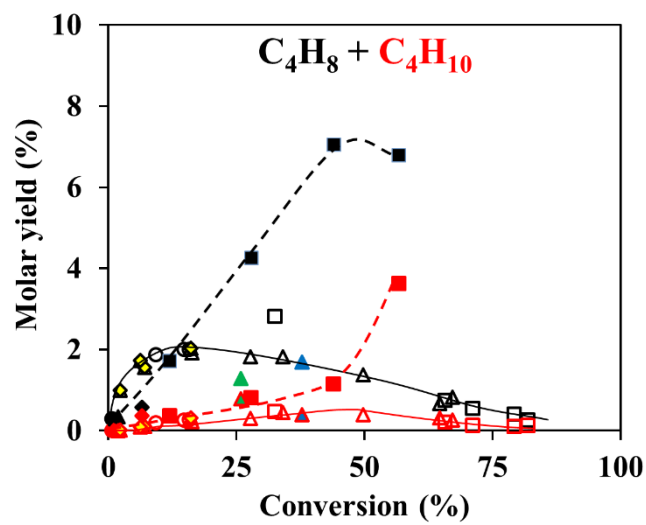
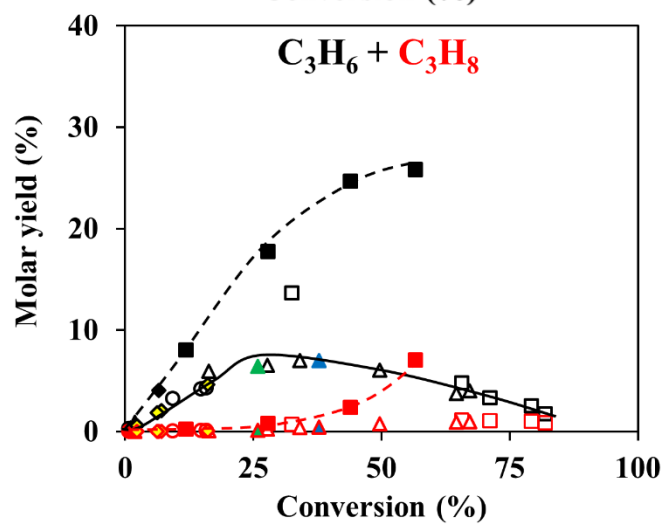
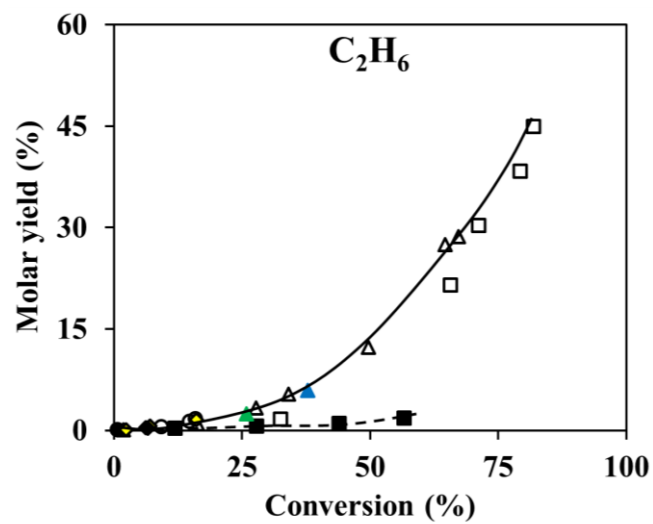
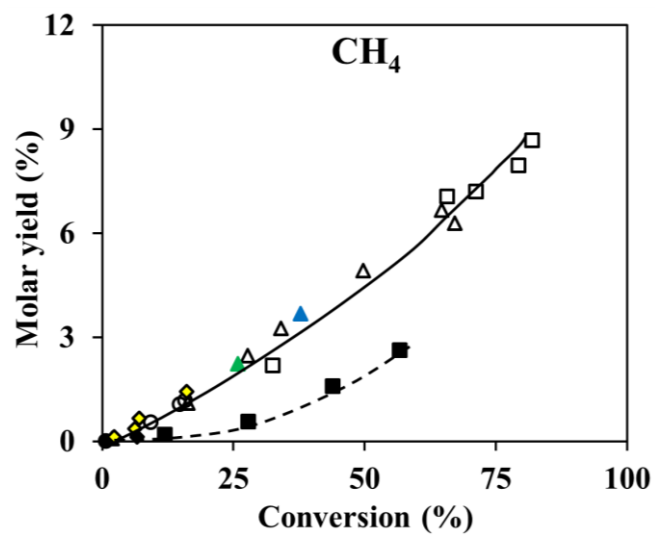


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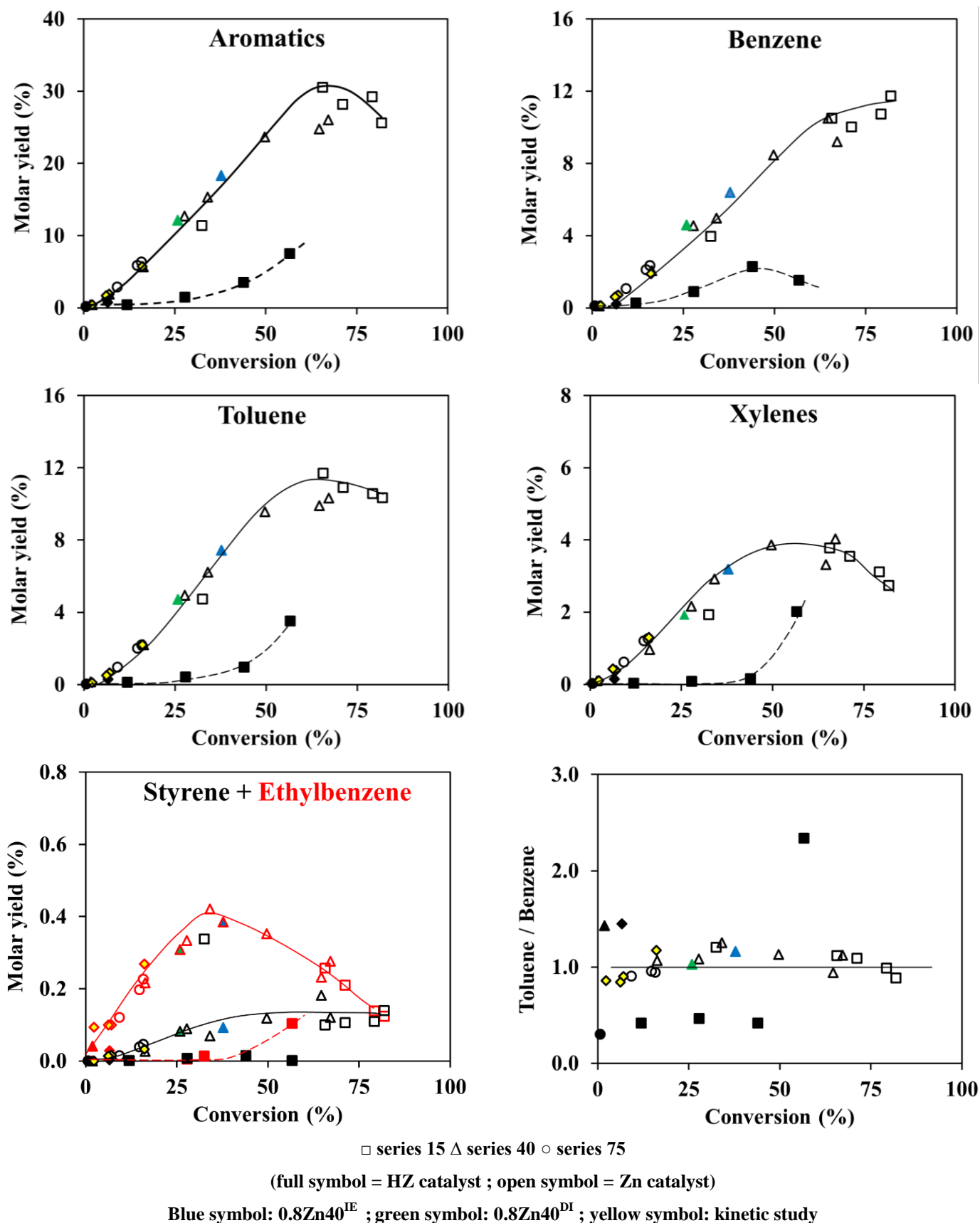


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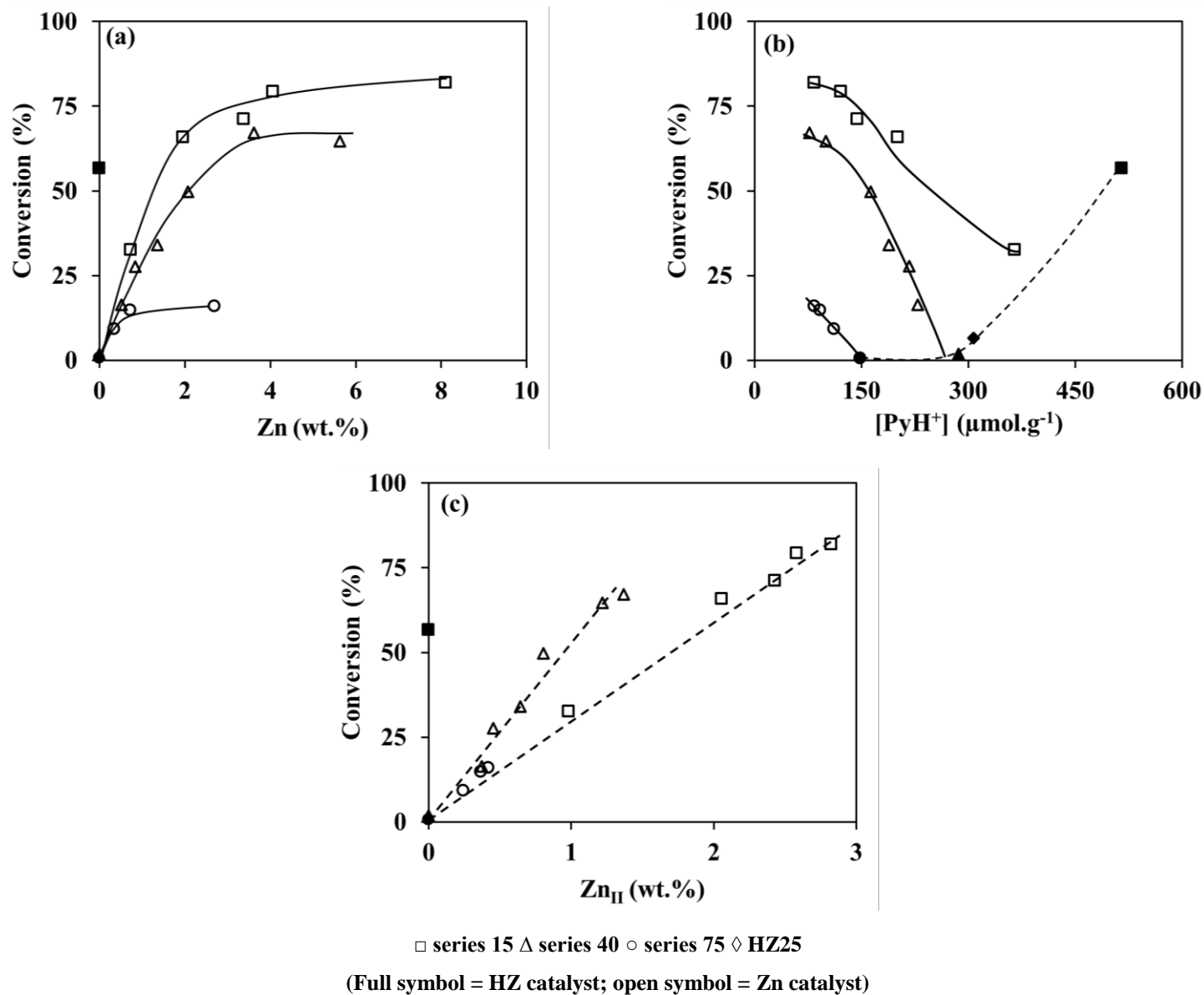
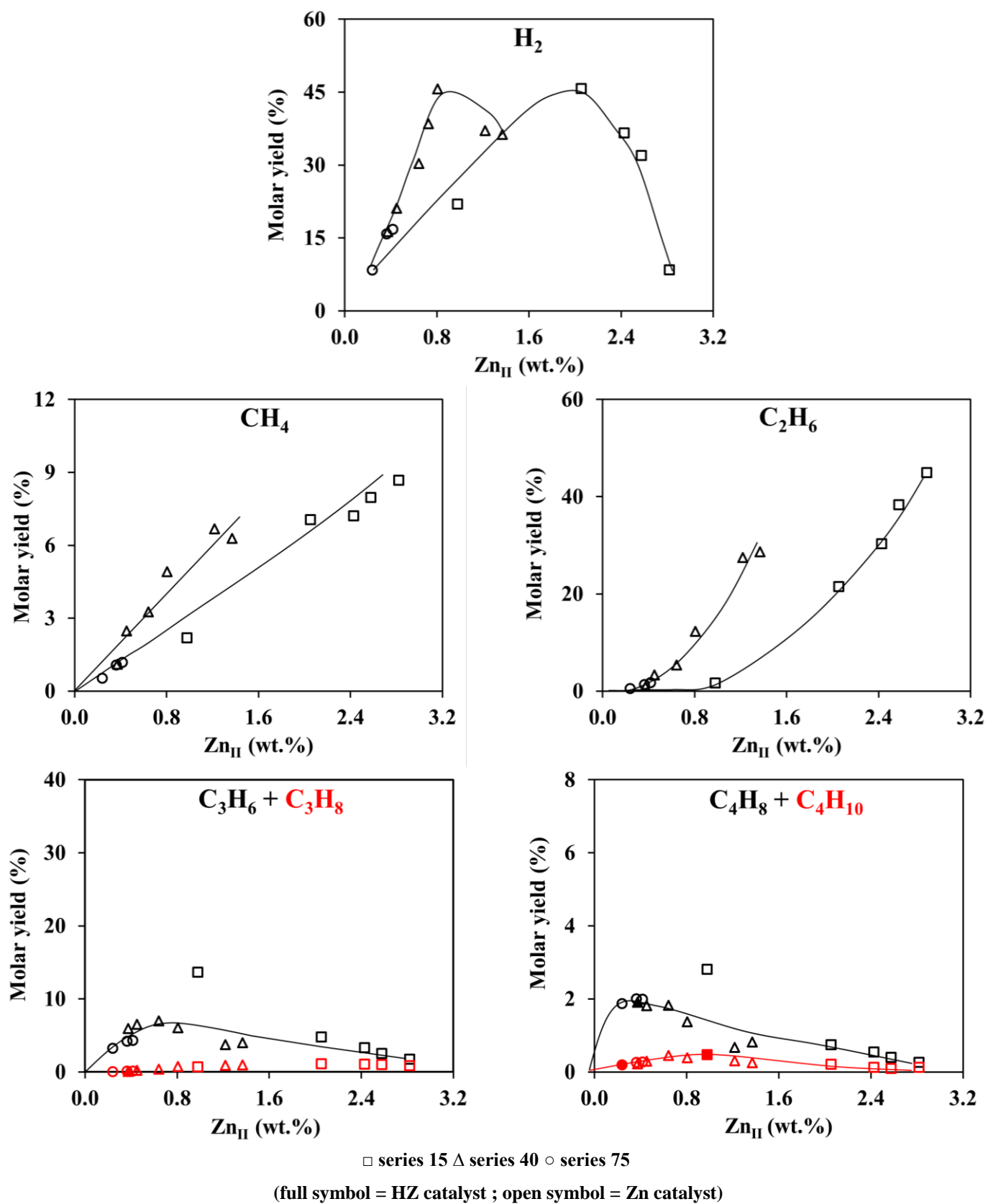


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(Operating condition: 500 °C, P= 1 atm, τ = 0.27 s)



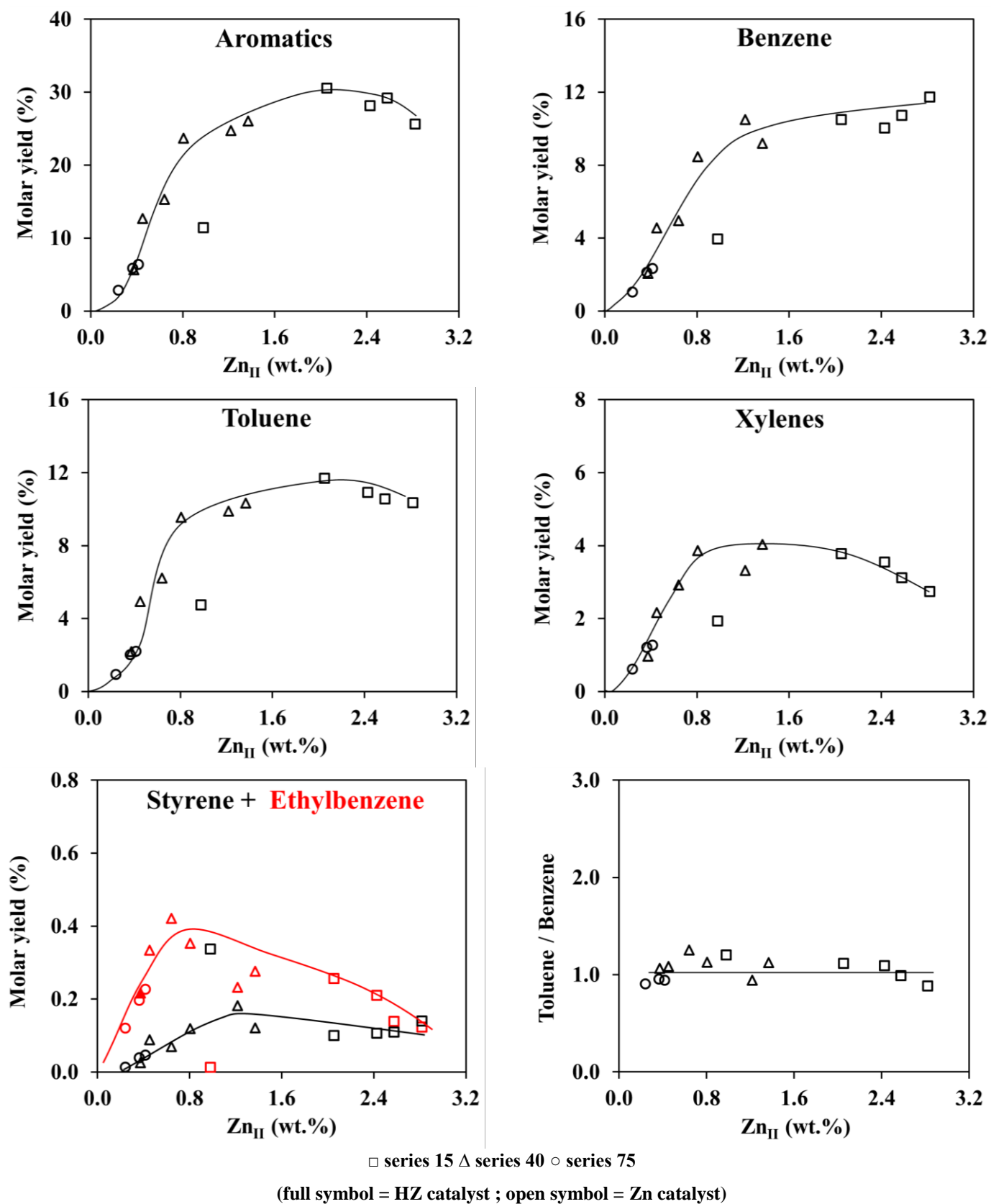


Figure 10: Molar yields of the products of ethylene transformation as a function of the content of oxo-binuclear Zn cation.

