Effect of zeolite acidity and mesoporosity on the activity of Fischer–Tropsch Fe/ZSM-5 bifunctional catalysts

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The effect of acidic properties and mesoporosity created by desilication on ZSM-5 zeolites was investigated to evaluate changes in product selectivity during Fischer–Tropsch synthesis (FTS) over Fe-based bifunctional catalysts. The reaction was studied at 300 °C, 10 bar, and H2:CO = 2:1, using a physical mixture of the iron-based FTS catalyst and zeolites with different Si/Al ratio. Hierarchical zeolites with micro- and mesoporosity were prepared by alkaline treatment. Higher acidity (lower Si/Al ratio) in the pristine zeolite was found to be responsible for cracking of heavy hydrocarbons and the formation of heavier aromatic products, while higher Si/Al ratio induced a higher selectivity towards gasoline-range products (isoparaffins and olefins). The presence of mesopores prompted a variable behavior depending on the final acidity of the resulting Fe-based hierarchical catalyst; zeolites that retained acidity led to a slight increase in C2-C4 paraffins due to overcracking of heavy molecules as a result of enhanced transport to the acidic sites through the mesopores. The products obtained with the Na+–containing alkali-treated zeolites with no acidity were similar to those obtained with the iron FTS catalyst alone, with most of the products in the paraffin range. Rather than improving the activity and selectivity to gasoline products, the better accessibility in the hierarchically-based Fe/ZSM-5 catalysts coupled to the preserved acidity of the zeolite induced the formation of aromatics and a higher amount of small paraffins (<C₄). This reinforces the idea of optimizing the catalyst towards a desired FTS hydrocarbon range through the control of its mesoporosity and acidity. Iron-based ZSM-5 catalysts with high Si/Al ratios and irrespective of the presence of mesoporosity shift the product distribution towards the formation of isoparaffins and lighter aromatics.

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1. Introduction

Fischer–Tropsch Synthesis (FTS) is a heterogeneously catalyzed polymerization reaction for the transformation of synthesis gas (CO + H₂, or syngas) into valuable hydrocarbons (gasoline, diesel, chemicals, etc.), which is suitable for the production of synthetic fuels from renewable sources of primary energy [1–3], such as biomass. This reaction produces a wide variety of products, from gases to heavy waxes. Since the discovery of the FTS process, one of the main prospects has been the improvement of activity and selectivity towards the desired products through catalyst optimization. Although cobalt, iron, nickel, and ruthenium exhibit functionality as FTS catalysts, only the first two are used for industrial applications [4]. Cobalt exhibits high selectivity to long chain paraffins and a higher resistance to deactivation than iron, the latter favoring the formation of olefins, aromatics and oxygenated compounds. Besides, iron catalysts work over a wide range of operational conditions and are generally active for water gas shift reaction (WGS) (CO + H₂O ⇌ CO₂ + H₂). This reaction produces hydrogen, and makes iron-based catalysts valuable when processing syngas with low H₂:CO ratios, such as those coming from biomass gasification [5,6].

One of the main drawbacks of FTS is the wide range of products obtained following the Anderson–Schulz–Flory (ASF) distribution [7,8]. This depends on a chain growth probability factor (α), which limits the maximum amount of a given product that can be obtained. Since temperature, pressure, feed gas composition, type of catalyst and composition, presence of promoters, and type of reactor are factors affecting the α value [9], designing adequate strategies to obtain a successful catalyst that maximizes a specific range of products (e.g. gasoline or diesel-range production) is challenging.
A common approach, which has been studied recently to drive the products towards hydrocarbons in the gasoline or diesel ranges, has been to use multifunctional catalysts [10–12]. These materials contain different types of active sites (acidic, metallic, etc.) with complementary functionalities. In the case of FTS, the use of acidic co-catalysts has been a sound choice since it narrows the distribution of products into the gasoline/diesel range by combining reactions of hydrocracking, olefin oligomerization, alkylation, branching and aromatization [13]. Many examples of this approach are available in recent literature, dealing with the use of a FTS metal catalyst combined with zeolites [3,14–18]. A common outcome of these studies has been to establish the importance of zeolite porosity and acidity in the performance of such multifunctional catalysts. The Brønsted acidity of the zeolite, due to the presence of Al in its structure, promotes secondary reactions, and therefore the formation of lighter hydrocarbons, both aromatic and branched [19]. Concerning pore structure, it may restrict the chain-growth process thus yielding lighter products, depending on the type of zeolite. Bessell found that cobalt supported on zeolite Y, mordenite and ZSM-5 gave active FTS catalysts, and that the acidity of the support determined the nature of the higher hydrocarbons being produced; the most acidic ZSM-5 supported catalyst produced branched products, while the mordenite channel system was responsible for linear-products [20]. The same author found that product selectivity was governed by the accessibility to the acidic sites within the pore structure rather than the overall acid strength when Co was supported in ZSM-5, ZSM-11, ZSM-12 or ZSM-34 [21]. Botes and Böhringer discovered that a catalyst containing iron and a highly acidic ZSM-5 zeolite (Si/Al ratio of 15) had a higher activity and selectivity towards aromatics and light paraffins, but a faster deactivation than a lower acidity zeolite (Si/Al ratio of 140) [22]. Martínez and López reassessed these findings using a FeCoK catalyst physically mixed with ZSM-5 [23].

Both aspects, pore structure and acidity, seem to be intimately related in FTS. However, the presence of micropores in zeolites often imposes strong diffusion limitations since it restricts the access to the active sites, and therefore it may limit the activity, selectivity and useful lifetime of the catalyst [24]. To overcome this issue, several studies on the effects of mesoporosity generation have been recently published for FTS catalysts based on cobalt/zeolite systems [25–28]. The use of these hierarchical zeolites produced an increase in CO conversion and selectivity towards \( \text{C}_5 - \text{C}_{11} \) compared to the untreated zeolites, due to the optimized hydrocracking and isomerization reactions occurring inside the newly-formed mesopores.

In this work we have investigated the effect of zeolite acidity and mesoporosity development in bifunctional Fe/ZSM-5-based catalysts. Mesopore formation was accomplished by the well-reported desilication method [29]. Since this treatment is prone to alter acidic properties in the zeolite, changes in product selectivity were systematically evaluated over non-acidic hierarchical Fe/ZSM-5 catalysts. To check effects specific for the zeolite, a comparison with a blank experiment containing no zeolite was also performed. A detailed study of the composition of liquid products has been fulfilled with the use of comprehensive two-dimensional gas chromatography mass spectroscopy (GCxGC/MS) [30].

2. Experimental

2.1. Synthesis of the catalytic materials

FTS catalysts were prepared by coprecipitation at constant pH. Aqueous solutions of the metal nitrates (Fe(NO\(_3\))\(_2\)·3H\(_2\)O, Cu(NO\(_3\))\(_2\)·3H\(_2\)O, Mg(NO\(_3\))\(_2\)·6H\(_2\)O, Ca(NO\(_3\))\(_2\)·4H\(_2\)O, KNO\(_3\), 1M of each) and the precipitating agent (Na\(_2\)CO\(_3\), 4 wt.% were simultaneously fed into a polypropylene vessel with a 905 Titrand automated titrator (Metrohm AG) equipped with two 800 Dosino\(^{\circ}\) dosing systems. The pH during precipitation in the stirred reactor vessel was maintained at a constant value of 8 (±0.2). After the addition of the appropriate ratio of reactants, the slurry was aged at 60 °C for 1 h under vigorous stirring. The precipitate obtained was filtered and washed thoroughly with deionized water, and dried overnight at 80 °C to yield the catalyst precursor (Fe-P). This sample was calcined in static air at 300 °C for 4 h using a heating rate of 5 °C/min (labeled as Fe). The addition of copper was intended to facilitate the reduction of iron oxides [31], while potassium enhances the surface basicity and the production of olefins [32]. The addition of magnesium increases the BET surface area of the catalyst, and leads to the formation of relatively smaller \( \alpha\text{-Fe}_2\text{O}_3 \) crystallites in the catalysts, facilitating the reduction and carburization [33].

Fe-zeolite bifunctional catalysts were prepared by physically mixing the Fe oxide with the same amount of a commercially ZSM-5 zeolite: Z40 (CBV 8014, Zeolyst International) and Z240 (Sud Chemie AG). Prior to any treatment, the as-received powders were calcined in static air at 550 °C for 6 h at 5 °C/min. Zeolites were subjected to alkaline treatments to create mesoporosity, following the procedure reported elsewhere [34]. Briefly, a 0.2 M NaOH aqueous solution was stirred at 500 rpm and heated at 65 °C, after which the zeolite was added (3.3 g of zeolite per 100 mL of alkaline solution), and maintained for 30 min. Afterwards, the zeolite suspension was cooled down in an ice-water mixture, and centrifuged. The resulting solid was washed with distilled water until pH neutral and dried at 100 °C. The solids were separated into two portions. The first ones were directly calcined in static air following the program described for the commercial zeolites, while the second portions were brought into the ammonium form via three successive exchanges in 0.1 M NH\(_4\)NO\(_3\) aqueous solution (1 g of zeolite per 100 mL of solution) and calcined in static air. All bifunctional catalysts were ground in the 100–300 μm particle size. Along the manuscript, the alkali-treated samples are generally identified by the code Zx-AT and Zx-AT-H, where x refers to the Si/Al ratio according to the manufacturer, AT refers to the alkali-treated zeolites, and H identifies the alkali-treated samples subjected to ultrior Na\(^+\) exchange.

2.2. Characterization techniques

The chemical composition of the materials and the alkaline content of the zeolites was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in a Spectro Arcos 165 spectrophotometer. Before analysis, the iron sample was dissolved in a 1% solution of HNO\(_3\). Zeolite samples were digested in 50 mL of 1% H\(_2\)SO\(_4\) and 1% H\(_2\)O\(_2\) mixture in a Berghof microwave. X-ray diffraction analysis was acquired by a Siemens EM-10110BU D5000 diffractometer. The angular 2θ diffraction range was between 5 and 70 °C for the iron-based catalyst 5 and 40 °C for zeolite samples, respectively. Data were collected with an angular step of 0.05° at 3 s per step. Cu-Kα radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. N\(_2\) adsorption was performed at –196 °C in a Quantachrome Quadrasorb-Si gas-adsorption analyzer. Before measurement, the iron precursor and calcined iron/zeolite samples were outgassed at 100 °C and 300 °C for 10 h, respectively. The BET method [35] was applied to calculate the total surface area. The t-plot method [36] was used to discriminate between micro- and mesoporosity. The mesopore size distribution was obtained by the BJH model [37] applied to the adsorption branch of the isotherm. The samples were also analyzed by transmission electron microscopy (TEM), which was performed in a JEOL JEM-1011 transmission electron microscope operated at 100 kV with point-to-point resolution of 0.2 nm. A
few droplets of sample suspended in ethanol were deposited on carbon-coated copper grids followed by evaporation at ambient conditions. Fourier transform infrared spectroscopy was carried out at 200 °C in a Vertex 7 spectrometer from Bruker using a diffuse reflectance (DRIFTS) accessory equipped with a Praying Mantis™ high-temperature reaction chamber (Harrick), ZnSe windows, and a MCT detector. The sample holder was filled with powdered zeolite samples (~3 mg) mixed with KBr, and carefully leveled off to reduce reflections of the sample surface and to ensure reproducible results. The sample was pretreated in N2 (5 Nml/min) at 400 °C for 60 min, using a heating ramp of 10 °C/min. Spectra were recorded in the range 1800–4000 cm⁻¹ by co-addition of 64 scans and a nominal resolution of 4 cm⁻¹.

2.3. Catalytic performance

The activity and selectivity of the catalysts were tested in a fully automated laboratory-scale fixed-bed catalytic reactor (Microactivity Reference, PID Eng&Tech, Spain). Experiments were conducted using 1.0 g of Fe catalyst and 1.0 g of zeolite, sieved to 100–300 μm, and mixed with 500 mg of quartz chips sieved to the same particle size. A blank experiment was also performed by mixing the Fe base catalyst (1 g) with quartz chips (1.5 g) as reference. The catalysts were loaded into the reactor tube and heated at 10 °C/min to 300 °C under N2 (20 Nml/min), and reduced with syngas (H2/CO molar ratio = 2) at the same temperature and 10 bar, while starting to monitor product formation. The reaction was prolonged for 48 h at constant temperature and pressure, using a weight hourly space velocity (WHSV) of 0.1 mol CO/fe-cat h, which is equivalent to a gas hourly space velocity (GHSV) of 2264 m³/feed/(m²/bed h). These parameters were calculated according to the weight of Fe catalyst for the WHSV, and the volume of bifunctional catalyst with the quartz chips for the GHSV. The reactor effluent passed through a cold trap kept at 2 °C and 10 bar to collect all liquid products (and waxes if present). The composition of the gaseous products (permanent gases and light hydrocarbons) was determined with an online gas micro-chromatograph equipped with a TCD detector (490 microGC, Agilent Technologies). The sensitivity of the detector to each analyzed compound (response factor) was determined periodically by their calibration against standards of certified gas mixtures using N2 as internal standard. Liquid products collected at low temperature were analyzed in a two-dimensional GC×GC system coupled to a mass spectrometer (Agilent 7890A), equipped with a flame ionization detector (FID) and mass spectrometry (MSD 5975C) using a differential flow modulator. The system consisted in two columns, a 30 m non-polar column (DB-5MS) and a 5 m polar column (HP-INNOWAX), giving rise to the orthogonal two-dimensional separation. The modulator isolates the eluent of the first column into a large number of adjacent small fractions, which are re-injected into the second column, resulting in a fast separation on this column (1.5 s). Detector signals were monitored with Agilent Chemstation software (Agilent). Data were converted with the GC-Image software (Zoex) for data processing.

CO conversion (X), product selectivity (Sj,k) and carbon balance (CB) were calculated according to Eqs. (1) to (3), where FCO,0 and FCO are the inlet and outlet molar flow rates of CO, FCO2 is the molar flow rate of CO2 produced, Fj,k is the molar flow rate of a product with j the number of carbons (1 ≤ j ≤ 22), and k denotes the type of product (aromatic, olefin or paraffin). Therefore, the selectivity definition in Eq. (2) refers only to hydrocarbon products and does not include carbon dioxide, unless stated otherwise.

\[ X = \frac{F_{CO,0} - F_{CO}}{F_{CO,0}} \]  
\[ S_{j,k} = \frac{j \cdot F_{j,k}}{F_{CO,0} - F_{CO} - F_{CO2}} \]  
\[ CB = \frac{F_{CO2} + \sum_{k=1}^{3} \sum_{j=1}^{22} (j \cdot F_{j,k})}{F_{CO,0} - F_{CO}} \] 

3. Results and discussion

3.1. Catalyst characterization

The molar Fe/Cu and Fe/Mg ratios of the as-prepared catalyst, determined by ICP-OES, were 16.7 and 0.82, which practically matched the nominal ratios of 20 and 0.67, respectively. Concerning commercial zeolites, their bulk molar Si/Al ratio was 38.9 for Z40 and 224 for Z240. Concerning the content of alkaline metals, sodium was the sole metal detected. The amount of Na⁺ in the non-treated catalysts (Z40 and Z240) and in the alkali-exchanged zeolites (Z40-AT-H and Z240-AT-H) was below the detection limit. In the case of sodic zeolites, Z40-AT and Z424-AT exhibited a 2.75% wt. and 1.11% wt. of Na⁺, respectively. These results indicate that sodium remained in the alkali-treated catalysts, and was removed successfully upon exchange with NH₄NO₃ followed by calcination. Fig. 1 shows the XRD patterns of the coprecipitated material (Fe-P), and its product after calcination. The as-prepared sample displayed...
a low-crystallinity pattern ascribed to the presence of pyroaurite (86-0181 ICDD pattern). The solid calcined at 300 °C showed characteristic reflections of the magnetite Fe3O4 structure (75-1609 ICDD pattern). No diffraction lines associated with any other iron oxide were detected. The characteristic X-ray diffraction pattern of the MFI structure was also confirmed in all commercial ZSM-5 samples, evidencing the typical high crystallinity of this structure, regardless of their Si/Al molar ratio. Alkali-treated zeolites without (Zx-AT) or with subsequent ion exchange (Zx-AT-H) retained their crystalline structure, although gave less intense signals in the diffractogram. This change is due to the silicon extraction process occurring during alkaline treatment [24].

The main physico-chemical properties of both the Fe-based catalyst and the treated zeolites are summarized in Table 1. The N2 adsorption isotherms at –196 °C of the Fe catalyst and its precursor in Fig. 2 exhibits a type IV isotherm with H3 hysteresis, which are characteristic of mesoporous materials with slit-shaped pores between aggregates of particles with fiber-like morphology. The BET surface area (ca. 150 m²/g) and pore volume (0.3 ml/g) of the iron catalyst and its precursor were very similar, indicating that the calcination step did not exert any important effect on the porosity of the derived oxide.

The N2 isotherms of the commercial zeolites exhibited the IUPAC type I behavior with a high uptake at low relative pressure, confirming their microporous character (Fig. 2). Both commercial zeolite samples showed typical BET surface areas (370–460 m²/g) irrespective of the Si/Al ratio. The micropore volume (Vmicro) (0.15–0.17 ml/g) was also characteristic of the MFI framework. The mesopore surface area (Smeso) (55–75 m²/g) responded to the crystal external surface, surface roughness of the crystals and the intercrystalline porosity derived from the aggregation of nanocrystals of less than 1 μm. The absence of a pronounced hysteresis loop in the adsorption-desorption isotherm indicates that the high values of Smeso should be ascribed to external surface area rather than to intracrystalline mesoporosity.

The two commercial zeolites were subjected to alkaline treatment in 0.2 M NaOH at 65 °C for 30 min (Zx-AT in Table 1), which are the optimal conditions for MFI zeolites [36]. The N2 isotherms of Z40-AT and Z40-AT-H were similar, and characteristic of hierarchical porous zeolites combining micro- and mesoporosity. They displayed an enhanced uptake at intermediate and high pressures (0.4–0.8) with H3 hysteresis. The largely parallel progression of the adsorption and desorption branches of the hysteresis loops, and the absence of a forced closure of the desorption branch at p/p0 = 0.45, give indication of the presence of accessible mesopores connected to the outer surface. The N2 isotherms of Z240-AT and Z240-AT-H showed adsorption at relative pressures above 0.7, indicating the formation of larger pores. The degree of silicon extraction and mesoporosity development were lower in Z240-AT compared to Z40-AT, as expected for the higher framework Si/Al ratio [38]. Indeed, the mesopore surface area in Z240-AT-H was twice that of its parent sample (129 m²/g vs 57 m²/g). The increase of mesopore surface area was from 73 m²/g in Z40 to 282 m²/g in Z40-AT-H. In parallel, the total pore volume of the treated materials increased at the expense of a reduction in the micropore volume. Alkali-treated materials with final ion exchange (samples Z40-AT, and Z240-AT) displayed intermediate Smeso and Vmicro values, probably due to some degree of blockage by Na cations inside the porous structures. The development of the mesoporosity was also confirmed by the BJH adsorption pore size distributions (Fig. 2, right), showing the formation of mesopores centered around 20 nm in Z40-AT, and 10 nm in Z40-AT-H. The blockage by Na+ ions in the pore channels of the alkaline-treated sample is responsible for the shift in PSD to higher values (pores centered at 20 nm). A much broader pore size distribution was found on Z240-AT and Z240-AT-H, in agreement with the lower degree of mesoporosity attained over the Z240 sample. This broadening is likely consequence of the formation of larger pores (>20 nm), which because of the diminishing surface to volume ratio at larger diameters make pore volume to grow faster than pore surface. Desilication of the zeolite to a Si/Al ratio of 25–50 has been considered to be the optimal range for silicon extraction while preserving acidity [38]. Excessive Si dissolution occurs in Z40-AT leading to larger pores, as evidenced in this sample and its corresponding ion-exchanged zeolite (Z240-AT-H). As expected, the desilication produced by NaOH treatment led to a decreased Si/Al ratio from 39 to 24 in Z40 and from 22 to 66 in Z240. The original crystallinity of the zeolites was not altered based on X-ray diffraction (Fig. 1, right).

Transmission electron microscopy (TEM) in Fig. 3 shows the presence of perforated crystals in Z40-AT and Z40-AT-H compared to the dense appearance of the microporous Z40 sample (with crystal sizes of 100–500 nm). A similar behavior was observed in the Z240-AT and Z240-AT-H samples, together with a more damaged structure than in Z40, which exhibited well-defined crystals with sizes in the range 150–200 nm.

Infrared spectroscopy in the OH-stretching region was carried out at 200 °C after treating the samples at 400 °C in N2, to qualitatively evaluate the acidity of the calcined and alkali-treated zeolites. As shown in Fig. 4, the zeolite samples show characteristic absorption bands at 3740 cm⁻¹, 3660 cm⁻¹, and 3600 cm⁻¹, assigned to terminal silanol groups (Si-OH) on the external surface, hydroxyl groups connected to extra-framework Al species (EFAL, Lewis acidity), and bridging hydroxyl groups associated with Brønsted acidity, respectively [39,40]. A priori, it is expected that the number of Brønsted sites increases with increasing the Al content, that is, when decreasing the Si/Al ratio [23]. This correlation was verified when the Si/Al ratio increased from 40 to 240, showing a qualitative decrease in intensity of the band at 3600 cm⁻¹. This latter absorption band completely vanished after alkaline treatment in both zeolites, due to the ion exchange with Na+. The spectrum of alkali-treated samples treated by ion exchange in NH4NO3 and calcined subsequently (Z40-AT-H and Z240-AT-H) showed a recovery of their Brønsted sites, albeit with a lower intensity compared to the non-treated samples, in agreement with both the loss of micropore volume and the absence of Na+ in the ICP-OES analyses. A progressive development of isolated silanol groups (band at 3740 cm⁻¹) was visible in the same samples, due to the formation of intracrystalline mesoporosity [34]; a slight increase in the amount of Lewis acid sites was discerned in alkali-treated samples compared to non-treated zeolites.

3.2. Fischer–Tropsch performance

The iron-based catalyst was directly reduced with syngas at the beginning of each reaction test to favor the formation of iron carbide species in order to improve its activity [31]. All reactions were performed under the following conditions: 300 °C, 10 bar, H2/CO = 2, and WHSV = 0.1 molCO/gFe-cat h (GHSV of 2264 m³ feed/(m³ bed h)). Permanent gases were analyzed on line, and liquid products were
collected and quantified off line through GCxGC/MS analysis. This technique has been considered to be superior to monodimensional gas chromatography to analyze the selectivity of the catalyst since it elucidates compounds with similar boiling points but different functionality, which tend to co-elute [30]. Besides, minor compounds present in low concentrations in the Fischer–Tropsch sample matrices can be separated, detected and quantified. This technique has been very useful to determine differences between all products obtained herein. Fig. S1 in Supplementary information exemplifies a typical two-dimensional contour plot of the liquid products obtained with the FeZ240-AT bifunctional catalyst (see Section 2.3 for analysis conditions). As a general trend the products had a wide range of elution times in the polar column (Y-axis), which correspond to linear or branched paraffinic compounds at the bottom, whereas minor products located at the top are aromatics. Carbon balance and global mass balance during the Fischer–Tropsch experiments were above 95% in all the reported experiments, indicating that there were no major losses of products during the experiments and that most products were accounted for.

3.2.1. Influence of Si/Al ratio of the untreated zeolite
An initial CO conversion of about 85% was found over the base Fe catalyst, which diminished to about 75% after 48 h (Fig. 5), thus showing a moderate deactivation during this period. After the addition of the zeolites, no influence of the Si/Al ratio on CO conversion was observed. In fact, the initial CO conversion was around 90% when using the FeZ40 catalyst, with a similar decay than in the Fe base catalyst, and only 75% with FeZ240. Despite its lower initial activity, the latter catalyst exhibited a more stable behavior upon time on stream.

The results in terms of selectivity are summarized in Table 2. The CO₂ selectivity was very similar in all cases, ca. 44%, indicating that the addition of zeolite was not affecting the WGS reaction, in which iron oxides are the active sites [41]. It is important to remark that the presence of Mg during synthesis might affect the FTS per-
Fig. 3. Transmission electron micrographs of the Fe catalyst and the native and treated zeolites.

Table 2
Selectivity and olefin to paraffin ratio of the Fe catalyst alone and mixed with commercial and alkali-treated zeolites.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity</th>
<th>( \text{O/P ratio} )</th>
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<tbody>
<tr>
<td></td>
<td>CO(_2)</td>
<td>Paraffin</td>
</tr>
<tr>
<td>Fe</td>
<td>0.44</td>
<td>0.52</td>
</tr>
<tr>
<td>FeZ40</td>
<td>0.44</td>
<td>0.22</td>
</tr>
<tr>
<td>FeZ40-AT</td>
<td>0.43</td>
<td>0.51</td>
</tr>
<tr>
<td>FeZ240</td>
<td>0.43</td>
<td>0.30</td>
</tr>
<tr>
<td>FeZ240-AT</td>
<td>0.43</td>
<td>0.50</td>
</tr>
<tr>
<td>FeZ240-AT-H</td>
<td>0.42</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* Calculated according to equation \( S_{j,k} = \frac{j}{F_{j,k} F_{CO_2}} \).

The Fe base catalyst exhibited a high selectivity towards paraffins in the range C\(_1\)-C\(_{20}\) (Fig. 6), with a very low olefin-to-paraffin ratio, and practically no aromatics. Addition of the commercial zeolites led to important differences in product selectivity (Fig. 7), i.e., the selectivity to aromatics increased from 2% (in the base Fe catalyst) to ca. 30% concomitantly to decreased paraffin selectivity in FeZ40 and FeZ240. The selectivity to C\(_3\)-C\(_4\) was similar (ca. 10%) for both bifunctional catalysts, while the selectivity in the range C\(_5\)-C\(_{12}\) (typical of gasoline) increased from 53% in the

formance thus leading to low hydrocarbon selectivity. Taking into account the important amount of CO\(_2\), comparable to previous publications [31], the results in the following figures were expressed as selectivity to hydrocarbons (Eq. (2), without CO\(_2\)). Most of the paraffins quantified in Table 2 are related to branched compounds (i.e. iso-paraffins).
base Fe catalyst to 67% in FeZ240, showing a progressive increase with the Si/Al ratio. FeZ40 and FeZ240 showed practically no differences in products selectivity (40% and 47% for paraffins and 55% and 50% for aromatics, at similar CO conversion levels of ca. 80% and 75%, respectively). Although these results seem to show subtle differences between catalysts, the general differences observed can be explained in terms of Brønsted acidity offered by the zeolites with different Si/Al ratio, as zeolites with higher Al content have higher amount of Brønsted acid sites \[ \text{FeZ40, FeZ240}. \] As previously observed in Fig. 4, the amount of acidic sites in Z40 is slightly higher than in Z240, thus facilitating the formation of aromatic products, especially, towards more complex structures in the most acidic catalysts, as shown below. The highest acidity in FeZ40 is likely responsible for the slightly increased methane selectivity, as expected from the introduction of zeolite \[ \text{FeZ40}. \]

An additional aspect to be considered is the particle size, since FeZ40 comprises larger crystals than in FeZ240. Previous studies observed an increased stability and higher concentration of isoparaffins and aromatics in the gasoline fraction \[ \text{FeZ40, FeZ240}. \] when using nanocrystalline ZSM-5 (with more available acid sites) compared to larger crystal size zeolites. In our particular case, both zeolite-based catalysts exhibit different crystal size and different acidity. Therefore, it can be inferred that selectivity differences found between FeZ240 and FeZ40 are mainly related to their acidity, although a certain crystal size contribution cannot be discarded (FeZ240 exhibits smaller crystal sizes but lower acidity, while FeZ40 crystals are larger but with higher acidity).

The vast majority of aromatic products was comprised in the C\text{7–C12} range, and was composed of branched benzenes (alkylbenzenes). The increased acidity in Z40 over Z240 led to the production of heavier aromatics, even reaching molecules with 14 carbons (i.e. branched naphthalenes). The percentage of lighter aromatics (7–10 carbons) increased in the opposite sense, that is, from Z40 to Z240, less A\text{8–A10} and more A\text{11,} compounds were formed in FeZ40 compared to FeZ240. This may imply that aromatization occurs in both the external acid sites and in Brønsted acid sites located inside the micropores (with diffusion constraints), which are poisoned upon reaction favoring the formation of heavier aromatics at the external acid sites. In contrast, the less acidic character of the FeZ240 catalyst induces the slightly higher formation of A\text{8–A10} products without suffering changes in activity along the 48 h time on stream.

These results confirm not only that the zeolite acidity is responsible for cracking of heavy hydrocarbons, and the formation of aromatics by oligomerization, cyclization, and dehydrogenation of primary short olefins produced over the Fe catalyst \[ \text{FeZ40, FeZ240}. \] but also that the degree of acidity (and in less extent, the crystal size)
induces noticeable differences in the distribution of aromatic products. In agreement with previous literature [44], our results also show that this transformation is motivated by a change in the ASF distribution, which decreases the C12 selectivity. The presence of acidic sites in the zeolites promotes cracking and isomerization reactions, and also, a high degree of aromatization in Fe-based bifunctional catalysts. Also, the increment in acidic sites in FeZ40, with low Si/Al ratio, led to the formation of more complex aromatic structures (>C11+).

3.2.2. Influence of mesoporosity

Primary hydrocarbons formed on active sites of a FTS are able to migrate into the zeolite micropores, where the above-mentioned processes occur. However, the products formed must diffuse out of the micropores of the zeolite, and this may partially lead to over-cracking towards lighter hydrocarbons [45]. In order to overcome this issue, desilication treatments were performed over selected zeolites to evaluate the effect of mesoporosity generation on the performance of Fe-hierarchical zeolites. The main effect of alkaline treatment is the extraction of framework silicon leading to an interconnected network of micropores and mesopores (and extensive surface area). Without subsequent ion exchange with NH4NO3, the hierarchical zeolite remained in the sodic form, and therefore, no Brønsted sites were present. This is in agreement with the content of Na+ in the alkali-treated zeolites as established by ICP-OES analysis, which were 2.75% and 1.11% Na+ in FeZ40-AT and FeZ240-AT, respectively. As expected, the amount of sodium in the most acidic zeolite is higher than in the zeolite with higher Si/Al ratio (i.e., less acidic).

In this work, we have evaluated the effect of mesoporosity development by measuring the catalytic performance using zeolites with or without Na+ exchange. A priori, the presence of Na+ in the alkali-treated zeolites was expected to provide a similar FTS performance than with the Fe base catalyst, if only acidity is considered. However, the effects of enhancement in mesoporous surface area and presence of sodium were investigated to evaluate possible changes in product distribution when no Na+ exchange was performed.

Fig. 5 shows CO conversion vs. time on stream for the alkali-treated samples with (FeZx-AT-H) or without (FeZx-AT) subsequent ion exchange. The activity of both FeZ40-AT and FeZ240-AT was around 5–8% lower than their parent counterparts, thus suggesting that the presence of sodium is affecting the catalytic performance. The addition of Na or K to FeCu/SiO2 catalysts has been reported to improve the catalytic activity and shift the product distribution to heavy hydrocarbons [46]. A typical decrease in methane selectivity, increase in low carbon olefin selectivity and shift to higher molecular weight hydrocarbons was observed when promoting Fe/CNT with sodium or potassium [47]. In other cases, K has decreased the activity of Fe-based FTS catalysts [48]. This leads to discrepancies due to the different catalysts systems, and the type of interaction between iron and the oxide support, which might finally mask the effect of the alkali promoter. In general, Na is known to be an electronic promoter since it can modify the adsorption of reactants on the active sites. These alkali promoters enhance CO chemisorption due to the iron tendency to withdraw electronic density from the alkali metal, thus increasing the strength of the Fe–CO bond, and therefore, weakening the intramolecular CO bond. The higher basicity also leads to less of the weakly bound H2 available at the surface, thus lowering the hydrogenation activity. This induces the increment of the olefin selectivity and high molecular products coupled to the decrease in methane formation [32,49]. In our case, the activity is only slightly reduced in the sodium-containing samples, but changes in selectivity due to interaction with Na on the external zeolite surface are in agreement with previous results in the literature (see below).

On the other hand, both FeZ40-AT-H and FeZ240-AT-H displayed again an increased CO conversion, especially in the latter catalyst, which is even slightly increased along the reaction. This can be explained by the fact that the presence of mesopores favored the transport of bulky products, thus avoiding deactivation by blocking and coke formation.

Concerning product selectivity, results are shown in Fig. 7. Products with >C15 obtained with the bifunctional catalysts were found in trace amount below the quantification limit of the instrument, and were not considered. Selectivity in FeZ40-AT and FeZ240-AT was substantially and qualitatively different from that obtained over FeZ40 and FeZ240. The results are summarized in Table 2, where most of the products were paraffins, a very small increase in the amount of olefins especially in the range C3–C4, and slight methane depletion was detected over both alkali-treated materials. These results would be in agreement with the increase in olefin content and decrease in methane when using alkali promoters [32]. In fact, these results are also quite similar to those of the product distribution of the Fe catalyst alone leading mainly to paraffins (Fig. 6), with minor differences: slightly lower selectivity to methane, formation of minor amount of olefins, and absence of products above C14 in the bifunctional catalysts (at least being quantifiable). This suggests that virtually no secondary reactions (hydrocracking, oligomerization, cyclization, etc.) occurred when using the non-acidic bifunctional catalysts (FeZ40-AT and FeZ240-AT), and Na behaves as a typical electron promoter. In contraposition, the presence of mesopores limited the size of the paraffins formed up to C14. Both FeZ40-AT and FeZ240-AT, with 2.75% and 1.11% of Na+, exhibited similar product distribution (Fig. 7) at similar degree of CO conversion (ca. 72%). Therefore, the effect of mesoporosity development in alkali-treated zeolites (without Na+ exchange, which do not retain their Brønsted acidity) is affecting the catalytic performance in these bifunctional catalysts, as even without acidic sites seemed to change the ASF product distribution when compared to the Fe catalyst without zeolite (no products with more than C14 were formed). In parallel, in these catalysts, Na interacted with the external surface of the zeolite thus acting as a promoter and leading to a slight modification of the selectivity towards olefins and methane.

As expected from the recovery of Brønsted acid sites (Fig. 4), the use of the acidic zeolites, FeZ40-AT-H, and FeZ240-AT-H led to a high C5–C12 selectivity again with respect to the Na-containing catalysts, due to cracking of heavy FT products over the acid sites. In parallel, the selectivity to C13+ was practically negligible, irrespective of the presence of mesopores in the alkali-treated and ion exchanged samples. The selectivity to methane was practically not affected upon alkaline treatment of the zeolites. Compared with untreated bifunctional catalysts, both FeZ40-AT-H and FeZ240-AT-H showed a decreased selectivity to the C5–C12 fraction, concomitantly to the slight increase in the C2–C4 carbon range (Fig. 7). The amount of aromatics marginally decreased in FeZ40-AT-H at the expenses of a slight increment in C2–C4 paraffins (Table 2). These results are better summarized in Fig. 8, where products are grouped into typical cuts according to the number of carbons. Not only the acidity of this material still favored cracking and isomerization, but also the better accessibility of the mesopores induced the formation of lighter compounds. In the case of FeZ240-AT-H, the alkaline treatment followed by ion exchange seemed to produce no significant effects, as the total amount of aromatics was practically equivalent to that in FeZ240. However, less acidic bifunctional catalysts (i.e., FeZ240 and FeZ240-AT-H) were more selective towards paraffins, olefins and lighter aromatic products with respect to bifunctional catalysts with low Si/Al ratio zeolites. It is important to mention that the selectivity of FTS catalysts is strongly dependent on both conversion level and on alkaline promotion (or poisoning). However, despite performing experiments...
at fixed WHSV rather than fixed conversion, the conversion level with all catalysts moved in a relatively narrow range (80–85% for the FeZ40-derived catalysts) and (75–85% for FeZ240-derived catalysts). Therefore, selectivity differences in all catalysts can be correlated with changes in acidity and mesoporosity, and less motivated by changes in CO conversion.

These results suggest that the presence of mesoporosity and acidity of these zeolites play a key role in modifying the gasoline-range selectivity. As previously reported, alkaline treatment and subsequent NH₄NO₃ ion exchange (followed by calcination) should lead to a partial recovery of the strong Brønsted acidity [29]. Following this, the increase in mesoporosity while keeping a certain level of acidity (similar or slightly below to that of the non-treated zeolites) seemed to somewhat hinder selectivity towards C₅-C₁₂ hydrocarbons; that is, the preserved acidity promotes cracking, aromatization, etc., and the presence of mesopores helps reaching the active acid sites with less diffusional constraints.

In summary, developing mesoporosity provided a better accessibility of the acidic active sites for cracking and aromatization, although for the gasoline-range objective (C₅-C₁₂) in FTS, this effect is partially detrimental. The Brønsted acidity, which is beneficial for cracking and aromatization reactions, was valuable to enhance the C₅-C₁₂ hydrocarbon range. However, the generation of small mesopores produced a slight increase in the C₂-C₄ fractions due to overcracking of heavy molecules in the acid sites. This effect was more pronounced for lower Si/Al ratios. Herein, the best performance towards C₅-C₁₂ products was achieved using a zeolite-containing bifunctional catalyst with higher Si/Al ratio (and intrinsic lower acidity), without direct influence on the presence of mesopores.

In this direction, the typical benefits achieved by hierarchical zeolites (possessing both micro and mesoporosity and preserved acidity) in a large number of heterogeneously catalyzed reactions [50] need to be optimized for each specific application and, more particularly, to the product/s of interest when complex reactions like FTS are concerned.

4. Conclusions

The conversion of syngas to hydrocarbons was carried out by using bifunctional catalysts comprising a physical mixture of a synthesized Fe catalyst and ZSM-5 zeolites with two different Si/Al

Fig. 7. Selectivity towards paraffins, olefins and aromatics over the different Fe-based bifunctional catalysts.

Fig. 8. Selectivity towards paraffins, olefins or aromatics over the different bifunctional catalysts. In each carbon number group, left graph: FeZ40 (○), FeZ40-AT (△), FeZ40-AT-H (□); right graph: FeZ240 (○), FeZ240-AT (△), and FeZ240-AT-H (□).
ratios (different inherent acidity). Zeolites were also subjected to alkalai treatment to develop a certain degree of hierarchical porosity, that is, the presence of micro- and mesoporosity. The results confirm that the zeolite acidity is responsible for the cracking of heavy hydrocarbons, and the formation of aromatics through oligomerization, cyclization and dehydrogenation of primary short olefins. The Si/Al ratio induced changes in the aromatic product composition. The increment in acidic sites (low Si/Al ratios) induced the formation of more complex aromatic structures. A higher Si/Al ratio in the zeolite led to higher selectivity towards the gasoline-range products. The formation of mesopores in alkalai-treated zeolites exerted a variable behavior depending on the final acidity of the material; ion-exchanged zeolites, which virtually recovered the acidity of the fresh, untreated zeolites, produced a slight increase in C2-C4 paraffins due an improved access to the acidic sites through the mesopores, and consequently, the overcracking of heavy molecules. However, the best performance towards the C5-C12 range hydrocarbons was accomplished with bifunctional catalysts with higher Si/Al ratios, irrespective of the presence of improved accessibility by mesopores. It is important to remark that the high degree of aromatization with these cata-
lysts (especially with the most acidic) is critical for gasoline-range hydrocarbons, thus needing further optimization. On the opposite side, Na⁺ containing catalysts behaved similarly to the iron base FTs catalyst, with most of the products in the paraffin range, although the promotion effect of this alkalai metal was evident through the slight decrease in methane and increment in olefinicity in the low carbon range.

These results demonstrate that the enhancement of accessibility does not always lead to better performance. In particular, the bifunctional iron/zeolite-based catalyst should exhibit weak acidity to reduce consecutive cracking and thus, to improve the selectivity to C5-C12 hydrocarbons. Therefore, tuning both the acidity and mesoporosity of iron-based bifunctional catalysts is an essential aspect to guide the FTs product distribution towards a specific hydrocarbon range. Additionally, the effect of incorporating iron FTs catalysts with alternative synthesis procedures in the structure of zeolites with customized mesoporosity and the use of high-silica zeolites are interesting points for further research.

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Appendix A. Supplementary data

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References
