Tailoring ZSM-5 Zeolites for the Fast Pyrolysis of Biomass to Aromatic Hydrocarbons


The production of aromatic hydrocarbons from cellulose by zeolite-catalyzed fast pyrolysis involves a complex reaction network sensitive to the zeolite structure, crystallinity, elemental composition, porosity, and acidity. The interplay of these parameters under the reaction conditions represents a major roadblock that has hampered significant improvement in catalyst design for over a decade. Here, we studied commercial and laboratory-synthesized ZSM-5 zeolites and combined data from 10 complementary characterization techniques in an attempt to identify parameters common to high-performance catalysts. Crystallinity and framework aluminum site accessibility were found to be critical to achieve high aromatic yields. These findings enabled us to synthesize a ZSM-5 catalyst with enhanced activity, which offers the highest aromatic hydrocarbon yield reported to date.

Introduction

The fast pyrolysis of lignocellulosic biomass represents a simple, cheap, and efficient approach to produce bio-based fuels and chemicals from renewable feedstocks.[1] In this process, solid biomass is heated to a high temperature (500–700 °C) to be converted thermochemically to light gases (CO, CO₂), solid char, and organic vapors, which can be further condensed to obtain the desired liquid bio-oil.[2] The ratio between the gas, liquid, and solid fractions is particularly sensitive to the heating rate. Fast heating rates on the order of 1000 °C s⁻¹ are required to achieve bio-oil yields of 60–70%.[3] The main byproducts are CO₂, CO, and H₂O, which result from decarbonylation, decarboxylation, and dehydration. These deoxygenation reactions are desired as they increase the energy density of the liquid fraction, thus its potential as a biofuel.[4] Fast pyrolysis is also attractive because this versatile technology can accommodate a wide range of feedstocks, which includes wood, switchgrass, and agricultural waste (e.g., corn stover). However, bio-oil is a complex mixture of more than 300 oxygenated compounds, such as anhydrosugars, organic acids, aldehydes, ketones, furanics, and phenolics,[5] and its high oxygen content and chemical complexity makes it unsuitable for direct use as a biofuel. Additional processes that involve one or several heterogeneous catalysts are required to decrease the oxygen concentration from ~45% to less than 7% and achieve stable blends with petroleum that allow refining.[6] Various catalytic deoxygenation processes have been investigated and reviewed recently.[7] Integrated approaches in which the catalyst is mixed directly with the biomass are appealing as pyrolysis and deoxygenation occur simultaneously in the same reactor. Notably, catalytic fast pyrolysis (CFP) using ZSM-5 zeolite as a catalyst produces in a single step benzene, toluene, xylene, and naphthalene, which can be used as building blocks by the petrochemical industry or further converted to gasoline-range hydrocarbons using hydrogenation processes already employed in refining.[8]

The isomorphous substitution of silicon with aluminum atoms in the well-defined crystal structure of zeolites generates strong Bronsted acid sites (BAS), which can catalyze a broad range of cracking, isomerization, and alkylation reactions. The performance of a zeolite for a given reaction depends on its acid site density, pore size, and crystallographic structure (pore network dimensionality, presence of large cages).[9] ZSM-5 is particularly desirable for reactions that involve small aromatics as its narrow pore size matches the dynamic diameter of benzene. Consequently, only molecules with a similar size and shape can diffuse in or out of the crystal, which makes it an excellent catalyst for the production of benzene, toluene, _para_-xylene, and naphthalene.[8d]

The ZSM-5-catalyzed fast pyrolysis of cellulose to aromatics has been investigated extensively.[2,8d,9b,10] Despite many efforts, commercial ZSM-5 samples from Zeolyst International offer the highest reported yields of aromatic hydrocarbons to

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date and, therefore, these catalysts were employed in most studies published recently.\(^{[11]}\) The reason for this excellent performance has not been identified yet, and the lack of structure–activity correlations currently constitutes a major barrier for the rational design of ZSM-5 catalysts for CFP.

Several studies were aimed to further improve the aromatics yield by enhancing diffusion and by passivating the outer surface of ZSM-5, two approaches used commonly in petrochemistry.\(^{[8d, 10a, c, e, 12]}\) Zheng et al. hypothesized that the slow diffusion of reactants and products in the ZSM-5 micropores is the main limiting factor to achieve a high performance.\(^{[10e]}\) Therefore, they proposed to shorten the diffusion path by decreasing the size of the ZSM-5 crystals. The authors compared 2 μm, 200 nm, and 50 nm crystals. Unfortunately, the results were ambiguous as the 200 nm crystals showed the highest aromatic yield but the 50 nm ZSM-5 gave the highest yield of desired benzene, toluene, and xylene (BTX) products. Additionally, reaction residence times were 50 s, which thus diminished any benefits from improved diffusion. Modest improvements in the overall aromatic yield were observed after the introduction of mesopores in the zeolite crystals by desilication.\(^{[10a]}\) Finally, passivation of the zeolite outer surface by silylation and dealumination was attempted to decrease the undesired conversion of pyrolysis vapors to coke on extra-framework aluminum sites.\(^{[10a]}\) However, these postsynthetic modifications did not impact the catalytic performance significantly either.

Here, we synthesized and fully characterized a series of ZSM-5 catalysts with different elemental compositions, crystal sizes, porosities, and acidities in an effort to identify structure–property–activity relationships. Through the investigation of these samples and comparison with commercial ZSM-5 from Zeolyst and Clariant, we show that crystallinity and extra-framework aluminum, parameters neglected in previous studies, play a key role in catalyst performance. These findings prompted us to investigate alternative synthesis methods. A remarkable ZSM-5 catalyst that offered the highest aromatic hydrocarbon yield to date was obtained.

**Results and Discussion**

ZSM-5 with a controlled particle size and mesoporosity was synthesized using a procedure developed by Petushkov et al.\(^{[13]}\) This method produces ZSM-5 nanocrystals (primary particles) of 5.5–40 nm that self-organize into mesoporous aggregates (secondary particles) of approximately 200 nm. The mesopore surface area and volume can be tailored for these samples by varying the hydrothermal treatment temperature between 130 and 190 °C if the gel composition is kept constant.\(^{[13]}\) The obtained zeolites were characterized fully to establish clear relationships between the catalytic activity and catalyst properties, specifically crystallinity, elemental composition, porosity, and acidity.

**Catalyst characterization**

SEM images (Figure 1) revealed that the ZSM-5 samples synthesized at 130–190 °C were homogeneous and composed of nanocrystals organized in 200–600 nm aggregates, in good agreement with the study of Petushkov et al.\(^{[13]}\) The elemental composition of each sample was determined by X-ray energy-dispersive spectroscopy (EDS) using an accelerating voltage of 15 kV. These conditions afforded a spatial resolution (analysis depth) of approximately 2 μm sufficient to obtain bulk chemical compositions for nanocrystalline samples. Measurements on commercial ZSM-5 of known chemical compositions confirmed that the silica-to-alumina ratio (SAR) values calculated from EDS analysis were accurate. The SAR values obtained for the laboratory-synthesized nanocrystalline ZSM-5 samples ranged between 49 and 53 (Table 1). The only deviation was observed for the zeolite prepared at the lowest temperature (130 °C). A low temperature seemed to be detrimental to Al in-
corporation in the zeolite framework and resulted in a SAR of 99.

Powder XRD patterns were acquired to study the crystal structure of the samples and the presence of amorphous material (Figure 2). An internal standard was mixed with each sample and used as a reference to calculate the relative crystallinity of the zeolitic material. Only diffraction peaks characteristic of the MFI framework type and internal standard were observed. In the present work, the relative crystallinity was calculated using the intensity of the characteristic reflections instead of the diffraction peak areas. Although both methods are common, the peak intensity is more sensitive to small variations in crystal structure. Temperature was found to have a beneficial effect on the crystallization process in good agreement with the results of Petushkov et al.\(^{13}\) The intensity of the reflections at \(2\theta = 23.08, 23.88, \) and \(24.36\) increased by 27% on going from a 130 to 190°C synthesis temperature. A lower crystallinity was accompanied by an increase of the amorphous phase in the sample, as indicated by a more pronounced amorphous scattering halo. Small peak shifts of \(2\theta = +0.1°\) were also observed for the least crystalline samples, for example, ZSM5-24-130, representative of a small contraction of the framework (smaller \(d\) spacing).

The nanostructuring of the catalyst increased the total surface area from 372 to 398–481 m\(^2\)g\(^{-1}\) (Table 1). A greater surface-to-volume ratio for these small crystals and their arrangement in aggregates resulted in a threefold enhancement of the mesoporosity compared to that of the commercial zeolite (Table 1). This increase is evident in the \(N_2\) physisorption isotherms at high \(P/P_0\) and in the pore size distributions (PSD; Figure 3). Although the commercial ZSM-5 displayed a type IV isotherm with a narrow H4 hysteresis typical of microporous materials organized in disordered mesoporous aggregates, all synthesized samples showed a more pronounced hysteresis loop characteristic of hierarchical materials.\(^{15}\) The PSD (calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) model) revealed a broad distribution of mesopores from 5 to 50 nm for samples synthesized at 130–150°C, whereas higher synthesis temperatures favored the formation of more compact aggregates. Pores upwards of 50 nm are significantly larger than those observed in MCM-41 or SBA-15 and, therefore, diffusion is expected to be improved significantly for the samples synthesized at 130 and 150°C.

Changes in acidity were probed by ammonia temperature-programmed desorption (NH\(_3\)-TPD; Figure 4) and FTIR spectroscopy of pyridinated samples (pyridine-FTIR; Figure 5), two complementary techniques commonly used for zeolite charac-

## Table 1. Synthesis conditions and characterization data for commercial and laboratory-synthesized ZSM-5 catalysts.

<table>
<thead>
<tr>
<th>Catalyst(^{a})</th>
<th>Conditions</th>
<th>SAR(^{b})</th>
<th>Surface area(^{c}) (m(^2)g(^{-1}))</th>
<th>Volume(^{d}) (cm(^3)g(^{-1}))</th>
<th>(V_\text{t_0})</th>
<th>(V_\text{t_0})</th>
<th>RC(^{e})</th>
<th>(27\text{Al FWHM}(^{f})</th>
<th>NH(_3)-TPD BAS peak(^{g}) center (°C)</th>
<th>area [a.u.]</th>
</tr>
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<tbody>
<tr>
<td>CBV2314</td>
<td>– –</td>
<td>23</td>
<td>372 274 98</td>
<td>0.202 0.127 100.0 5.9</td>
<td>408 86</td>
<td></td>
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<tr>
<td>ZSM5-24-130</td>
<td>24 130</td>
<td>98.6</td>
<td>481 230 251</td>
<td>0.348 0.105 81.0 5.6</td>
<td>366 30</td>
<td></td>
<td></td>
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<tr>
<td>ZSM5-24-150</td>
<td>24 150</td>
<td>49.2</td>
<td>438 254 184</td>
<td>0.364 0.117 86.7 5.8</td>
<td>387 39</td>
<td></td>
<td></td>
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<tr>
<td>ZSM5-24-170</td>
<td>24 170</td>
<td>52.9</td>
<td>398 248 150</td>
<td>0.273 0.114 100.9 5.4</td>
<td>409 66</td>
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<tr>
<td>ZSM5-24-190</td>
<td>24 190</td>
<td>52.3</td>
<td>421 243 178</td>
<td>0.291 0.111 102.5 5.3</td>
<td>413 68</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ZSM5-OPT</td>
<td>20 180</td>
<td>34.4</td>
<td>318 244 74</td>
<td>0.159 0.113 100.7 4.9</td>
<td>432 147</td>
<td></td>
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</table>

\(^{a}\) CBV2314: commercial ZSM-5; ZSM5-24-x: nanocrystalline ZSM-5 synthesized with various hydrothermal treatment temperatures (x = 130–190°C) using the method of Petushkov et al.\(^{13}\) ZSM5-OPT: microcrystalline ZSM-5 synthesized using a recipe adapted from Kleinwort.\(^{14}\) 

\(^{b}\) Silica-to-alumina ratio calculated from EDS analysis. 

\(^{c}\) Specific surface areas determined from \(N_2\) physisorption using the BET (total) and t-plot (micropores) methods. 

\(^{d}\) Volume (total) and t-plot (micropores) methods. 

\(^{e}\) Relative crystallinity calculated based on the intensity of the main diffraction peaks. Results were normalized to the commercial CBV2314. 

\(^{f}\) Full width at half maximum (FWHM) of the \(^{27}\text{Al SSNMR spectroscopy peak} that corresponds to framework Al.

\(^{g}\) Peak center and area for the contribution that corresponds to strong BAS in the NH\(_3\)-TPD curves.

Figure 2. (top) Powder XRD patterns obtained for commercial (CBV2314) and nanocrystalline samples synthesized at various temperatures. (bottom) The addition of an internal standard allowed us to scale the patterns and compare characteristic MFI peaks.
The NH$_3$-TPD curves obtained for similar zeolites measured under the same conditions provides valuable information on changes in the total (Lewis and Brønsted) acid site density within a sample series. A net increase in acidity with synthesis temperature, independent of elemental composition is illustrated in Figure 4. These results suggest a better aluminum insertion in the zeolites. Although it is difficult to distinguish Lewis from Brønsted acid sites by NH$_3$-TPD, Bates et al. demonstrated a direct correlation between the contribution at 366–413°C and N-propylamine decomposition. Therefore, this TPD peak can be assigned unambiguously to strong BAS associated with framework Al atoms. An integration of this contribution (Table 1) supports an increase in BAS with synthesis temperature, in good agreement with the improved Al insertion in tetrahedral framework sites at the expense of amorphous Al species. This interpretation is also consistent with pyridine-FTIR spectroscopy and $^{27}$Al solid-state nuclear magnetic resonance (SSNMR) spectroscopy (vide infra). In addition, the BAS peak center shifted from 366 to 413°C with the increasing synthesis temperature, which indicates the presence of stronger BAS in the more crystalline samples.

Changes in acidity were further investigated by pyridine-FTIR spectroscopy as this probe molecule generates distinct IR-active vibrations if chemisorbed on Lewis or Brønsted acid sites (Figure 5). Interestingly, the integration of the peak at $\tilde{v} = 1550$ cm$^{-1}$ revealed similar concentrations of Lewis acid sites, independent of the synthesis parameters. The concentration of BAS ($\tilde{v} \approx 1550$ cm$^{-1}$) increased with the synthesis temperature following the trend 130°C < 150°C < 170°C < 190°C. This trend is consistent with the changes observed in the $^{27}$Al SSNMR spectra (Figure 6 and Figures S1 and S2). The obtained SSNMR spectra displayed two main peaks centered at $\delta = 55$ and 0 ppm, which corresponds to tetrahedrally coordinated framework aluminum atoms (Al$_{\text{tet}}$) and octahedral extra-framework Al species (Al$_{\text{oct}}$), respectively. The isomorphous substitution of framework Si with Al in the tetrahedral coordination creates negative framework charges that are balanced by protons to give zeolites their characteristic strong Brønsted acidity. The linear correlation between BAS (H$^+$) and tetrahedrally coordinated Al atoms allows the quantification of strong BAS in protonic zeolites by SSNMR spectroscopy. In contrast to chemisorption techniques, SSNMR spectroscopy probes the total number of strong BAS (associated with framework Al), regardless of their accessibility. Therefore, the fact that SSNMR spectroscopy (Al$_{\text{tet}}$ peak), NH$_3$-TPD, and pyridine-FTIR spectroscopy share the same 130°C < 150°C < 170°C trend of the synthesis temperature indicates that all the BAS are accessible and titrated in the equilibrated samples if NH$_3$ and pyridine are given sufficient...
time to diffuse inside the pore network. At this stage, it is also important to remember that the samples synthesized at 130 and 150 °C present the highest mesopore surface area and volume (Table 1). Yet, these samples are the least acidic. These results indicate that our series of nanocrystalline ZSM-5 samples is fundamentally different from the zeolites studied by Puértolas et al.\[19\] These authors identified a clear porosity–acidity correlation for mesoporous zeolites prepared by desilication. Hence, porosity, acid site density, and catalytic activity followed the same trend. In contrast, all the techniques used in the present study indicate that the number of strong BAS increases with the synthesis temperature, whereas the amount of amorphous material in the samples decreases, as indicated by XRD. Therefore, higher synthesis temperatures (170–190 °C) enhance Al insertion in the zeolitic framework at the expense of Al atoms involved in amorphous, NMR-invisible, extra-framework material, with an optimum at 170 °C for the gel composition selected for this work.

The complex relationship between the characterized properties reveals why clear structure–activity correlations have not yet been identified for zeolite-catalyzed fast pyrolysis. The combination of techniques used in this work is expected to provide unique insights into these correlations.

Catalytic performance

The synthesized samples were tested for the CFP of cellulose to aromatic hydrocarbons. Yields and selectivities to the most important products are reported in Figure 7. Notably, the CFP reaction is performed typically at a high temperature between 600 and 800 °C. The optimal temperature (the temperature that affords the highest yields) varies, which depends on the configuration of the pyrolyzer used for the tests. Although pyroprobes are operated typically at 600–650 °C, micropyrolyzers perform better at 650–700 °C.\[20–29\] Here, we chose to perform the reaction at 700 °C by using a micropyrolyzer on the basis of previous optimizations of our setup.\[29\] Cellulose and catalyst were brought to the target temperature within 500 ms, and the overall reaction proceeded within a few seconds. Only aromatic hydrocarbons were detected under these conditions, of which benzene, toluene, xylene, and naphthalene accounted for more than 70% of the detected products.

Significant differences in activity were observed for the nanocrystalline zeolites with yields to aromatic hydrocarbons in the range of 15–30%. This broad difference in catalytic performance cannot be attributed to variations in the elemental composition as commercial ZSM-5 samples from Zeolyst and Clariant with SAR values of 23 to 55 achieved similar yields under our reaction conditions (27.5 ± 1.0% Table S1). Interestingly, the laboratory-synthesized zeolites with the highest mesoporosity (ZSM-5-24-130 and ZSM-5-24-150) performed very differently and gave yields of 15 and 27%. These results are important: although mesoporosity and a small crystal size may enhance intracrystalline diffusion, other parameters play a more prominent role in the production of aromatic hydrocarbons. This interpretation is consistent with previous work for which only minor improvements in BTX production were achieved if mesopores were introduced in zeolite crystals.\[30\]

A comparison of the reference CBV2314 with the hierarchical ZSM-5 synthesized at 150, 170, and 190 °C provided interesting insights into the parameters that govern the catalytic activity. These four zeolites achieved similar yields (24–29%) although they exhibit a very different crystal size, aggregate size, porosity, and acidity. Notably, ZSM-5-24-170 achieved the same yield as commercial ZSM-5 (CBV2314) although it had 25% fewer BAS and a lower microporous volume, which were both reported to be critical to achieve a high aromatic hydrocarbon yield for the CFP of cellulose.\[10a–e\]

Key features and aromatic yields for the least active (ZSM-24-130) and the best catalysts (ZSM-5-24-170 and CBV2314) were compared in a radar plot to identify key differences visually and guide future rational catalyst design (Figure 8). The overlapping areas in the plot reveal that the best catalysts are highly crystalline and present a strong acidity. These observations were consistent for the commercial Zeolyst and Clariant zeolites (Table S2, Figure S3) as well as laboratory-synthesized ZSM-5. Surprisingly, mesoporosity ($S_{meso}$) and total surface area

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Figure 6. $^{27}$Al SSNMR spectra of the commercial (CBV2314) and synthesized ZSM-5 samples. The peaks at δ = 55 and 0 ppm are characteristic of Al atoms in framework and extra-framework sites, respectively.

Figure 7. Aromatic yield and selectivity to the main aromatic hydrocarbons obtained for the CFP of cellulose at 700 °C. The tests were performed by using a micropyrolyzer equipped with online GC–MS analysis.
Correlations also emerged between catalytic activity and Al Td NMR carbon production under our reaction conditions. New correlations also emerged between catalytic activity and Al Td NMR peak intensity and shape. Correlations between Al Td peak intensity, acidity, and catalytic activity were identified and have already been discussed in previous sections. However, these correlations failed to explain why ZSM5-24-170 achieved the same aromatic yield as commercial ZSM-5 with 50% fewer acid sites. A more in-depth analysis of the SSNMR spectroscopy results revealed interesting trends in the shoulder at $\delta \approx 50$ ppm (Figure S1) and in the full width at half maximum of the Al Td peak (Table 1). These observations could be consistent with the presence of extra-framework amorphous silica-alumina in the commercial zeolite as well as in the ZSM5-24-130 and ZSM5-24-150 samples (also revealed by XRD). Therefore, as a next step, we explored alternative gel compositions and hydrothermal treatment conditions that favor the growth of highly crystalline ZSM-5 samples with strong acidity and enhanced Al insertion in the zeolitic framework as these parameters seem critical to achieve high yields (vide infra).

**Synthesis of ZSM-5 with enhanced CFP performance**

The negligible amount of amorphous materials identifiable by XRD in samples synthesized at high temperature suggests that a significant increase in bulk crystallinity would be difficult to achieve. However, disordered surface species (e.g., amorphous extra-framework silica-alumina) have been proposed to block a vast majority (>$99\%$) of pore openings in small (<50 nm) MFI crystals.[23] These blockages are particularly difficult to characterize by aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM), AFM, and even chemical sorption.[21] Although most acid sites remain accessible to probe molecules under equilibrium conditions, frequency-response investigations demonstrated that these inorganic species hamper the diffusion of bulky molecules under reaction conditions. Clearly, these effects are expected to also take place for larger crystals, in particular for very fast reactions such as CFP. We hypothesized that tuning the synthesis conditions to decrease the formation of these disordered species would also improve Al insertion into the zeolitic framework and enhance the catalytic activity.

Highly ordered (defect-free) zeolites are of particular importance for membrane applications in which intercrystal diffusion paths and varying pore sizes are detrimental to membrane performance.[22] Research in this field has established that heterogeneous nucleation growth techniques and extended crystal growth times are advantageous for single-phase MFI synthesis.[22] Through these synthesis techniques, we can minimize defect formation and generate highly ordered crystals at the expense of mesoporosity.

The synthesis of a highly ordered ZSM-5 catalyst was adapted from a recipe by Kleinwort.[14] The method utilizes a seeding step and long crystallization time to ensure a highly homogeneous and crystalline ZSM-5. SEM images of the obtained sample revealed microcrystals organized in aggregates of 3–5 $\mu$m, that is, approximately one order of magnitude larger than the nanocrystals studied in the first part of this work (Figure 9). Characterization by XRD (Figure S4) confirmed that the crystallinity of the sample was similar to commercial ZSM-5 (relative crystallinity (RC) = 100.7\%). However, AC-HRTEM and selected area electron diffraction (SAED) showed differences in the structure and amorphous content for the two samples (Figure 10 and Figures S5 and S6). Small (20–50 nm) crystalline domains with a significant number of grain boundaries and low-contrast areas that could correspond to amorphous regions were imaged for the commercial Zeolyst CBV2314. The corresponding SAED pattern was consistent as it showed the coexistence of highly crystalline (bright spots) and amorphous (diffuse spots) regions. In contrast, the optimized ZSM-5 crystals have a well-aligned network of micropores that extends over hundreds of nanometers. The high crystallinity of the sample was further confirmed by SAED.

As expected, the mesoporous surface area and volume were minimal (sample ZSM5-OPT in Table 1). $N_2$ physisorption showed a near-type I isotherm characteristic of microporous materials and the PSD displayed only few pores with a width greater than 1 nm (Figures S7 and S8). Hence, although the relative crystallinity determined by XRD is similar for both samples, the optimized ZSM-5 exhibits long-range order with micropores free of any amorphous material.

The existence of pore blockages in both samples was further studied by $N_2$ uptake kinetic studies (Figure 11). These time-
resolved N₂ adsorption experiments provide significant insights into the diffusion of small molecules with dynamic diameters well below the pore size of the zeolite. The uptake experiments start after evacuating the samples and reaching a base pressure of 10⁻⁵ mmHg. Thus, the uptake kinetic traces provide direct information on the accessibility (and blockage) of the microporous network of the zeolite. Diffusion in the commercial ZSM-5 is slow and the adsorbed volume reached a plateau after ≈50 s (Figure 11). In comparison, the uptake for the optimized ZSM-5 was approximately one order of magnitude faster despite the larger crystal and aggregate sizes (Figure 9). These experiments, together with AC-HRTEM images and SAED patterns, support the presence of an amorphous phase inside the pores of the commercial zeolite and that may impact its catalytic activity.

The optimized ZSM-5-catalyzed fast pyrolysis of cellulose produced 32% yield of aromatic hydrocarbons, a 12% increase compared to commercial CBV2314 tested under the same conditions (Figure 7). To the best of our knowledge, this is the first time that the performance of Zeolyst ZSM-5 has been surpassed. Notably, this excellent performance was obtained with microporous micron-sized crystals. Therefore, this experiment is consistent with the conclusions drawn from the first part of this work and confirms that although nanostructuring the zeolite crystals or inserting mesopores and mesovoids may help inter- and intracrystalline diffusion, other parameters have a significantly more pronounced impact on the CFP activity and the formation of the desired aromatic hydrocarbons.

Further analysis of the microcrystalline ZSM-5 by NH₃-TPD, pyridine-FTIR spectroscopy, and ²⁷Al SSNMR spectroscopy (Figures 12–14) confirmed that the synthesis conditions we used to minimize defects also enabled a better insertion of Al in the zeolitic framework and, as a result, the formation of more homogeneous and stronger BAS. Although the sample presents a SAR of 34.4, thus a 50% lower Al content than that of the commercial ZSM-5, NH₃-TPD revealed a significant increase in strong acid sites (Figure 12). Conversely, pyridine-FTIR spectros-
The ZSM-5 zeolite catalyzes the fast pyrolysis of cellulose with a high selectivity to small aromatic hydrocarbons (benzene, toluene, xylene, naphthalene), which find applications as bio-based chemicals or as gasoline-range fuels after additional hydrogenation. The unique size and shape selectivity of ZSM-5 based chemicals or as gasoline-range fuels after additional hydrogenation. The unique size and shape selectivity of ZSM-5 catalysts are strong enough to retain pyridine at the desorption temperature used for pyridine-FTIR spectroscopy. However, the NH3 desorption activation energy for AIOH sites is lower than that of BAS. Therefore, AIOH would not appear in the strongest acid site region of TPD (above 350 °C). Further FTIR spectroscopy studies using collidine and 2,6-di-tert-butylpyridine (DTBPy), two probe molecules too large to diffuse inside the ZSM-5 micropore network, were performed to locate these AIOH sites and obtain additional information on acid site accessibility. The absence of any signal for this sample series (Figure S9) demonstrates that the extra-framework AIOH species are located inside the pore network, in good agreement with the N2 uptake experiments. These measurements also ruled out any significant contribution from external acid sites and any porosity–acidity correlation for CFP. This interpretation is also supported by 27Al SSNMR spectroscopy results (Figure 14): the peak that corresponds to tetrahedral aluminum increases in intensity and becomes narrower, which indicates more Al in highly symmetric framework sites than for the commercial sample. We used the radar plot shown in Figure 15 to highlight the critical parameters for high catalytic activity and provide further insight into the key factors that need to be further optimized. A comparison of the results for commercial and optimized ZSM-5 reveals that the increase in aromatic hydrocarbon yield can be assigned to a higher Al ratio in framework sites and, reciprocally, less Al in extra-framework surface species that block pores and, potentially, catalyze undesired reactions.

Conclusions

The ZSM-5 zeolite catalyzes the fast pyrolysis of cellulose with a high selectivity to small aromatic hydrocarbons (benzene, toluene, xylene, naphthalene), which find applications as bio-based chemicals or as gasoline-range fuels after additional hydrogenation. The unique size and shape selectivity of ZSM-5 towards these compounds is well established and understood. However, the importance of other structural parameters for the efficient transformation of pyrolysis vapors into aromatics remained to be elucidated. It was proposed previously that strong Bronsted acid sites located inside the pores of the zeolite catalyze a series of deoxygenation, cracking, alkylation, and aromatization reactions. This hypothesis was based primarily on analogies with the reactions of methanol to olefins and methanol to hydrocarbons. Here, we have demonstrated that amorphous silica-alumina surface species, even present in small concentrations, impact the diffusion of bulky reactants, lower the amount of Al in framework sites, and, consequently, alter the Bronsted acid site density and strength. These observations were shown to hold without exception regardless of the catalyst manufacturer or synthesis method. On the basis of this finding, we designed a highly crystalline zeolite with minimal crystalline defects and amorphous material through the adaptation of techniques developed for zeolite membrane synthesis. This approach allowed us to further study the role of zeolite crystallinity as well as the nature of its acid sites. The yield to the desired products increased by 12% and for the first time surpassed the aromatic hydrocarbon yield obtained for commercial ZSM-5 tested under the same conditions. This work sets the foundation for future mechanistic studies and for the design of new zeolitic materials optimized for catalytic fast pyrolysis.

Experimental Section

Catalyst synthesis

Reference ZSM-5 samples in their ammonium form were purchased from Zeolyst International and used here for comparison: CBV2314, CBV3024E, CBV5524G, and CBV8014 with SiO2/Al2O3 = 23, 30, 50, and 80, respectively. The samples were calcined in air at 550 °C for 10 h (ramp: 5 °C min⁻¹) before characterization and catalytic testing. ZSM-5 nanocrystals with controlled particle size and mesoporosity were synthesized according to a procedure published previously. Briefly, a clear gel with the following molar composition of 25:1:5:4:1000 TEOS/NaAlO₂/TPAOH/TPABr/H₂O...
Cined at 550°C and collected by centrifugation (5000 rpm, 30 min) and washed twice with water. The system was determined using the NIST LaB6 standard. All data and calcination at 550°C for 24 h. The synthesis temperature was varied between micro- and mesoporosity. The N$_2$ rate of adsorption experiments were performed by dosing 5 cm$^3$ g$^{-1}$ of N$_2$ to a sample under vacuum (10 μmHg).

N$_2$ adsorption/desorption isotherms and N$_2$ uptake were measured by using a Micromeretics ASAP 2020 system at 77 K. Zeolite powder (50–60 mg) was degassed at 200°C (heating ramp: 5°C min$^{-1}$) for 12 h under vacuum. The specific surface area was calculated using the BET method. The BJH model with Faas correction was applied to the adsorption branch of the isotherm to calculate the PSD. The t-plot method was used to discriminate between micro- and mesoporosity. The N$_2$ rate of adsorption experiments were performed by dosing 5 cm$^3$ g$^{-1}$ of N$_2$ to a sample under vacuum (10 μmHg).

SEM images were acquired by using a FEI Quanta 250 FEG operated at 10 kV. The samples were coated with 2 nm of Ir for conductivity. X-ray analysis was performed by using an Oxford Instruments Aztec$^{TM}$ energy-dispersive spectrometer (EDS) system equipped with an X-Max 80 detector. EDS spectra were typically recorded at 15 kV, which corresponds to a beam penetration depth of ≈2 μm.

For HRTEM and SAED, the samples were dry-dispersed on a holey carbon grid. Images and diffraction patterns were acquired by using an FEI Titan 80–300 equipped with an aberration corrector on the objective lens. The microscope was operated at an acceleration voltage of 300 kV. To minimize the effect of the electron beam, a low current density was used.

NH$_3$-TPD was performed by using a Micromeretics AutoChem II 2920. Zeolite powder (50 mg) was pretreated at 550°C (heating ramp: 10°C min$^{-1}$) in 10 mL min$^{-1}$ He for 1 h to desorb any moisture from the surface. The sample was then cooled to 50°C and ammonia was adsorbed for 30 min (20 mL min$^{-1}$ of 10 vol% NH$_3$ in He). The sample was then purged at 100°C under flowing He for 90 min. NH$_3$ desorption was recorded by heating the zeolite from 100 to 700°C using a 10°C min$^{-1}$ ramp. Curves were normalized using the same mass. Peak areas were determined using a Gauss analysis in OriginPro 9.1 software.

FTIR spectroscopy was performed by using a Bruker Vertex 80 spectrometer with a Harrick Praying Mantis diffuse reflection (DRIFTS) attachment. Samples were first pyridinized or adsorbed with DTBPY for 48 h. Desorption occurred at 150°C over 4 h for pyridine and 1 h for DTBPY to remove any physisorbed species. 2% pyridinized zeolite/KBr mixture was made, mixed and ground by mortar-and-pestle, and sieved through a 45 μm sieve. DTBPY samples were ground by mortar-and-pestle and sieved through a 45 μm sieve. The samples were then analyzed using OPUS 7.0 software. Absorbance from 4000–1000 cm$^{-1}$ was collected using 32 scans at a 4 cm$^{-1}$ resolution for pyridine and 128 scans at 2 cm$^{-1}$ resolution for DTBPY.

SSNMR spectroscopy was performed by using a Bruker Avance II spectrometer with a 14.1 T wide-bore magnet using a 4 mm triple resonance magic-angle spinning (MAS) probe in double resonance mode. TopSpin 3.0 software was used for data acquisition and processing. The operating frequencies for $^1$H and $^{27}$Al on this spectrometer are 600.13 and 156.38 MHz, respectively. The samples were first rehydrated in a humidifier for 48 h at RT. The powders were then packed into a Kel-F rotor insert and the insert was placed in a 4 mm MAS rotor. Samples were spun at a frequency of 5 or 12 kHz, with the slower speed required for some samples if spinning sidebands from the downfield peak interfered with the

Catalyst characterization

Powder XRD patterns were collected by using a Siemens D 500 diffractometer using CuK$_\alpha$ radiation, a diffracted-beam monochromator (graphite), and a scintillation detector. Data were recorded in the 2θ range of 5–50° using a step size of 0.05° and a dwell time of 3 s per step. The instrument broadening of the diffraction system was determined using the NIST LaB$_6$ standard. All data were analyzed using Jade software version 9.5. Test specimens were prepared by mixing the bulk sample with an internal standard (high purity corundum, Alfa Aesar, verified using NIST 674b standards zincite, rutile, and cerianite). The mixture consisted of 0.150 g of sample and 0.100 g of corundum. All measurements were made by using an analytical balance and recorded to the nearest 0.1 mg. Then the components were mixed in an agate mortar-and-pestle. After mixing, the material was removed from the mortar, quickly recombined, and then placed back into the mortar-and-pestle for a second mixing cycle. This produced a homogeneous powder that contained 40% internal standard by mass. Specimens for XRD analysis were prepared by placing 0.20 ± 0.03 g of powder into the cavity of a zero-background holder (MTI Corporation zero diffraction plate, size 20 mm diameter by 1 mm deep). The powder was compacted into the cavity with a glass slide. Relative crystallinity was calculated by summing the peak maxima for each sample at the characteristic peaks 2θ ≈ 23.08, 23.88, and 24.36°. Intensities are reported relative to the commercial sample (CBV21341) that was taken as 100%.

The operating frequencies for 1H and 27Al on this spectrometer are 600.13 and 156.38 MHz, respectively. The samples were first pyridinized or adsorbed with DTBPY for 48 h. Desorption occurred at 150°C over 4 h for pyridine and 1 h for DTBPY to remove any physisorbed species. 2% pyridinized zeolite/KBr mixture was made, mixed and ground by mortar-and-pestle, and sieved through a 45 μm sieve. DTBPY samples were ground by mortar-and-pestle and sieved through a 45 μm sieve. The samples were then analyzed using OPUS 7.0 software. Absorbance from 4000–1000 cm$^{-1}$ was collected using 32 scans at a 4 cm$^{-1}$ resolution for pyridine and 128 scans at 2 cm$^{-1}$ resolution for DTBPY.
resonance of the upfield peak. The temperature was stabilized at 298 K. Spectra were acquired using a 90–1–180–1–detect Hahn echo pulse sequence with a 2.5 μs 90°–27°Al pulse and an echo period of one rotor period (200 μs at 5 kHz spinning speed or 83 μs at 12 kHz spinning) under 1H dipolar decoupling at 62 kHz. Typically, spectra were acquired with 2048 scans and a recycle delay of 1.5 s.

Catalyst testing

Catalytic pyrolysis experiments were conducted by using a micro-
pyrolyzer (PY-2000IS, Frontier Laboratories, Japan) equipped with an autosampler (AS-1020E, Frontier Laboratories, Japan). A de-
tailed description of the setup can be found in previous stud-
ies[2b, 25]. All CFP experiments were performed in situ. The zeolite
was synthesized by a modified version of the method described in a previous publication.

The total moles of carbon in the aromatic products were de-
fined as the molar ratio of carbon in a specific product to the
final product distribution was reported as molar carbon yield, de-

calized either by a mass spectrometer detector (MSD) or a flame

tor split ratio was set to 100:1. Separated pyrolysis vapors were an-
d at 12 kHz spinning or

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Playing nice: The interplay of zeolite structural characteristics is studied to identify parameters common to high-performance catalysts in catalytic fast pyrolysis. Crystallinity and accessibility to framework Al atoms is critical to achieve high aromatic yields. These findings allow us to synthesize a ZSM-5 catalyst with enhanced catalytic properties, which offers the highest aromatic hydrocarbon yield reported to date.


Tailoring ZSM-5 Zeolites for the Fast Pyrolysis of Biomass to Aromatic Hydrocarbons