Impact of Controlling the Site Distribution of Al Atoms on Catalytic Properties in Ferrierite-Type Zeolites†

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Zeoites with the ferrierite (FER) topology are synthesized using a combination of tetramethylammonium (TMA) cations with differently sized cyclic amines (pyrrolidine (Pyr), hexamethyleneimine (HMI), and 1,4-diazabicyclo[2.2.2]octane (DAB)). Using these organic structure-directing agents (SDAs), low Si/Al ratios and concentrated synthesis mixtures favor the crystallization of FER materials. Increasing the size of the cyclic amine or decreasing the aluminum content leads to the crystallization of other phases or the creation of excessive amounts of connectivity defects. TMA cations play a decisive role in the synthesis of the FER materials, and their presence allows the use of HMI to synthesize FER. Proton MAS NMR is used to quantify the accessibility of pyridine to acid sites in these FER samples, where it is found that the FER + HMI + TMA sample contains only 27% acid sites in the 8-MR channels, whereas FER + Pyr and FER + Pyr + TMA contain 89% and 84%, respectively. The constraint index (CI) test and the carbonylation of dimethyl ether (DME) with carbon monoxide are used as probe reactions to evaluate how changes in the aluminum distribution in these FER samples affect their catalytic behavior. Results show that the use of Pyr as an SDA results in an increased concentration of acid sites in the 10-MR channels.

1. Introduction

Zeolites are crystalline solids composed of silicon and aluminum oxides arranged in a three-dimensional network of uniformly shaped micropores (<2 nm) of tunable topology and composition. They represent one of the most important classes of heterogeneous catalysts and are used in several large-scale industrial processes where they mostly serve as strong, shape-selective Bronsted acids. Acid sites in zeolites are commonly generated when protons balance the negatively charged framework induced by the presence of tetrahedrally coordinated aluminum (Al) atoms. The activity and selectivity of a given reaction catalyzed by zeolites is determined by the material’s structure, that is, by the size and shape of the channels and cavities, and by the distribution and relative concentration of Al atoms in the framework. Locating, and subsequently controlling, the position of active sites within the zeolite structure continues to be an elusive problem with enormous relevance to shape-selective catalysis.

Amines and quaternary ammonium cations are often used as structure-directing agents (SDAs) during zeolite synthesis to obtain specific crystal phases. The interaction of the SDA with the inorganic host is a complex process that continues to be heavily studied in order to understand and rationalize how changes in the properties of the SDA, for example, size, rigidity, and charge distribution, can be related to changes in framework topology and active site distribution. In recent years, the synthesis of increasingly complex organic cations has resulted in the creation of new zeolite frameworks, thereby shedding light on the distinctive relationship between the SDA and the framework obtained. Similarly, recent reports have shown how the use of a specific combination of known SDAs in the absence of inorganic cations can alter the distribution of active sites within zeolites with the same framework topology. Although it is clear that the particular choice of SDA has a strong impact on the self-assembly process of the zeolite structure, the effects on the distribution of acid sites, at present, remain unresolved. There are very limited data on SDA structure influencing the Al site distribution in zeolites.

Here, we report on structure–function relations between specific SDA combinations and aluminum distribution within the framework for zeolites with the ferrierite (FER) topology synthesized using combinations of tetramethylammonium (TMA) cations with differently sized cyclic amines (pyrrolidine (Pyr), hexamethyleneimine (HMI), and 1,4-diazabicyclo[2.2.2]octane (DAB)). In addition, parameters influencing the nucleation and crystallization of FER, including water concentration and Al content, were also included in the experimental design. We note that FER was chosen because its qualities are ideal for this study. First, the FER structure has four nonequivalent T-sites distributed among two different channel systems, thereby drastically changing the accessibility of certain reactive molecules to active sites. Specifically, the FER structure consists of channels of 10-membered (10-MR) rings running parallel to the [001] direction, 8-MR channels running parallel to the [010] direction, and 6-MR channels running parallel to the [001] direction, where the intersection of an 8-MR and a 6-MR channel creates a [866^68^5] cage, known as the “ferrierite cavity” that is accessible only through 8-MR windows (see Figure S1 in the Supporting Information). Second, FER can be synthesized using a variety of SDAs in the absence of inorganic cations, making it possible to influence the Al charge compensation exclusively with the SDA. Finally, there exists precedent in the literature regarding the use of mixtures of organic SDAs to influence the distribution of Al within the framework of FER. Specifically, Perez-Pariente et al. observed a higher degree of active site occupation in the...
ferrocyanide when two particular SDAs were used in media free of inorganic cations.5

Changes in the Al distribution within the framework of FER samples were investigated using two different techniques. First, pyridine accessibility to active sites was quantified with $^1$H MAS NMR. Pyridine was chosen as a probe molecule because it strongly interacts with Bronsted acid sites located within 10-MR channels, but its size precludes it from interacting with sites located within 8-MR channels. Second, two probe catalytic reactions sensitive to the location of active sites within the zeolite’s channels, namely, the constraint index (CI) test and the carbonylation of dimethyl ether (DME) with carbon monoxide, were used.

The CI test, originally designed by Haag and co-workers to search for shape-selective catalytic behavior in zeolites,8 compares the reaction rates for the cracking of n-hexane (n-C$_6$) and its isomer, 3-methylpentane (3-MP), under competitive conditions (eq 1). A higher CI value is obtained from preferential cracking of n-C$_6$ compared to the branched 3-MP, which is excluded in sterically constrained environments. Thus, CI values > 12 are obtained with small-pore zeolites (e.g., 8-MR channels), and CI values < 1 are usually observed in large-pore zeolites that showed no steric exclusion of 3-MP (e.g., zeolite beta, which contains only 12-MR channels).

$$CI = \log(\text{rate } n\text{-C}_6\text{ conversion})/\log(\text{rate } 3\text{-MP conversion})$$

For our purposes, this test is a useful tool in identifying changes within a zeolite containing active sites located in different channel systems. In the case of FER, a contribution of sites located within 10-MR and 8-MR channels will be observed, resulting in an average CI number between 7 and 15. However, a successful selective displacement of active sites from the 10-MR channels to the cavities should be reflected in CI values higher than 12 because 3-MP will be almost completely excluded. Conversely, the displacement of catalytic sites contained within the 8-MR channels should result in a decrease in the average CI value because the catalytic behavior will be governed by active sites located within the more accessible 10-MR channels.

The low-temperature carbonylation of DME with CO using acidic zeolites, recently discovered by Iglesia and co-workers, represents one of the most remarkable examples of active site specificity in zeolites known to date.9–11 It was shown, by way of detailed kinetic analyses, that a direct correspondence exists between DME carbonylation rates and the number of acid sites located in the 8-MR channels or “side pockets” of mordenite (MOR) and in the cavities FER. Interestingly, it was reported that this reaction does not proceed with other zeolites, such as beta, NaY, or ZSM-5. This “enzyme-like” specificity was further rationalized and corroborated with theoretical calculations performed by Corma et al., where one T-site in MOR was identified as the most active.12 Hence, the carbonylation reaction can be used as an extremely sensitive probe to measure the effect that a particular SDA has on selectively populating the active site in FER responsible for catalyzing this reaction.

2. Experimental Section

2.1. Zeolite Synthesis. Synthesis gels were prepared such that the total concentration of organic groups acting as SDAs was constant. The reaction mixtures had the following compositions: SiO$_2$/xAl$_2$O$_3$/yTMAOH/(0.54 – y)H$_2$O where Y was either Pyr, HMI, or DAB, x was either 0.02 or 0.033, y was either 0.06 or 0.0 (depending if a mixture or a single SDA was used), and z was either 5 or 15.

Synthesis mixtures were prepared by adding a colloidal suspension of silica (LUDOX, Sigma-Aldrich, 40 wt %) and alumina (Catapal, SASOL) to an aqueous solution containing the SDAs. The solution was stirred and then allowed to reach the desired water ratio by evaporation. Finally, hydrofluoric acid (Mallinckrodt, 52 wt % in water) was added dropwise, resulting in a thick gel. This gel was then stirred by hand for an additional 5 min and then introduced into a 25 mL Teflon-lined stainless steel autoclave (Parr Instruments) and heated at 423 K under autogenous pressure for either 14, 30, or 60 days. The solids were recovered by filtration, extensively washed with water, and dried overnight at 373 K. Next, the solids were calcined at 853 K (0.01667 K s$^{-1}$) under flowing air (1.667 cm$^3$ s$^{-1}$) for 6 h to remove the organic content located within the crystalline material.

Commercial samples of ferrierite (denoted as FER-OH) (Si/Al = 10) and mordenite (denoted as MOR) (Si/Al = 10) were obtained from Zeolyst, exchanged with 1 M NH$_4$NO$_3$ (1 g in 50 mL) three times at 353 K for 12 h each. These samples were transformed to the acid form by calcination under flowing air (1.667 cm$^3$ s$^{-1}$) at 853 K (0.01667 K s$^{-1}$) for 6 h.

2.2. Characterization. $^{27}$Al, $^1$H, and $^{13}$C solid-state MAS and CPMAS NMR spectra were recorded using a Bruker DSX 500 spectrometer operating at 11.7 T with 500.2, 130.3, and 125.8 MHz for $^1$H, $^{27}$Al, and $^{13}$C nuclei, respectively, using a Bruker 4 mm CPMAS probe. Typically, spinning rates of 15 kHz were used for $^1$H and $^{27}$Al nuclei and 8 kHz for the $^{13}$C nucleus. In addition, MAS spectra were recorded after applying a 4 µs-π/2 pulse for $^1$H, a cross-polarization contact time of 1 ms for $^{13}$C CPMAS, and a 0.3 µs-π/18 pulse for the $^{27}$Al nucleus.

For pyridine adsorption experiments, calcined and hydrated zeolites were first packed in a 4 mm zirconia rotor, and the entire rotor was placed inside a 150 mm × 5 mm o.d. glass NMR tube. The NMR tube was then attached to a vacuum line and evacuated at 453 K for 30 min and allowed to cool to room temperature while maintaining the evacuation. Dry helium gas was introduced to the sample before the rotor was exposed to air, and the rotor was closed immediately with a tight-sealing Kel-F cap. This procedure was found to be efficient in avoiding introduction of moisture into the sample. Deconvolution of $^1$H MAS NMR spectra for quantification was performed using OriginPro 8 software (OriginLab Corp, Northampton, MA).

Powder X-ray diffraction patterns were collected with a Scintag XDS 2000 diffractometer using Cu Kα radiation. Organic content was determined by thermogravimetric analysis (TGA) using a Netzsch STA 449 C apparatus with alumina crucibles heated in air at 10 K/min. Nitrogen adsorption was carried out on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature (77 K). Scanning electron microscopy (SEM) images were recorded on a LEO 1550 VP FE SEM at an electron high tension (EHT) of 10 kV. Elemental and chemical analysis data were obtained from Galbraith Analytical Laboratories (Knoxville, TN).
of the effect of the amine's size on the nucleation and crystallization of the zeolite. Second, literature reports have shown that TMA cations direct the formation of small cavities in zeolites, as is the case of the FER cavity. Indeed, Perez-Pariente and co-workers used TMA cations in conjunction with SDA to influence the distribution of Al atoms in FER. Therefore, the incorporation of TMA in our design would allow us to study the “cooperative effect” of utilizing two organic SDAs during the nucleation process. Third, the concentration of aluminum atoms in the synthesis gel can play an important role in the final distribution of active sites within the framework. As described by Cejka et al., zeolites with Si/Al < 20 may contain Si–Al arrangements described as “Al pairs” [Al–O–(Si–O)_{1.2}–Al] and “single” Al atoms [Al–O–(Si–O)_{3}–Al], which are known to have different catalytic behaviors. For this reason, synthesizing the same zeolite with two different Si/Al ratios is important. Fourth, the water content is known to drastically affect the nucleation process. A more concentrated gel will result in faster nucleation and crystallization of a given phase. Consequently, two different water-content levels, one dilute and one concentrated, were included in this study.

The synthesis results shown in Figure 1 clearly show preferential compositions and conditions for the formation of crystalline phases. Specifically, crystalline phases were only observed when concentrated gels (H$_2$O/Si = 5) containing Pyr or HMI were used. After 60 days at 453 K, crystalline phases failed to appear in samples that were amorphous at 14 days. FER topology for these materials was confirmed by XRD for Pyr and Pyr + TMA samples with the Si/Al ratio of 15 (see Figure S2 in the Supporting Information). Interestingly, when the larger HMI amine was used, FER topology was observed only in the sample containing TMA ions. Decreasing the aluminum in the synthesis gel resulted in the formation of materials related to FER but not in a complete crystalline form. After 14 days of crystallization, the diffraction patterns for those materials possessed lower peak intensities than their completely crystalline counterparts and also show the presence of amorphous SiO$_2$ (see Figure S2 in the Supporting Information, samples 2, 6, and 18). The XRD pattern did not change after 30 days of hydrothermal treatment at 453 K. The difference in crystallinity between samples containing two different amounts of Al can be explained as follows: The unit cell of the ferrierte is formed by 36 atoms in tetrahedral coordination. Referring to the data in Table 1, the FER + Pyr and FER + Pyr + TMA samples synthesized with the theoretical Si/Al ratio of 15 show a Si/Al ratio after crystallization of 13.1 and 17.0, respectively. $^{27}$Al MAS NMR spectra for these samples confirm that most
Al atoms are in tetrahedral coordination (see Figure 2), which translates into materials containing \( \sim 2.1 \) to \( 2.5 \) Al atoms per unit cell. Thermogravimetric and elemental analyses (see Figure S3 in the Supporting Information and Table 1) reveal that these materials contain the equivalent of approximately four organic molecules per unit cell. Therefore, the positive charges introduced by the organic SDAs have to be balanced by Al atoms, fluoride anions, or structural defects, that is, silanol groups. Because these samples are crystalline, the charge balance appears to close without the presence of high concentrations of defects. On the other hand, when the higher Si/Al ratio is used, the aluminum content per unit cell approaches \( 1.4 \), which is much lower than the positive charges introduced by the organic SDAs. Consequently, a large amount of structural defects is required to balance those positive charges, which creates too many connectivity defects to complete the crystallization of the FER structure.

An increase in size of the cyclic amine from Pyr to HMI results in the crystallization of the FER phase only in the presence of TMA cations. The presence of TMA as a co-SDA favors the nucleation of FER due to the ability of the small quaternary cation to template the FER cavities. The \( ^{27}\text{Al} \) MAS NMR spectrum for the calcined sample (see FER + HMI + TMA in Figure 2) reveals that more than \( 80\% \) of the aluminum is in tetrahedral coordination. We observed that, in the absence of TMA, MCM-22, a zeolite with a bidirectional 10-MR pore system, is obtained. This result indicates that the HMI molecule is too large to template the small cavities present in FER, thereby favoring the nucleation of the medium-pore MCM-22 zeolite, where HMI can properly fit. When the Si/Al ratio is increased, that is, the number of Al atoms per unit cell decreases, rather than obtaining MCM-22 or FER structures with a large number of connectivity defects, either pure MCM-22 or a mixture of phases consisting of MCM-22 and FER is achieved. Finally, amorphous materials are obtained when the size of the cyclic amine is further increased from HMI to DAB.

Three crystalline materials with the FER topology were obtained using different combinations of SDAs. Importantly, the three FER samples show similar physical characteristics, having comparable Al contents (see Table 1), micropore volumes (see Table 1), crystal sizes, and morphologies, that is, thin platelike crystals agglomerated in \( \sim 20 \mu \text{m} \) spherulites (see Figure 4). This suggests that any differences in catalytic activity and pyridine accessibility between samples are a consequence of the particular SDA combination used rather than a result of differences in physical features. We evaluated the acid-site distribution of these FER samples by quantifying the accessibility of deuterated pyridine and by evaluating their catalytic performance in the CI test and DME carbonylation reactions.

Accessibility of pyridine to the channels of FER was quantified using \( ^{1}\text{H} \) MAS NMR. The \( ^{1}\text{H} \) NMR spectrum of

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\text{TABLE 1: Si/Al Ratios, Thermogravimetric Analyses Data, and Micropore Volume of Calcined FER Materials}
\]

<table>
<thead>
<tr>
<th>chemical analysis (wt%)</th>
<th>C/N molar ratio</th>
<th>TGA(^a) (wt %)</th>
<th>micropore volume (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FER + Pyr</td>
<td>13.2</td>
<td>6.93</td>
<td>2.12</td>
</tr>
<tr>
<td>FER + Pyr + TMA</td>
<td>17.0</td>
<td>6.72</td>
<td>1.61</td>
</tr>
<tr>
<td>FER + HMI + TMA</td>
<td>17.2</td>
<td>8.60</td>
<td>2.00</td>
</tr>
</tbody>
</table>

\(^a\) Measured from elemental analysis. \(^b\) Weight loss measured in the 473–1123 K range.
dehydrated aluminosilicate zeolites contains four relevant signals for this study: a resonance at 1.7 ppm assigned to silanol groups, a resonance at 2.0 ppm assigned to disturbed silanol groups, that is, silanol groups that have another –OH group in the vicinity, a resonance at 3.8 ppm assigned to acidic Si–OH–Al protons, and a resonance at 4.8 ppm assigned to disturbed acidic Si–OH–Al protons.18 The interaction of deuterated pyridine molecules with Bronsted acid sites generates a chemical shift of ∼12 ppm. Therefore, because pyridine cannot interact with Bronsted sites located within 8-MR channels or cavities, pyridine adsorption in a zeolite, such as FER, will shift all signals associated with acid sites in the 10-MR and the remaining signal at 3.8 ppm will correspond to the number of acid sites located in the 8-MR channels or cavities. Here, deuterated pyridine is adsorbed into a commercial MOR sample (Zeolyst CBV21A, Si/Al = 10) and the 3.8 ppm signal is used as an external standard to quantify sites located within 8-MR channels. Indeed, detailed characterization studies performed on this MOR sample by Iglesia and co-workers show that 58% (2% of the acid sites are located within the 8-MR channels.10,11 Upon performing the deuterated pyridine adsorption on the FER samples, 1H MAS NMR quantification of the number of acid sites located in the 8-MR channels yielded values of 89% ± 2%, 84% ± 3%, and 27% ± 5%, for FER + Pyr, FER + Pyr + TMA, and FER + HMI + TMA, respectively (see Table 2 and Figure 5). A commercial ferrierite sample (Zeolyst, Si/Al = 10) synthesized in alkaline media yielded 53% ± 6% of acid sites located in the 8-MR channels. The results for FER + Pyr, FER + Pyr + TMA, and FER-OH are in agreement with accessibility results reported by Perez-Pariente and co-workers obtained by infrared spectroscopy.5 Surprisingly, when compared to FER synthesized in an alkaline media, FER samples synthesized in the presence of Pyr show a preferential sitting of the acid sites in the FER cavity, whereas FER synthesized in the presence of HMI shows a preferential acid-site sitting in the 10-MR channels. These results clearly show that the particular combination of SDAs used has a strong impact on the number of sites located within 8-MR channels.

The CI number as a function of time of reaction is shown in Figure 6. For all samples, the CI number did not remain constant over time. Specifically, FER-OH, FER + Pyr, and FER + Pyr + TMA showed initial CI numbers > 12 that slowly declined to a steady-state value of ∼7.0. Conversion data reveal that the cracking rate of 3-MP remains constant, whereas the cracking rate of n-C8 slowly decreases over time, resulting in a gradual decline in CI number. This catalytic behavior is representative of the presence of acid sites in both channel systems of FER and also points at faster deactivation rates for sites located within

Figure 4. SEM images of (A) FER + Pyr, (B) FER + Pyr + TMA, and (C) FER + HMI + TMA.

TABLE 2: Steady-State Methyl Acetate Synthesis Rates for Various FER Samples and Percentage of Acid Sites Inaccessible to Pyridine Molecules and, Therefore, Related to the Amount of Acid Sites Located in the 8-MR Channels

<table>
<thead>
<tr>
<th>steady-state methyl acetate synthesis rate [mol/g atom Al h]</th>
<th>Si/Al</th>
<th>EFAI*a</th>
<th>Si/Altet,b</th>
<th>acid sites in 8-MR channels</th>
<th>mmol Al8-MR/g cat</th>
</tr>
</thead>
<tbody>
<tr>
<td>FER-OH</td>
<td>0.9</td>
<td>10.0</td>
<td>3.8</td>
<td>10.4</td>
<td>53% ± 6%</td>
</tr>
<tr>
<td>FER + Pyr</td>
<td>1.3</td>
<td>13.2</td>
<td>4.0</td>
<td>13.7</td>
<td>89% ± 2%</td>
</tr>
<tr>
<td>FER + Pyr + TMA</td>
<td>0.8</td>
<td>17.0</td>
<td>2.1</td>
<td>17.4</td>
<td>84% ± 3%</td>
</tr>
<tr>
<td>FER + HMI + TMA</td>
<td>&lt;0.1</td>
<td>17.2</td>
<td>20.0</td>
<td>21.5</td>
<td>27% ± 5%</td>
</tr>
<tr>
<td>MOR</td>
<td>10.0</td>
<td>11.5</td>
<td>11.3</td>
<td>20.0</td>
<td>58% ± 3%</td>
</tr>
</tbody>
</table>

*a EFAI = Extraframework aluminum (%), calculated from 27Al MAS NMR. *Si/Altet = Si/Al ratio considering only Al in tetrahedral coordination. These values have been calculated from the 1H MAS NMR spectra after adsorption of deuterated pyridine.
the 8-MR channel system. At times on-stream under 30 min, the CI numbers for FER + Pyr and FER + Pyr + TMA are much higher than the CI numbers for FER-OH, which is consistent with the higher concentration of acid sites located within 8-MR calculated from the pyridine adsorption study (see Table 2). Interestingly, sample FER + HMI + TMA showed a notably different catalytic behavior in comparison to other FER samples. Specifically, at short times on-stream, the CI number was <2 and it gradually increased over time to reach a steady-state value of ~7.0. A similar behavior whereby the CI number increased over time was reported by Zones and Harris for SSZ-25\textsuperscript{19} and by Carpenter et al. for certain MOR samples.\textsuperscript{20} This result suggests that the contribution to the CI number of sites located within 8-MR channels of FER + HMI + TMA is negligible, and therefore, its catalytic behavior is dominated by acid sites located within the 10-MR channels. Indeed, as seen in the data listed in Table 2, the number of acid sites located within 8-MR channels in this sample is much lower when compared with that of the other FER samples.

Differences in DME carbonylation rates observed between FER samples further support the strong influence that particular SDA combinations exert on the acid site distribution. As shown by the data in Figure 7, DME carbonylation rates increase in parallel with the number of acid sites located within 8-MR channels of different FER samples, which is consistent with the reports by Iglesia and co-workers whereby a direct relationship between DME carbonylation rates and the number of acid sites in the 8-MR side pockets of MOR was observed.\textsuperscript{10,11} FER + Pyr shows the highest steady-state MA synthesis rates, followed by FER-OH, FER + Pyr + TMA, and, last, by FER + HMI + TMA, in direct correspondence with the number of acid sites located within their 8-MR channels (see Table 2). FER + HMI + TMA shows a DME carbonylation rate that is an order of magnitude lower (<0.1 mmol MA (g Al atom)\textsuperscript{-1} h\textsuperscript{-1}) than the rate observed for other FER samples, thus becoming the first example of a FER-type material in acid form and free of alkaline cations that shows virtually no carbonylation activity.

The catalytic results provide strong evidence indicating that the synthetic procedure used in the present study can be used to selectively populate T-sites in either the 8-MR or the 10-MR of FER, depending on the particular SDA combination used. Thus, the mechanisms of how the SDAs influence Al site distribution merit further study. Variable-temperature solid-state NMR spectroscopy is commonly used to study the dynamics of organic molecules present in the as-synthesized form of zeolites.\textsuperscript{21} Generally, molecules occluded within the pores of a zeolite that are not sterically prevented from isotropic reorientation (i.e., the molecule can rotate freely within the pore) and that do not have strong electrostatic interactions with the framework will show a characteristic band sharpening as the temperature increases due to the onset of isotropic reorientation.\textsuperscript{13C CP MAS and 13C single-pulse MAS NMR variable-temperature experiments performed on sample FER + HMI + TMA in the 298–503 K temperature range are shown in Figure 3a,b. The signals associated with both SDAs are present in the sample, with signals assigned to HMI showing a larger degree of broadening when compared with the signal assigned to TMA (see Figure 3a), indicating a lower degree of mobility or a higher anisotropy with respect to TMA. Interestingly, it is observed that, at all temperatures, up to 503 K, the SDAs do not undergo isotropic reorientation. Thus, because both SDAs are not sterically hindered in the pores, it is concluded that strong electrostatic interactions are preventing the SDAs from undergoing such reorientation. This result is in sharp contrast with results obtained by Gies et al., where it is shown that electrically neutral amines used to synthesize nonasil readily undergo isotropic reorientation in the 5\textsuperscript{12}G\textsuperscript{12} cage.\textsuperscript{22} Importantly, such strong organic–inorganic interactions between the SDA and the framework as the ones observed for the HMI molecule in FER are expected to influence aluminum sitting by inducing it to
preferentially occupy specific framework sites near the vicinity of the SDA. Indeed, theoretical calculations performed by Gomez-Hortiguera et al. involving the relative stability of different T-sites in the presence of mixtures of SDAs suggest that cyclic amines with NH2+ groups have a stronger ability to interact with Al than TMA because stronger H-bond interactions can be developed with the negative charge associated with the incorporation of Al atoms.6 Thus, the specific location and relative orientation of the cyclic amine in the zeolite framework will be responsible for biasing the Al distribution toward a particular T-site. In this case, the size difference between HMI and Pyr has a tremendous effect on the aluminum distribution in FER.

A more complete understanding and controlling of the structure-function between SDAs and aluminum distribution in zeolite materials continues to be a subject of interest. The work of Perez-Pariente and co-workers and the results shown here demonstrate that ferrierite appears to be a good zeolite type to investigate further the mechanistic details of how SDAs can alter Al site distributions.

4. Conclusions

The experimental design for the synthesis of materials with the FER topology using three differently sized cyclic amines (Pyr, HMI, and DAB) revealed that low Si/Al ratios and concentrated reaction mixtures are more favorable for the crystallization of the correct phase. Increasing the size of the cyclic amine or decreasing the Al content leads to the crystallization of other phases or the creation of excessive amounts of connectivity defects. Interestingly, TMA plays an important role in the crystallization, thereby allowing the use of a large cyclic amine, such as HMI, to synthesize FER when used in conjunction with TMA cations. Probe reactions and pyridine accessibility tests showed that the particular combination of SDAs used strongly influenced the distribution of acid sites within the framework of FER. Using Pyr, in the presence or absence of TMA cations, generated materials with acid sites mostly within the 8-MR channels, whereas using HMI in conjunction with TMA cations generated materials with acid sites located mostly within the 10-MR channels. Variable-temperature NMR studies indicated that very strong electrostatic interactions exist between cyclic amines used as SDAs and the framework, thereby making it possible for the amine to change the distribution of active sites within the zeolite depending on its physicochemical properties and its relative location/orientation within the zeolite’s framework.

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Supporting Information Available: Representation of the FER structure, XRD patterns of the synthesized materials, and thermogravimetric analysis of the fully crystalline ferrierite materials. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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