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Synthesis and characterization of Fe- and [Fe,Al]-MCM-22 zeolites

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Abstract

The synthesis of Fe-MCM-22 zeolite is reported for the first time. Its structure and characteristics are similar to those of the MCM-22 zeolite. The aluminum is in a framework tetrahedral position in the [Fe,Al]-MCM-22 samples. The white color of the samples, the increase of the $^{29}$Si and $^{27}$Al NMR linewidths with increasing Fe content and the constancy of the (Fe+Al)/u.c. values all suggest that Fe is also incorporated in tetrahedral position of the framework.

Keywords: Characterization; MCM-22; Iron; Synthesis; Zeolite

1. Introduction

MCM-22 is synthesized under hydrothermal conditions using an organic template (generally hexamethyleneimine) and inorganic cations [1,2]. The hexagonal structure contains two different independent porous systems. The first consists of a two-dimensional sinusoidal channel system, accessible through 10-ring apertures. The layers containing this channel system are linked together by oxygen bridges forming large supercages characterized by 12-ring apertures of 7.1 Å inner free diameter and an inner height of 18.2 Å [3,4].

In recent years the properties of MCM-22 have been thoroughly investigated [5–7]. Dealuminated acid forms of MCM-22 have been characterized, concluding that the acidic properties are very similar to a H-ZSM-5 zeolite [6]. Synthesis parameters for the preparation of MCM-22 zeolite have been optimized. Only a low Si/Al ratio is convenient for the synthesis of pure MCM-22 [7].

$^{27}$Al and $^{29}$Si MAS NMR studies on as-synthesized and dealuminated samples revealed that the framework silicon and aluminium atoms are located on at least five crystallographically non-equivalent tetrahedral (T) sites [6]. Certain $^{29}$Si NMR lines were characterized by T sites that are distant from template molecules [8].

Catalytic properties, cracking of alkanes, isomerization of m-xylene, hydroisomerization of n-decane, etc. were also studied but they are only mentioned in this context.

In this paper we report for the first time the synthesis and characterization of Fe-MCM-22 zeolite. While this paper was being examined by the referees a short communication appeared in the literature [9].
Two different methods of synthesis are necessary in order to obtain [Fe,Al]-MCM-22 and pure [Fe]-MCM-22, respectively. For example, pure [Fe,Al]-MCM-22 was obtained by mixing 0.31 g of Al(OH)₃ (Platz and Bauer), 6.4 g of NaOH (Carlo Erba, 30% weight solution in water) and 7.2 g of fumed SiO₂ (Serva) in 64.8 g of distilled water, so obtaining a solution named A. At the same time, 2.58 g of Fe(NO₃)₃·9H₂O (Merck) was dissolved in 32.4 g of distilled water, forming the solution named B. After complete homogenization solution B was added drop by drop to solution A. Finally, the synthesis mixture was obtained by adding 5.95 g of hexamethylenimine (HMI, Aldrich). The experimental protocol is similar to that used for the preparation of ferrilisicate ZSM-5 zeolites [9-12]. For the procedure of synthesis reported here, white [Fe,Al]-MCM-22 (samples 2, 3, 4, see Table 1) products were obtained and brown [Fe]-MCM-22 (sample 5). The general composition of the gels was: 6Na₂O–30SiO₂–aAl₂O₃–6Fe(NO₃)₃–HMI–1350H₂O with a = 0, 0.2, 0.5 and 0.8 and b = 2, 1.6, 1 and 0.4, respectively. (Note that Al₁ + Fe = 2 in the gel.) A white crystalline sample of [Fe]-MCM-22 (sample 1, Table 1) was synthesized using the following procedure: 2.58 g of Fe(NO₃)₃·9H₂O and 7.2 g of fumed SiO₂ were added to 64.8 g of distilled water in order to obtain an iron silicate gel. Simultaneously, 6.4 g of NaOH (30% weight solution in water) was added to 32.4 g of distilled water. This solution was added drop by drop to the iron silicate gel and, after complete homogenization, 5.95 g of hexamethylenimine (Aldrich) was mixed, obtaining the final synthesis mixture: a = 0 and b = 1.6 in the gel.

Syntheses were carried out in PTFE autoclaves under dynamic conditions (33 rounds per minute) at a temperature of 150°C. The crystallinity of the samples was determined by comparing the intensity of the peaks in X-ray diffraction spectra with the reference spectrum of an MCM-22 sample previously synthesized and taken as standard. X-ray diffraction spectra (d = 3.42 or 26.1°) for the as-synthesized and calcined samples were collected on a Philips PW1710 diffractometer. A Cu Kα lamp was powered with 40 kV and 20 mA. Data were acquired in the 2θ range 5–40° with a step size of 0.02° and a step time of 5 s.

Samples 2, 3 and 4 exhibit 100% crystallinity after 7 days of synthesis of the reaction mixture. Samples 1 and 5 show complete crystallization only after 11 days. In Table 1 the reaction mixture ratios are reported.

Samples were calcined in dry air flow of 10 cm³/min at a temperature of 600°C for 6 h. The heating rate was 1°C/min.

Measurements of nitrogen adsorption at 77 K were carried out using a Micromeritics ASAP 2010 apparatus. About 80 mg of the calcined sample was degassed at 473 K and ~10⁻⁸ mmHg before the acquisition of data. Thermal analysis (DSC and TG) was carried out using a Netsch Model STA 400. The samples were run from room temperature to 800°C at a rate of 10°C/min under 15 cm³/min flow of dry air.

Atomic absorption analyses were carried out with a Shimadzu AA-660 spectrometer. About 200 mg of the calcined samples was dissolved with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al+Fe</th>
<th>Fe/Al</th>
<th>OH/tet.</th>
<th>Na/tet.</th>
<th>HMI/tet.</th>
<th>H₂O/tet.</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>8</td>
<td>0.38</td>
<td>0.38</td>
<td>0.48</td>
<td>42.9</td>
<td>White</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>4</td>
<td>0.375</td>
<td>0.375</td>
<td>0.47</td>
<td>42.2</td>
<td>White</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1</td>
<td>0.375</td>
<td>0.375</td>
<td>0.47</td>
<td>42.2</td>
<td>White</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>0.25</td>
<td>0.375</td>
<td>0.375</td>
<td>0.47</td>
<td>42.2</td>
<td>White</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>8</td>
<td>0.375</td>
<td>0.375</td>
<td>0.47</td>
<td>42.2</td>
<td>Brown</td>
</tr>
</tbody>
</table>

*a tet = moles Si + moles Al + moles Fe.*
5 ml of HF and 2 ml of H$_2$SO$_4$ and diluted in distilled water at the desired volume.

EPR spectra were reported at room temperature on a Bruker BER-420 spectrometer with a TE102 rectangular cavity.

The NMR spectra were recorded either on a Bruker MSL400 or on a CXP200 spectrometer. For $^2$Si (39.7 MHz), a 6 μs ($\theta = \pi/2$) pulse was used with a repetition time of 6.0 s. For $^{29}$Al (104.3 MHz), a 1.0 μs ($\theta = \pi/12$) pulse was used with a repetition time of 0.1 s. For $^{13}$C (50.3 MHz), a 15 μs ($\theta = \pi/2$) pulse was used with proton high power decoupling.

For IR studies, thin self-supporting wafers of each sample were prepared and outgassed under vacuum, in a home-made cell, at temperatures of 550°C for 3 h. The IR spectra were taken on a FT-IR Bruker IF728 with a resolution of 2 cm$^{-1}$.

The ion exchange experiments were carried out as follows: 0.5 g of the calcined product was treated three times with a 1 M NH$_4$NO$_3$ aqueous solution (10 ml solution/g of solid) at 80°C. After each ion exchange the solid was filtered and washed with distilled water. The NH$_4$ form was calcined in air at 550°C for 6 h. The so-obtained H form of the products was ion exchanged with a 1 M KCl solution following the same procedure as the first exchange. The K form of the microporous solid was dried for 12 h at 120°C.

Transmission Mössbauer spectroscopy was also used to determine the site occupied by iron. The technique provides information about the local environment of the $^{57}$Fe nuclei randomly distributed throughout the sample by measuring the perturbation of nuclear levels resulting from the interaction with local, internal magnetic fields and with the external electric field. The Mössbauer measurements were made using a $^{57}$Co source in a Rh matrix with an activity of 50 mCi. The specimen of interest was placed between the source and a Si(Li) detector where 14.4 keV γ rays resulting from the recoilless resonant absorption of $^{57}$Fe nuclei within the specimen were detected.

3. Results and discussion

The X-ray powder diffractogram shows clearly that the as-synthesized solid has the structure of MCM-22 zeolite [Fig. 1(a)]. Tables 2 and 3 show the comparison between the line positions and their relative intensities for the sample MCM-22 and the literature data [1]. Before calcination most of the lines are broad and overlap. The calcined Fe-MCM-22 sample also shows the characteristics of calcined MCM-22 [5] [Fig. 1(b) and Tables 2 and 3].

SEM photographs of the as-synthesized Fe-MCM-22 samples 2, 3 and 5 are shown in Fig. 2. They are very similar to those reported for the MCM-22 zeolite samples [7,13]. The thin platelets of ca. 1–2 μm diameter frequently form spherical aggregates of ca. 10–15 μm and the morphology does not depend on the Fe content. Calcination of the samples did not affect the morphology of the crystals.

In Table 4 are reported the content of iron, aluminum and sodium determined by atomic absorption and the content of the organic molecule trapped in the zeolite channels determined by thermogravimetric analysis. The values are expressed in moles per 100 g of activated samples.

![Graph](image-url)
Table 2
Comparison between X-ray powder diffraction patterns of as-made sample 3 and precursor MCM-22

<table>
<thead>
<tr>
<th>As-made</th>
<th>MCM-22*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d(hkl)$</td>
<td>$I_{rel}$</td>
</tr>
<tr>
<td>13.63</td>
<td>57.6</td>
</tr>
<tr>
<td>12.51</td>
<td>70.9</td>
</tr>
<tr>
<td>11.30</td>
<td>51.9</td>
</tr>
<tr>
<td>9.17</td>
<td>48.4</td>
</tr>
<tr>
<td>8.94</td>
<td>34.7</td>
</tr>
<tr>
<td>6.76</td>
<td>29.7</td>
</tr>
<tr>
<td>6.08</td>
<td>28.3</td>
</tr>
<tr>
<td>4.44</td>
<td>33.3</td>
</tr>
<tr>
<td>4.08</td>
<td>57.4</td>
</tr>
<tr>
<td>3.95</td>
<td>58.8</td>
</tr>
<tr>
<td>3.79</td>
<td>48.0</td>
</tr>
<tr>
<td>3.58</td>
<td>48.2</td>
</tr>
<tr>
<td>3.44</td>
<td>100</td>
</tr>
<tr>
<td>3.39</td>
<td>53.8</td>
</tr>
<tr>
<td>3.07</td>
<td>31.2</td>
</tr>
<tr>
<td>2.69</td>
<td>29.8</td>
</tr>
<tr>
<td>2.38</td>
<td>29.7</td>
</tr>
<tr>
<td>2.34</td>
<td>27.3</td>
</tr>
</tbody>
</table>

* From Ref. [5].

Table 3
Comparison between X-ray powder diffraction patterns of calcined sample 5 and calcined MCM-22

<table>
<thead>
<tr>
<th>Calcined</th>
<th>MCM-22 calcined*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d(hkl)$</td>
<td>$I_{rel}$</td>
</tr>
<tr>
<td>12.34</td>
<td>71.0</td>
</tr>
<tr>
<td>11.07</td>
<td>50.3</td>
</tr>
<tr>
<td>8.95</td>
<td>58.3</td>
</tr>
<tr>
<td>6.16</td>
<td>55.8</td>
</tr>
<tr>
<td>5.34</td>
<td>37.7</td>
</tr>
<tr>
<td>4.38</td>
<td>36.5</td>
</tr>
<tr>
<td>3.91</td>
<td>61.3</td>
</tr>
<tr>
<td>3.75</td>
<td>45.9</td>
</tr>
<tr>
<td>3.36</td>
<td>40.4</td>
</tr>
<tr>
<td>3.42</td>
<td>100</td>
</tr>
<tr>
<td>3.30</td>
<td>43.6</td>
</tr>
<tr>
<td>3.21</td>
<td>40.5</td>
</tr>
<tr>
<td>3.06</td>
<td>28.2</td>
</tr>
<tr>
<td>2.68</td>
<td>28.4</td>
</tr>
<tr>
<td>2.37</td>
<td>26.4</td>
</tr>
<tr>
<td>2.34</td>
<td>25.2</td>
</tr>
</tbody>
</table>

* From Ref. [5].

The ratio of the amount of HMI decomposed at high temperature to that decomposed at low temperature varies from 1/0.65 to 1/1.2. The low temperature HMI species were shown to occupy the interlayer supercages in MCM-22 zeolite, while the high temperature HMI species are occupying the intralayer zig-zag channels [5]. The HMI/u.c. values vary from 9.2 to 9.6. The occupation of the supercages is characterized by 3.9–5.8 HMI/u.c., while the intralayer occupancy varies from 4.3 to 5.8. (These values were computed from a formula weight of one unit cell equal to 4825 given in Ref. [5].) As the (Fe + Al)/u.c. values are close to 4.3 and the Na/u.c. values are only equal to 0.14 (or 0.44), almost half of the HMI species have to be in the protonated form neutralizing the framework negative charges.

The two different HMI species cannot be shown by the $^{13}$C NMR spectrum, because it is not well resolved due to the presence of the paramagnetic...
Fe(III) in the framework (Fig. 4). Note that only the $^{13}$C NMR spectrum of the low Fe-containing sample 4 could be measured.

The Al atoms are well introduced into the structure in a tetrahedral form. Indeed, the chemical shift of ca. 54 ppm characterizes tetrahedral species of Al(OSi)$_4$ configuration (Fig 5 and Table 5). It is not possible to detect different Al species in the structure, as was the case for MCM-22 zeolite [5,6], because of the line broadening due to the Fe(III) species, although some asymmetry can be recognized in the spectrum.

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe$^a$ (× 10$^{-2}$ mol%)</th>
<th>Al$^a$ (× 10$^{-2}$ mol%)</th>
<th>Si/Al + Fe</th>
<th>Na$^a$ (× 10$^{-2}$ mol%)</th>
<th>K$^+$ (Al + Fe) (%)</th>
<th>Fe$_{eq}$ (× 10$^{-2}$ mol%)</th>
<th>HMI$^b$ (× 10$^{-2}$ mol%)</th>
<th>DSC peaks (°C)</th>
<th>HMI$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8</td>
<td>—</td>
<td>19.9</td>
<td>0.28</td>
<td>0.40</td>
<td>40</td>
<td>19</td>
<td>377.6–8</td>
<td>466.3–11</td>
</tr>
<tr>
<td>2</td>
<td>7.4</td>
<td>1.6</td>
<td>17.1</td>
<td>0.56</td>
<td>0.48</td>
<td>36</td>
<td>20</td>
<td>384.1–10</td>
<td>479.4–10</td>
</tr>
<tr>
<td>3</td>
<td>5.3</td>
<td>4.1</td>
<td>16.4</td>
<td>0.91</td>
<td>0.71</td>
<td>49</td>
<td>20</td>
<td>385.7–9</td>
<td>490.8–11</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>6.3</td>
<td>15.8</td>
<td>0.30</td>
<td>0.83</td>
<td>10</td>
<td>20</td>
<td>384.4–11</td>
<td>502.8–9</td>
</tr>
<tr>
<td>5</td>
<td>9.3</td>
<td>—</td>
<td>16.5</td>
<td>0.69</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>376.7–8</td>
<td>464.6–12</td>
</tr>
</tbody>
</table>

$^a$ Atomic absorption.

$^b$ Thermal gravimetry.
in competition and the introduction of a total of 4.3 = (Fe + Al)/u.c. is favored in our reaction conditions.

The 29Si NMR spectra of the samples are centered at ca. −110 ppm (Fig. 7 and Table 6). They do not show any fine structure due to the presence of paramagnetic Fe(III) species, which lead to line broadening. The NMR linewidth increases linearly with increasing Fe content of the samples (Fig. 5). The increase is much smaller for the calcined samples suggesting that part of the Fe(III) ions have left the zeolite framework.

The color of the as-made samples is white except for sample 5, where some brownish color was detected, showing the presence of extraframework Fe-containing species.

EPR results were used to characterize the Fe species in the zeolite samples. One typical spectrum of sample 3 is recorded in Fig. 8 and Table 7 shows the $g$ values of the various Fe-containing species. Despite the great importance of the EPR technique in characterizing the various paramagnetic species, no clear-cut interpretation has been given until now. For example, the species characterized by a $g$ factor of 2.0 are considered octahedral [14,15], while such species are described as framework tetrahedral species in Ref. [16]. The signal at $g = 2.3$ is considered as the $g_z$ contribution of the octahedral species [14,15]. Finally, at $g = 4.3$ can be found the framework tetrahedral species, the intensity of which is higher at low temperatures [14]. This species can be included in the EPR signal observed at low magnetic field, where only the middle of the spectrum was computed to be between 4.23 and 4.56. The latter species are considered as deformed tetrahedral species.

The Mössbauer spectra of the Fe-MCM-22 as-made samples confirm the presence of tetrahedral Fe(III) ions (Table 8 and Fig. 9). The spectra of samples 1 [Fig. 9(a)] and 5 [Fig. 9(b)] were decomposed by attempting to use two doublets, one for the tetrahedral configuration of Fe, and one for the octahedral configuration. The resulting parameters are listed in Table 8. The isomer shift of tetrahedrally coordinated Fe(III) is equal to 0.18 mm/s for both samples. Octahedrally coordinated Fe(III) is detected in sample 5 and is characterized by higher isomer shift (0.32 mm/s) and quadrupolar splitting (0.93 mm/s). These
values are in good agreement with those reported in the first genuine publication by Meagher et al. [17] and later confirmed by others [18–20]. It is
Fig. 7. $^{29}$Si NMR spectra of [Fe,Al]-MCM-22 samples 3 and 4. Sample 3 as-made (a); sample 4 as-made (b); sample 3 calcined (c); sample 4 calcined (d).

Table 6

$^{29}$Si NMR data of precursor Fe-MCM-22 samples (a) and calcined Fe-MCM-22 samples (b)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ (ppm)</th>
<th>$\Delta H$ (Hz)</th>
<th>$\delta$ (ppm)</th>
<th>$\Delta H$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-113$</td>
<td>$400$ (1000)</td>
<td>$-113$</td>
<td>$400$ (1000)</td>
</tr>
<tr>
<td>2</td>
<td>$-106$</td>
<td>$1300$</td>
<td>$-109$</td>
<td>$800$</td>
</tr>
<tr>
<td>3</td>
<td>$-108$</td>
<td>$1100$</td>
<td>$-110$</td>
<td>$750$</td>
</tr>
<tr>
<td>4</td>
<td>$-110$</td>
<td>$850$</td>
<td>$-109$</td>
<td>$700$</td>
</tr>
<tr>
<td>5</td>
<td>$-108$</td>
<td>$1500$</td>
<td>$-110$</td>
<td>$1000$</td>
</tr>
</tbody>
</table>

interesting to note that despite the brownish color of sample 5, the amount of tetrahedral Fe(III) is still high (some 87%).
Table 7: FT-IR and ion exchange measurements were carried out on the calcined samples. Indeed, both techniques are very important to assess the framework or extraframework position of the M(III) elements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>g</th>
<th>3.463</th>
<th>2.307</th>
<th>1.985</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.268</td>
<td>2.440</td>
<td>2.017</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.559</td>
<td>2.440</td>
<td>2.017</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.497</td>
<td>2.449</td>
<td>2.011</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4.381</td>
<td>2.437</td>
<td>2.012</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.464</td>
<td>2.451</td>
<td>2.160</td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Mössbauer isomer shift (IS), quadrupole splitting (QS) and relative intensities ($I_{rel}$) of Fe-MCM-22 as-made samples taken at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>$I_{rel}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(III)$_{tetra}$</td>
<td>0.18</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>Fe(III)$_{octa}$</td>
<td>0.18</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>Fe(III)$_{octa}$</td>
<td>0.32</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The presence of the 3640 cm$^{-1}$ band in sample 1 strongly suggests that Fe(III) occupies a tetrahedral framework position in this Fe-MCM-22 material [9]. Fe-MCM-22 sample 5 also contained tetrahedral framework Fe(III) (see for example the above Mössbauer spectra), the calcined sample does not show clearly the presence of Fe(III) in the framework. The higher wavenumber observed for Si(OH)$_2$Fe with respect to Si(OH)$_2$Al groups [9] also suggests that the Brønsted acidity of Fe-MCM-22 is much weaker than that of Al-MCM-22.

The ion exchange capacities are very interesting.

FT-IR and ion exchange measurements were carried out on the calcined samples. Indeed, both techniques are very important to assess the framework or extraframework position of the M(III) elements.

The introduction of M(III) elements into the tetrahedral framework of zeolites generates Si(OH)$_2$M Brønsted acid sites. This is clearly shown in Fig. 10, where the 3800–3400 cm$^{-1}$ region is expanded. The position of the maximum of the 3620 cm$^{-1}$ band shifts to higher wavenumbers when the Al content of the sample decreases. The values of the maxima are 3622 cm$^{-1}$ for sample 4, 3627 cm$^{-1}$ for sample 3, 3639 cm$^{-1}$ for sample 2 and 3640 cm$^{-1}$. The band at ca. 3730 cm$^{-1}$ stems from internal SiOH groups. The presence of the 3640 cm$^{-1}$ band in sample 1 strongly suggests that Fe(III) occupies a tetrahedral framework position in this Fe-MCM-22 material [9]. Fe-MCM-22 sample 5 also contained tetrahedral framework Fe(III) (see for example the above Mössbauer spectra), the calcined sample does not show clearly the presence of Fe(III) in the framework. The higher wavenumber observed for Si(OH)$_2$Fe with respect to Si(OH)$_2$Al groups [9] also suggests that the Brønsted acidity of Fe-MCM-22 is much weaker than that of Al-MCM-22.

The ion exchange capacities are very interesting.
The $K/(Al+Fe)$ ratios are reported in Table 4. All show that a great part of the Fe is in a tetrahedral framework position in the Fe-MCM-22 zeolites. The Brønsted acidity and the ion exchange capacity show that a non-negligible part of Fe(III) remains in tetrahedral framework position even after air calcination of the samples. The synthesis of Fe-containing MCM-22 could open new routes for catalysis involving oxido-reduction reactions.

### Acknowledgements

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### References


### Table 9

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V$ (cm$^3$/g)</th>
<th>$d$ (Å)</th>
</tr>
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<tr>
<td>1</td>
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<td>0.221</td>
<td>12.64</td>
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<tr>
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<td>12.65</td>
</tr>
<tr>
<td>3</td>
<td>308</td>
<td>0.236</td>
<td>12.65</td>
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<tr>
<td>5</td>
<td>334</td>
<td>0.241</td>
<td>12.91</td>
</tr>
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</table>

In conclusion, the constancy of the $(Fe+Al)/u.c.$ values in the as-made samples, the white color of the as-made samples, the Mössbauer spectra, the dependence of both the $^{27}$Al and $^{29}$Si NMR linewidths on the Fe content of the samples all show that a great part of the Fe is in a tetrahedral framework position in the Fe-MCM-22 zeolites. The Brønsted acidity and the ion exchange capacity show that a non-negligible part of Fe(III) remains in tetrahedral framework position even after air calcination of the samples. The synthesis of Fe-containing MCM-22 could open new routes for catalysis involving oxido-reduction reactions.