TUNING ACID SITES DISTRIBUTION OF ZEOLITE FERRIERITE
AND IMPACT ON ITS CATALYTIC PERFORMANCE

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ABSTRACT
Zeolite ferrierite has been synthesized following our synthesis strategy to control the distribution of acid sites in the zeolite framework. Different combinations of two templates have been employed as structure directing agents, in the absence of inorganic cations. The amount of bridging OH groups inside the ferrierite cavity, accessible only through 8-ring windows, relative to that in the 10-ring channels, has been found to strongly depend on the specific combination of structure directing agents employed in the synthesis. A good correlation between the acid sites accessibility and catalytic activity has been found. The catalytic performance of ferrierite samples prepared following our synthesis strategy has advantages compared to that of ferrierite obtained following the conventional procedure, employing pyrrolidine as structure directing agent, and in the presence of sodium. This synthesis route may be extended to other suitable zeolite materials.

Keywords: ferrierite, acid sites distribution, n-butene isomerization, combination of templates.

INTRODUCTION
The activity and selectivity of a zeolite in a catalytic reaction is the result of a combination of several factors, the microporous structure and the number and distribution of acid sites among them. Zeolite ferrierite possesses medium-pore 10-ring channels and smaller cavities, accessible through 8-membered rings. Its complex porous structure allows for a high degree of complexity in the distribution of acid sites. We have recently developed a synthesis strategy to tailor the acid sites distribution of ferrierite based on an appropriate combination of organic molecules used as structure directing agents (SDAs) [1]. The synthesis is carried out in fluoride medium to avoid the presence of inorganic cations. Therefore, the negative charge associated to the incorporation of Al in tetrahedral sites, substituting Si, is counter-balanced exclusively by the positive charge of the organic SDAs, which allows controlling aluminum sitting. We report here the results on acid sites accessibility and catalytic activity of ferrierite samples prepared with selected combinations of organic SDAs, showing the strong impact of the different SDAs on the properties of the final product. M-xylene and n-butene isomerization reactions are studied, the latter being of applied interest, as ferrierite is employed at the industrial scale.

EXPERIMENTAL
The molar composition of the synthesis gels was: 0.06 SDA1: 0.48 SDA2: 0.48 HF: 0.03 Al2O3: 0.96 SiO2: 4.6H2O, SDA1: tetramethylammonium (TMA); SDA2: 1-benzyl-1-methyl-pyrrolidinium (BMP) or pyrrolidine (PIRR). A synthesis using pyrrolidine as the only SDA was also performed (SDA1=SDA2=PIRR). The samples will be referred to as FER-BMP-TMA, FER-PIRR, FER-PIRR-TMA, where the word FER is followed by the names of the organic templates employed in each case. A ferrierite sample was prepared in alkaline medium in the presence of Na+ as a reference (FER-1H). Solid products were characterized by XRD (PANalytical X’Pert PRO-MPD diffractometer, CuKα radiation), thermal analysis (Perkin-Elmer TGA7 instrument, heating rate 20 °C/min, air flow 30 mL/min, temperature
range 20-900 °C), chemical CHN analysis (Perkin-Elmer 2400 CHN analyzer), ICP-AES (Optima 3300 DV Perkin-Elmer) and SEM/EDX (Jeol JSM 6400 Philips XL30, operating at 20 kV). Acid sites distribution between the ferrierite cavity and the 10-ring channel has been determined by FTIR measurements with pyridine as probe molecule, following the procedure described by Witchterlová et al., based on the known constrained access of pyridine to the ferrierite cavity [2]. Transmission FTIR spectra were recorded using a Nicolet 5ZDX FTIR spectrometer provided with an MCT detector. The samples were pressed into self-supporting wafers, placed in a glass cell and activated in vacuum at 400°C for 8 h. The sample was contacted with pyridine vapour (8 Torr) at 150°C and subsequently degassed at 150 °C for 30 min, and then the FTIR spectrum was recorded. Pyridine was again dosed and the cell was evacuated for 30 min prior to recording the FTIR spectrum. A series of FTIR spectra at increasing total contact time of the sample with pyridine were obtained. M-xylene isomerization was carried out in a fixed bed reactor at 350 °C and atmospheric pressure, with molar ratio N2/m-xylene = 5.3. The isomerization of n-butene was performed in a fixed bed reactor, at 400 °C and atmospheric pressure, with molar ratio N2/butene = 4 and WHSV = 25 h⁻¹.

RESULTS AND DISCUSSION

Ferrierite zeolite was the product obtained in all the three different syntheses performed, although slightly broader peaks were observed in the XRD pattern of the sample FER-BMP-TMA [3]. The Si/Al molar ratio of the solids was ca. 15.5, which corresponds to an aluminum content of about 2.2 Al atoms per unit cell. The SEM images showed that the samples FER-PIRR and FER-PIRR-TMA crystallize as aggregates (ca. 10×22 μm) composed of smaller plate-like crystals, whereas the sample prepared with BMP+TMA crystallized as needles of about 7 μm in length. Clear differences were found in the accessibility of pyridine to the acidic hydroxyl groups depending on the SDAs employed in the synthesis [4]. This can be associated with the relative tendency of the SDA located in the FER-cage to pump Al to this cage, which may lead to a high proportion of acid sites located in non-accessible positions of the ferrierite cavity, decreasing that of sites exposed to the 10-ring channel. Thus, FER channel can possess much higher Si/Al ratio than the average value in the crystal. The differences in acid site distribution have a strong impact in the catalytic behavior of the samples. The activity in m-xylene isomerization increases with the relative population of acid sites in the 10-ring channel, accessible to m-xylene. The same trend is observed for isomerization of n-butene to isobutene [5], being the most active sample at short reaction times the conventional FER-1H sample. However, its deactivation is fast (Fig. 1, up): at 720 min, its activity decreases by 70 %, whereas for the samples prepared following our synthesis strategy, this activity decay is significantly slower. Besides, these samples show a much higher selectivity to isobutene (> 90 %), compared to the conventional sample (Fig. 1, down), as a result of their low tendency to yield the by-products formed in the dimerization/oligomerization of butene followed by cracking [5]. This is probably due to their low proportion of acid sites in the accessible positions of the 10-ring channel, which would hinder non-selective reactions, thus increasing the resistance to deactivation of these catalysts. Further studies by measuring CO₂ adsorption heats showed consistent results regarding acid sites distribution between the non-accessible cavity locations and the more accessible 10-ring channel [6]. These results constitute another indirect evidence for the differences in acid sites distribution among our ferrierite samples. In order to obtain direct proof of these differences, ²⁷Al MQ MAS NMR measurements were recently performed [7]. Interestingly, they show two separate signals on the isotropic chemical shift projection, which would correspond to Al atoms in two different chemical environments, although we cannot assign each signal to Al atoms in a particular T site. To our knowledge, this is unique evidence of the possibility of
modifying, and eventually tailoring, the distribution of acid sites in zeolites, a long sought target in zeolite science. Besides, our synthesis route is reproducible, since ferrierite samples have been prepared in the same synthesis conditions in the laboratory of Prof. Davis (Caltech, U.S.A.), obtaining similar results [8].

Table 1. Accessibility of the Brønsted acid sites to pyridine found in the IR adsorption experiments for the samples synthesised with the different combinations of SDAs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of acid sites accessible to pyridine</th>
</tr>
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<tbody>
<tr>
<td>FER-PIRR-10d</td>
<td>10</td>
</tr>
<tr>
<td>FER-PIRR-TMA-10d</td>
<td>18</td>
</tr>
<tr>
<td>FER-BMP-TMA-20d</td>
<td>36</td>
</tr>
<tr>
<td>FER-1H*</td>
<td>52</td>
</tr>
</tbody>
</table>

*: Ferrierite sample obtained following the conventional synthesis procedure.

Fig. 1. \( n \)-butene conversion (up) and selectivity to isobutene (down) vs. time on stream for the samples prepared with the different combination of SDAs, and different heating times (days).
CONCLUSION

We have designed a synthesis strategy that allows gaining an effective control on acid site distribution in the zeolite ferrierite framework. The amount of bridging OH groups inside the ferrierite cavity, accessible only through 8-ring windows, relative to that in the 10-ring channels, has been found to strongly depend on the specific combination of SDAs employed in the synthesis. A good correlation between the acid sites accessibility and catalytic activity has been found. This synthesis strategy may be extended to other suitable zeolite materials.

ACKNOWLEDGEMENT

A.B.P. is thankful for the support of the European Community under a Marie Curie Intra–European Fellowship for Career Development (7th Framework Programme). Funding from the Spanish Ministry of Economy (project MAT2012–31127) is greatly acknowledged.

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