The synthesis of SSZ-39 using mixtures of isomeric, organic structure directing agents

Michiel Dusselier1, Joel E. Schmidt1, Roger Moulton2, Barry Haymore2, Mark Hellums2 and Mark E. Davis1*
1Chemical Engineering, California Institute of Technology Pasadena, CA 91125, USA
2Sachem, Inc., 821 East Woodward St., Austin, TX 78704 USA
*mdavis@cheme.caltech.edu

Introduction

The AEI molecular sieve topology has 8 membered ring (MR) openings leading to a 3D channel system with symmetric pores of 3.8 Å and cages of 7.3 Å in diameter [1]. Lately, there is growing interest in such 8MR materials for environmental catalysis and gas separations [2]. Besides the methanol-to-olefins (MTO) reactions, an important application of aluminosilicate versions of small pore zeolites is the selective catalytic reduction (SCR) of NOx in flue and exhaust gases [3]. The current catalyst for mobile vehicle use is Cu-SSZ-13 zeolite (CHA topology). Recently, Moliner et al. demonstrated superior SCR and improved stability over Cu-SSZ-13 with Cu-SSZ-39, an aluminosilicate with the AEI topology [4]. The synthesis of SSZ-39 is limited to tight control of the inorganic compositions of the gel and the need for an organic structure-directing agent (SDA). Here, we show the synthesis of SSZ-39 using isomeric mixtures of SDAs that might provide lower costs routes to the production of SSZ-39.

Materials and Methods

The organic SDAs were prepared by Sachem Inc. or synthesized from lupetidines. 13C-CP MAS spectra were recorded on a Bruker 500 MHz spectrometer. SEM imaging and Si/Al determination were performed on a ZEISS 1550 VP microscope with an energy dispersive spectrometer. X-ray diffraction (XRD) was collected on a Rigaku MiniFLEX II. In a general synthesis, the SDA was combined with additional base and water in a 23 mL-Teflon-lined reactor. Then, a silica source was added (sodium silicate, PQ) as well as faujasite CBV500 (Zeolyst) for providing a source of alumina. The stirred mixture was then sealed and placed in a rotating oven at 140 °C (typical molar SDA:Si ratio of 0.14).

Results and Discussion

Lupetidines are synthesized by hydrogenation of lutidines. The separation of isomers of these organics can be highly determining to the cost of the overall resulting SDA and zeolite. Using diastereoisomer as well as structural isomer mixtures of these quaternized SDAs, shown in Figure 1, pure SSZ-39 could be made over a range of isomer ratios as listed in Table 1. The syntheses with different diastereoisomer mixtures had identical kinetics, yields and Si/Al ratios, and yielded pure SSZ-39 according to their XRD patterns.

Both isomers were found to be incorporated in the zeolite structure as observed by solid state NMR results (Figure 2). 13C-CP MAS NMR is able to distinguish between cis and trans isomers of the SDAs within the zeolite. With the structural isomer SDA mixture, SSZ-39 synthesis was also possible, but the zeolite preferentially incorporated the cis-2, isomer over the cis-3,5. Since syntheses with the pure cis-2,6 isomer (not shown) tend to favor mordenite formation over SSZ-39, it is possible that the cis-3,5 is preferentially involved in nucleation.

Table 1. Synthesis of SSZ-39 with mixed isomers of quaternized lupetidines

<table>
<thead>
<tr>
<th>Si</th>
<th>Al</th>
<th>SDA mixture</th>
<th>Ratio</th>
<th>NaOH</th>
<th>H2O</th>
<th>Time</th>
<th>Result*</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.067</td>
<td>cis-3,5:trans-3,5</td>
<td>98:2</td>
<td>0.51</td>
<td>28</td>
<td>6days</td>
<td>SSZ-39</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>0.067</td>
<td>cis-3,5:trans-3,5</td>
<td>75:25</td>
<td>0.51</td>
<td>28</td>
<td>6days</td>
<td>SSZ-39</td>
<td>6.3</td>
</tr>
<tr>
<td>1</td>
<td>0.067</td>
<td>cis-3,5:trans-3,5</td>
<td>50:50</td>
<td>0.51</td>
<td>28</td>
<td>6days</td>
<td>SSZ-39</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>0.033</td>
<td>cis-3,5:trans-3,5</td>
<td>98:2</td>
<td>0.61</td>
<td>28</td>
<td>5days</td>
<td>SSZ-39</td>
<td>8.8</td>
</tr>
<tr>
<td>1</td>
<td>0.067</td>
<td>cis-3,5: cis-2,6</td>
<td>49:51</td>
<td>0.54</td>
<td>28</td>
<td>3.7days</td>
<td>SSZ-39</td>
<td>6.5</td>
</tr>
</tbody>
</table>

*trace ANA impurity found in some samples

Figure 2. 13C-CP-MAS NMR of A) 48:52 cis:trans-3,5 isomer B) 48:52 cis:trans-3,5 C) SSZ-39 made with the 48:52 mixture. D) SSZ-39 made with the 98:2 mixture. c = cis, t = trans.

Significance

The synthesis of SSZ-39 is currently of great interest for use in a number of important reactions. Our results: i) show a possible cheaper route to the commercial synthesis of zeolite SSZ-39, and ii) reveal fundamental information on the structure direction of SSZ-39 using both pure and mixed isomer SDAs. Control over the synthesis of SSZ-39 renders this material available for investigation of the structure-property relationships for 8MR zeolites that show excellent performance in both MTO and SCR (LEV, SSZ-13, SSZ-16, SSZ-39).

References