Alkaline leaching for synthesis of improved Fe-ZSM5 catalysts

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Abstract

Fe-ZSM5 catalysts were fully Fe-exchanged by pretreating the parent zeolite with base a solution prior to the Fe-exchange. The catalysts prepared in this way showed very low amount of inactive FeOx and improved performance in N₂O decomposition. Alkaline leaching breaks down the zeolite crystals – which shorten the diffusional lengths – and the Fe-exchange is completed. The improved performance is related to the higher amount of Fe exchanged into the Brønsted sites.

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1. Introduction

Fe-zeolites are very active catalysts for several reactions (a.o. N₂O decomposition, SCR of NOx with hydrocarbons, benzene-to-phenol). Their application range is being spread due to the bio-mimetic approach, trying to simulate natural Fe-containing enzymes.

The most applied methods for preparing Fe-zeolites are based on ion-exchange, both gas–solid (chemical vapour deposition, CVD) [1–3] and liquid phase (wet ion-exchange, WIE) [4]. Liquid phase has the advantages of technical simplicity, less corrosive (CVD produces HCl) and probably more reproducible catalysts.

Different variants to the Feng and Hall’s protocol on ion-exchanged Fe-ZSM5 have been developed [5–10]. Despite the simplicity they still present several drawbacks: (i) low exchange degree is usually achieved on ZSM5 (much lower than for CVD) and (ii) large amounts of inactive FeOx are formed when the process is extended in time aiming to increase the exchange level.

During preparation of Fe-ZSM5 we have systematically achieved less than half of the full exchange capacity. Visualizing the zeolite’s agglomerates in Fig. 1 – top, it contains large crystals ~2 μm. Such large diffusional paths combined with the low surface diffusion coefficients for zeolites (typically 10⁻⁸ cm²/s) make the exchange rather slow. The time required to diffuse the cations along those microchannels would imply days. Extending time may pursue its full exchange. However, an undesired process – Fe(III) hydrolysis to inactive FeOx – takes place in parallel. The situation is illustrated in Fig. 1.

Higher (if not full) exchange can alternatively be achieved by shortening the diffusional lengths. That is by decreasing the particle size of the zeolite. Unlike acid leaching, which mostly removes framework Al, alkaline treatments preferentially extract Si as reported by Mobil Oil in [11]. We will make use of the desilication effect of NaOH solutions and present a new approach based on fracturing the crystals-agglomerates. The properties of the resulting Fe-(extra-)exchanged catalysts will be discussed based on the TPR data and N₂O-decomposition performance.
2. Materials and methods

2.1. Alkaline leaching and Fe-ion exchange

The zeolite was acquired from Alsi Penta (AP-SM27). It consists of an ammonium form with a Si/Al ratio of 12.5 (measured). The sample also contains some traces of Fe (470 ppm).

The alkaline treatments were carried out with a 0.2 M NaOH solution (75 ml/g zeolite). The mixture was heated at 353 K under reflux during 30 and 120 min. These periods were representative of mild and severe conditions, upon a preliminary screening. The samples were washed by filtering with deionized water, dried, and finally exchanged twice with NH4NO3 (0.5 M, 353 K for 1 h) to recover the NH4-form.

Iron was incorporated by wet-ion exchange (WIE) on the as-received sample (reference) and alkaline-modified samples (30 and 120 min). Ion-exchange was carried out at pH 2.5 for a targeted Fe loading of 2.0 wt% (close to full exchange for Fe(III)). After washing and drying, the catalysts were calcined in air at 773 K for 4 h. The modified samples are denoted afterwards as Fe-AT-30 and Fe-AT-120, where AT means alkali-treated and the number is the leaching time, in minutes.

2.2. Characterization techniques

Elemental analysis of the catalysts was done by ICP-OES (Perkin-Elmer Optima 3000DV (axial)). The morphology of the solid particles was visualized by scanning electron microscopy (SEM). Images were recorded with a Philips XL 20 microscope at 10 kV. Samples were coated with gold to improve contrast. Temperature-programmed reduction with H2 was done in a commercial Micromeritics TPD/TPR 2900 apparatus, using a high purity mixture of 10 vol% H2/Ar. Calibration was done with CuO (99.999% metal basis, Aldrich). The samples were pretreated in He at 423 K for 1 h. After cooling down, they were flushed with the reduction mixture at room temperature to get the baseline stabilized, and start the temperature program (ramping rate of 10 K/min). The gas at the reactor outlet was monitored by a TCD detector after passing through a cold trap to remove the produced water.

2.3. N2O-decomposition activity tests

Activity tests were carried out in a six-flow reactor [19] using 50 mg of catalyst particles (125–250 mm). The catalysts were tested in N2O/He (4.5 mbar N2O) at a total pressure of 3 bar for a space time of $W/F^O(N_2O) 900$ kg · s · mol$^{-1}$ (where $W$ is the catalyst mass and $F^O(N_2O)$ the molar flow of N2O in the feed). The reactor outlet was analyzed by gas chromatography (Chrompack CP 9001). Before reaction the catalysts were treated in He at 673 K for 1 h, and cooled down to the starting reaction temperature. After switching to reaction mixture (1 h stabilization time) the activity was measured.

3. Results and discussion

Two particular conditions were chosen for mild (AT-30) and severe (AT-120) leaching. We first checked
whether basic leaching is able to break down the crystals. Visualization of the samples morphology was done by SEM. Large zeolite agglomerates (2–4 µm) of different morphologies were observed for the as-received zeolite (Fig. 2A). A significant change is detected upon alkaline treatment. Large crystals were cracked down into smaller sizes < 1 µm (Fig. 2B). The long-order crystallinity of the zeolite was not altered as deduced by XRD (Fig. 3). Similar results were observed for long-time treatment (AT-120). SEM pictures therefore anticipate that diffusional limitations have been sufficiently minimized to allow full Fe-exchange.

This was confirmed by elemental analyses (ICP) in Table 1. Fully exchanged Fe-ZSM5 samples were prepared upon both alkaline pretreatments. The Si/Al decreases only after prolonged treatment. This indicates that for the AT-30 sample only a small fraction of Si atoms is involved for crystal-size reduction, not detectable by ICP. N₂-physisorption data (not shown) revealed that mesoporosity is only developed for 120-min treatment. However, it is irrelevant for the exchange process, since AT-30 treatment is sufficient to allow full exchange. For comparison, an untreated Fe-ZSM5 catalyst is included in Table 1. Its exchange capacity only reached 30% employing an excess of Fe-salt during ion-exchange.

TPR measurements gave more experimental evidence for the total exchange. Large proportions of clustered FeOₓ are detected for the unmodified Fe-ZSM5 (Fig. 4A). On the contrary, the base-modified catalysts only contained Fe-exchanged species located at 700 K (Fig. 4B and C). Therefore, the Fe is incorporated on the Brønsted exchange sites.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe target (%)</th>
<th>Fe ICP (wt%)</th>
<th>Si/Al (mol)</th>
<th>FeOₓ (wt%)b</th>
</tr>
</thead>
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<tr>
<td>ZSM-5</td>
<td>–</td>
<td>468 a</td>
<td>12.5</td>
<td>–</td>
</tr>
<tr>
<td>Fe-ZSM5</td>
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<td>0.86</td>
<td>13.4</td>
<td>30</td>
</tr>
<tr>
<td>Fe-AT-30</td>
<td>2.00</td>
<td>1.93</td>
<td>13.0</td>
<td>2</td>
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<tr>
<td>Fe-AT-120</td>
<td>2.00</td>
<td>1.98</td>
<td>10.9</td>
<td>2</td>
</tr>
</tbody>
</table>

a Concentration of Fe (ppm) found in the parent zeolite.

b Percentage calculated from TPR data.

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**Fig. 2.** Scanning electron microscopy pictures of the parent ZSM5 (A) and alkaline treatment AT-30 (B).

**Fig. 3.** XRD patterns of the parent ZSM5 (A) and base-treated AT-30 (B).

**Fig. 4.** H₂-TPR profiles of the (A) Fe-ZSM5 (un-treated), (B) Fe-AT-30 and (C) Fe-AT-120 catalysts. Conditions: 5% H₂/Ar; ramping rate, 10 K min⁻¹.
The activity of these catalysts for N\textsubscript{2}O-decomposition at 750 K is given in Fig. 5. Results with other Fe-based untreated ZSM-5 samples are also included for comparison. In agreement with TPR, an improvement in the N\textsubscript{2}O-decomposition performance was observed. The activation energy analysis does not show meaningful differences between treated and un-treated samples. Therefore, the activity increase is attributed to the larger proportion of active Fe exchanged in the zeolite matrix, as compared with the untreated catalysts. For the Fe-AT-120 sample a slightly higher activity was observed, which is ascribed to the created mesoporosity. This implies better diffusional transport through the newly formed mesochannels. However, the role is not very relevant for N\textsubscript{2}O-decomposition since the molecules involved (N\textsubscript{2}O, N\textsubscript{2} and O\textsubscript{2}) are rather small compared to the microchannels dimension.

The use of caustic washing was reported by Mobil Oil [20], and utilized afterwards as a routine method, for purifying large-crystal zeolites. Concentrated aqueous base solutions preferentially dissolve smaller crystals and amorphous fractions. Caustic treatment was then used for Al enrichment and thus enhancing their catalytic properties in acidic forms [11]. Nowadays, the applicability has been redrawn for obtaining micro-mesostructured zeolites [12–18], based on the intracrystalline nature of the porosity development as later demonstrated [17,18]. To the best of our knowledge, its use for diminishing crystal size has not been reported yet (as indicated in Fig. 2). However, our approach may not be generally applicable to full range of Si/Al. For low Si/Al, as our sample, fractioning is more favorable. A large fraction of weak Si–O–Al bonds can be the precursors for fractioning. These are not present for high silica zeolites and therefore the intracrystalline pathway is preferentially developed. On the other hand, the breaking down process can also be understood as a massive dislodgement of the crystal agglomerates by removing the (more) amorphous parts. Discrimination between both proposed mechanisms is difficult.

Summarizing, the N\textsubscript{2}O-decomposition performance for Fe-ZSM5 is improved by facilitating the Fe-exchange process without the formation of FeO\textsubscript{x}. This is achieved by a controlled base leaching prior to the WIE. Mild conditions of leaching (NaOH 0.2 M, 353 K for 30 min) allow full exchange.

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References