Short communication

Recyclable swelling solutions for friendly preparation of pillared MWW-type zeolites

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1. Introduction

Lamellar zeolites or so-called two-dimensional (2D) zeolites are a class of microporous crystalline materials whose structure is propagated in only two dimensions [1,2]. These zeolites are initially formed by a 2D lamellar zeolitic precursor, and after calcination, 2D precursors are transformed into 3D zeolites by topotactic condensation. The MCM-22 zeolite was synthesized for the first time by Mobil Oil Co. and belongs to MWW (Mobil Twenty Two) framework topology which is formed by two independent porous systems being both accessible through ten-membered rings windows. One porous system is defined by sinusoidal and bidirectional channels with 0.52 nm of internal diameter. The second porous system is based on supercavities with a free internal diameter of 0.71 nm delimited by twelve-membered rings with an internal height of 1.82 nm. The consecutive supercavities are connected between them through ten-membered rings windows [3]. Its lamellar zeolitic precursor (P)MCM-22 is formed by the stacking of individual lamellae (thickness of 2.5 nm each one) which have an elevated amount of silanol groups (≡Si-OH) on their external surface. Consequently, the connection between these lamellae is by H-bonding with a possible participation of hexamethylenimine (HMI) molecules as the structural directing agents that are occluded between the lamellae. The separation between lamellae of the (P)MCM-22 offers great versatility to generate hierarchical lamellar architectures such as pillared [4], disordered [5] and delaminated [6], which can be applied in different fields such as catalysis, separation, adsorption, purification, enzyme immobilization and environmental remediation [7–12]. In catalysis, lamellar zeolites have received increasing attention as potential materials that can replace the existing commercial zeolites [2,13–16].

Among open lamellar architectures, pillaring allows for the creation of mesopores by the stabilization of inorganic pillars between MWW lamellae [4]. Before the pillaring procedure, a swelling of (P)MCM-22 is required which involves a complex procedure where the stoichiometry is not completely established [4]. Swelling of (P)MCM-22 involves the breaking of interlamellar bonds of partially condensed silanol groups and hydrogen bonds. This requires a high pH obtained by the exchange of Br⁻ or Cl⁻ ions of the cationic surfactant hexadecyltrimethylammonium halides CTABr/Cl for OH⁻ ions by the mixing of CTABr/Cl and tetrpropylammonium or tetramethylammonium hydroxide solutions [17–19]. The swelling procedure could be carried out at elevated (80 °C) and ambient temperatures, which directly affects the integrity of lamellae [20]. Moreover, swelling/pillaring shares the same reagents (surfactant, solvent, hydroxide medium and silicate

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source) as the M41S-type mesoporous materials and an undesired formation of mesophases competitors could be formed [21]. Furthermore, the swelling/pillaring procedure is associated with high costs, labor, and volume of the reactants and wastewater production [14,22]. The high costs are related with the use of concentrated surfactant solutions (~29–40 wt%) and the expensive resins for the exchange Br⁻ or Cl⁻ ions of the surfactants for OH⁻ ions. In addition, for the swelling procedure, the weight ratio of swelling solutions/[P]MCM-22 = 29.5 generate a high volume of surfactant solution with a high pH which raises concerns about the wastewater treatment and the potential harm to ecosystem and human health [23]. Consequently, post-synthesis modification is still challenging for its larger-scale implementation. To minimize the use of starting reactants for the synthesis of porous materials, studies involving the reuse of non-reacted solutions after the separation of products for microporous and mesoporous materials, such as FAU, MFI, BEA, LTA, AIPO-34 and MCM-41 were reported, and in most cases a compensation of reactants and/or pH was necessary [24–30]. To the best of our knowledge, there are no studies involving the recycling of reactants from the post-synthetic modifications of zeolites. Herein, we explore the reuse of the swelling solution of [P]MCM-22 without complementation of reactants or pH to obtain a more economic and eco-friendly production of MWW-type pillared materials.

2. Experimental

2.1. Synthesis of MCM-22 precursor

Synthesis of [P]MCM-22 precursor was carried out with a Si/Al = 25 M ratio similar to the literature precedent [31]. For the synthesis, 0.37 g of NaOH (Sigma Aldrich) and 0.37 g of NaAlO₂ (Riedel de-Haën) were dissolved in 81.18 g of distilled water. In a next step, 4.98 g of HMI (Sigma Aldrich) and 6 g of silica (Aerosil 200, Degussa) were added to the mixture and stirred for 2 h. After, the gel was placed in a Teflon-lined stainless steel autoclave under rotation autoclaves (60 rpm) for 7 days at 135 °C.

2.2. Swelling precursor

Swelling of the precursor was done according to the literature [19]. The procedure was carried out at room temperature with 1.8 g of [P]MCM-22, 7.2 g of distilled water, 35.0 g of an aqueous solution of (P)MCM-22, 7.2 g of distilled water, and reuses 1-2-3-4 were named SwR1-SwR2-SwR3-SwR4, respectively.

2.3. Pillaring

The pillaring procedure was carried out at 80 °C for 24 h with stirring under a nitrogen atmosphere and the weight ratio of swollen precursor/TEOS was 0.2. The resultant material was calcined at 540 °C (temperature ramp rate 3 °C min⁻¹) under N₂ flow (1 mL s⁻¹) and synthetic air (1 mL s⁻¹) for 8 h. The surfactants and TEOS used were from Sigma Aldrich. Pillared samples were named “pill”.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>d₀₀₁ (nm)</th>
<th>pH</th>
<th>Loss [%]</th>
<th>S_BET</th>
<th>V_p[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P]MCM-22</td>
<td>3.2</td>
<td>2.7</td>
<td>21.8</td>
<td>–</td>
<td>–</td>
<td>810</td>
</tr>
<tr>
<td>MCM-22</td>
<td>1.9</td>
<td>4.5</td>
<td>13.6</td>
<td>37.9</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>Sw</td>
<td>2.0</td>
<td>4.2</td>
<td>13.5</td>
<td>33.8</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>Sw-pil</td>
<td>1.9</td>
<td>4.5</td>
<td>13.5</td>
<td>39.9</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>SwR1</td>
<td>2.1</td>
<td>4.1</td>
<td>13.4</td>
<td>37.9</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>SwR2</td>
<td>1.9</td>
<td>4.5</td>
<td>13.4</td>
<td>37.9</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>SwR3</td>
<td>2.1</td>
<td>4.1</td>
<td>13.4</td>
<td>37.9</td>
<td>–</td>
<td>777</td>
</tr>
<tr>
<td>SwR3-pil</td>
<td>1.9</td>
<td>4.5</td>
<td>13.4</td>
<td>37.9</td>
<td>–</td>
<td>777</td>
</tr>
</tbody>
</table>

[^d] pH of swelling.  
[^b] Total weight loss by TGA.  
[^c] m² g⁻¹.  
[^d] cm³ g⁻¹.

Fig. 1. XRD patterns of precursor, calcined, swollen materials after reuse 1, 2, 3 and 4 of the swelling solution and pillared Sw and SwR3 samples.

2.4. Characterization

Powder XRD patterns of synthesized materials were analyzed on PANalytical Cubix fast diffractometer, using Cu-Kα1 radiation and an X'Celerator detector in Bragg-Brentano geometry in the regions of 5–40°. Powder XRD patterns in the low-angle region (1.8–20°) were recorded on Bruker D2-Phaser using Cu-Kα1 radiation and Lynxeye detector in Bragg-Brentano geometry. Nitrogen adsorption isotherms at -196 °C were measured with a Micromeritics ASAP 2010 manometric adsorption analyzer. Before the measurements were taken, the samples were outgassed for 12 h at 300 °C. The specific surface area (S_BET) was calculated by the BET method from the nitrogen adsorption data in the relative pressure range from 0.06 to 0.11. The total pore volume (VTP) was obtained from the adsorbed amount of N₂ at a relative pressure of approximately 0.99. The external surface area (Sext) was estimated using the t-plot method. The pore size distribution (PSD) was obtained using BJH method with nitrogen adsorption branch data.

Elemental analysis was determined by inductively coupled plasma - atomic Emission Spectrometry (ICP-OES) on a Varian 715-ES after dissolution of the solids in a HNO₃/HF solution. Thermogravimetric analysis (TGA) measurements were done in a Mettler-Toledo TGA/SDTA851E analyzer in air flux with a heating range of 10 °C min⁻¹.

Scanning electron microscopy (SEM) analysis were recorded on a ZEISS Ultra 55 microscope operating at 2 kV and transmission

[^d] pH of swelling.  
[^b] Total weight loss by TGA.  
[^c] m² g⁻¹.  
[^d] cm³ g⁻¹.

Fig. 1. XRD patterns of precursor, calcined, swollen materials after reuse 1, 2, 3 and 4 of the swelling solution and pillared Sw and SwR3 samples.
electron microscopy analysis (TEM) was recorded on a Philips CM10 operating at 100 kV.

3. Results and discussion

Fig. 1 shows the XRD patterns of precursor, calcined MCM-22 and swollen materials after the reuses of swelling solution. For swollen materials, the overlapping of (101) and (102) diffraction peaks was observed to a broad band, and the (00l) diffraction band was shifted to lower angles for the swollen samples until the third reuse, (SwR3) which indicates that precursors are swollen [32]. The values of d-spacing after swelling are shown in Table 1 and did not indicate a substantial decrease after each reuse compared to the first swelling. The XRD pattern of the SwR4 sample was different from other swollen samples and was associated with a small portion of swollen MWW lamellae. It was previously reported that swelling at elevated temperatures (80 °C) decreases the pH (from 13.8 to 12.9) after swelling that is associated with the formation of monosilicic acids and other oligomer silicates from the dissolved silica. On the other hand, the pH is approximately similar to the starting pH with swelling at room temperature [20]. Indeed, this was the main reason that we chose the swelling at room temperature and the consequent reuse of the swelling solution without pH adjustments. The pH values are shown in Table 1 where the starting pH of 13.6 decreases to 13.4 up to the third reuse. For the fourth reuse, a pH of 13.1 was found.

To quantify the organic material present in the swollen precursors, TGA analyses were performed and are shown in Fig. A.1 (supplementary content) while total weight loss values are shown in Table 1. In general, the total weight losses are higher than 33% for all swollen samples which indicates that the recycled swelling solution remained appropriate for the procedure up to the third reuse. Interestingly, the total weight losses did not indicate a gradual decrease of the organic content as the reuses increase. We believe that the decrease of the pH is the main reason for the partial swelling of precursor SwR4. The chemistry associated with the separation of lamellae is based on the high pH (OH−) necessary to react with the silanol groups (≡Si-OH) on the surface of MWW lamellae to form deprotonated silanol groups (≡Si-O−). These negative charged groups repel each other and attract cationic surfactant molecules (CTA+, TPA+) populating the interlamellar region at the same time [33]. Thus, we can presumed that the adjustment of the pH to the starting values (~13.6) could open the possibility of increasing the reuse of the solution to more than three times.

To evaluate the stabilization of silica inorganic pillars between MWW lamellae, the first swollen sample (Sw) and the sample swollen with the third reuse (SwR3) were pillared and the XRD patterns are shown in Fig. 1. It was observed that the broad band at 8-10° and the (00l) peaks were maintained after pillaring. In addition, (001) and (003) were maintained and indicated a long-range ordering of the lamellar structure. The d-spacing of 4.5 nm of the SwR3-pil sample indicated galleries regions of 2.0 nm (thickness of an MWW lamella with 2.5 nm subtracted). ICP-OES

![Fig. 2. Nitrogen adsorption isotherms (a) and pore size distribution (b) of the SwR3-pil and Sw-pil pillared samples and MCM-22 zeolite.](image_url)

![Fig. 3. SEM images of samples (a) SwR3-pil, (b) Sw-pil and TEM images of (c) SwR3-pil and (d) MCM-22.](image_url)
values showed an increase of the Si/Al ratio of the precursor from 23 to 34 and 36 for Sw-pil and SwR3-pil samples, respectively. These results indicate the deposition of silica in the pillared materials.

Nitrogen adsorption isotherms of SwR3-pil, Sw-pil and the MCM-22 zeolite are shown in Fig. 2a. It was observed that pillared materials SwR3-pil and Sw-pil present an isotherm with a high amount of nitrogen adsorbed at low pressures due to the strong adsorbent-adsorbate interaction. The pressures between $p/p_0$ 0.1–0.4 correspond to the phenomenon of capillary condensation in the mesopores region due to pillaring. The MCM-22 zeolite isotherm is type-I, with the highest nitrogen capacity adsorbed at pressures $p/p_0$ <0.1 which is typical of microporous material. The pore size distribution is shown in Fig. 2b and indicates supermicropores and small mesopores (2–4 nm) as a result of pillaring for the pillared materials SwR3-pil and Sw-pil present an isotherm with a high degree of lamellar ordering using the recycled swelling solutions without any addition of reactants or pH adjustment up to the third reuse. This approach was shown to be beneficial and economically viable (reuse of chemical reagents and reduction of the cost of production in the chemical industry) and environmentally friendly by the reduction of waste generated.

Acknowledgements


Appendix A. Supplementary data

Supplementary data related to this chapter can be found at http://dx.doi.org/10.1016/j.micromeso.2017.06.045.

References
