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Additional Information

The influence of ethanol-assisted washes to obtain swollen and pillared MWW-type zeolite with high degree ordering of lamellar structure

Anderson Joel Schwanke^{a*}, Urbano Díaz^b, Avelino Corma^b, Sibelegher^a

^a Universidade Federal do Rio Grande do Norte, Laboratório de Peneiras Moleculares, 59078-970, Natal, RN, Brasil

*anderson-js@live.com

^b Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, 4602, Valencia, España

Resume: We studied the influence of the ethanol as washing solvent to obtain swollen and pillared MWW-type zeolites with long-range ordering of lamellar structure. The diffractogram results showed that the increase number of washes increase the degree order of lamellar structure. The thermogravimetric results showed a considerable removal of the weakly interacted surfactant molecules after the third wash. The washes with ethanol did not remove the surfactant strongly interacted with the MWW structure. The pillared material after the third wash showed long-range ordering of lamellar structure, surface area of 728 m² g⁻¹, mesopores sizes of 2 - 4 nm and morphology characteristic of pillared MWW-type zeolites.

Keywords: ethanol extraction, MWW, MCM-22, swelling, pillaring, hierarchical zeolites

anderson-js@live.com

udiaz@itq.upv.es

acorma@itq.upv.es

sibelepergher@gmail.com

1. Introduction

Zeolites are a class of microporous crystalline materials formed by the union of tetrahedral (Si, Al, P, Ti, Ge, Ga, Fe, Nb, etc) units linked by oxygen atoms and widely used as catalysts, adsorbents, molecular sieving, ion-exchangers and supports [1, 2]. According to International Zeolite Association, there are more than 230 zeolite topologies, and most part have tridimensional structures obtained by direct synthesis or after calcination [3]. On the other hand, few topologies form lamellar zeolitic precursors (LZPs) propagated in only two-dimensions [4]. The LZPs offer great versatility to create open pore structures (pillared, exfoliated, disordered, desilicated, hybrid) with improved access for larger molecules than the microporous channels of zeolites (less than 1 nm) [5-8]. Among the best example of lamellar zeolitic precursors, the LZP of the MCM-22 (MWW topology) zeolite is the most versatile for post-synthetic modifications. The LZP of the MWW zeolite possesses a sinusoidal 10-ring channels and 12-ring hemicavities on the external surface, and after its calcination of LZP, the silanol groups are condensate on the surface of MWW lamellae and form internal supercavities by the union of hemicavities trough 10-ring windows [5].

In order to obtain open lamellar pore structures, and particularly, pillared-MWW materials, the individual MWW lamellae of the LZP are separate with a swelling procedure using cationic surfactants in high pH media [9]. The intercalation chemistry involves the deprotonation the silanol groups ($\equiv\text{Si-O}$) on the surface of each MWW lamellae. The negative charged groups on surface of MWW lamella repel each other, and simultaneously, attract the cationic surfactant molecules and filling the interlamellar region [10]. Consecutively, a pillaring agent, such as tetraethylortosilicate (TEOS), is added and rigid SiO_2 pillars are stabilized after calcination. The MCM-36 was the first pillared zeolite with a hierarchical structure of mesopores (interlamellar regions between MWW lamellae) and micropores (of each individual lamella). This MWW-type pillared material showed higher adsorption capacities for bulky hydrocarbon molecules, enzymes, and catalytic activity than the microporous MCM-22 zeolite [11-13].

However, the swelling procedure of LZP of the MWW-type materials still considered a complex procedure with a stoichiometry not completely defined and associated with cost and time consuming [11, 14, 15]. These factors still challenging for the large-scale implementation of lamellar zeolites with open pore architectures. Thus, several efforts have been focused to obtain a better understanding between swollen and pillared MWW-type materials as well as more economical and friendly routes. The swelling procedure was studied using soft (25 °C) or aggressive (80 °C) treatments showing that structural integrity and long-range ordering of lamellar structure were obtained with soft swelling procedure [16]. Recently, we reported the influence of molecular dimensions of swelling agents (C_{12}TA^+ , C_{16}TA^+ , C_{18}TA^+) combined with soft and aggressive swelling procedures to obtain tunable properties such as surfactant

accommodation between lamellae, surface area, pore sizes and acidic nature [7]. Furthermore, an economical and eco-friendly procedure based on the reuse of the recyclable swelling solution was reported and showed that is possible to obtain swollen MWW-type LZP for three times with no compromise the physicochemical properties of the pillared material [17].

Another procedure is fundamental to obtain swollen and pillared materials with long-range ordering of lamellar structure. The swollen LZP must be washed to remove the excess of weakly interacted surfactant of the MWW structure. This procedure avoids the interaction of the excess of surfactant with TEOS and the possible formation of undesirable mesophases [18]. It was reported that is necessary successive washes with high centrifugation cycles from 10 to 40, with 10 000 rpm and 10 minutes each one [16].

The use of washing solvents in order to partial or total surfactant removal – and reuse - was reported for some porous materials such as MCM-41, SBA-15 and HMS [19-21]. In other cases, the remaining surfactant interacted with the inorganic structure serve to adsorb molecules of specific interest [22, 23]. As far as we know, there are no alternative procedures of partial removal of surfactant from swollen MWW-type zeolites in the current literature. Here, we explore the influence of the use ethanol as washing solvent with a simple alternative to the successive cycles of washes and centrifugation to obtain swollen and pillared MWW-type materials.

2. Experimental

2.1 Synthesis of MWW-type LZP

Synthesis of LZP precursor was carried out with a Si/Al = 25 molar ratio similar to the reported literature [24]. For the synthesis, 9.50 mmol of sodium hydroxide (NaOH, Sigma Aldrich) and 4.51 mmol of sodium aluminate (NaAlO₂, Riedel de-Haën), were added in 4.51 mol distilled water under magnetic stirring. Consequently, 50.22 mmol of hexamethylenimine (HMI (Sigma Aldrich) and 100 mmol of fumed silica (SiO₂, Aerosil 200, Degussa) were added to the mixture and stirred for 2 h. After, the resulting gel was added in a Teflon-lined stainless steel autoclave under rotation autoclaves (60 rpm) at 135 °C for 7 days. The autoclaves were quenched and the resultant solid was filtered with deionized water until the pH = 7. The LZP was dried at 60 °C for 12 h. The tridimensional zeolite MCM-22 used as reference was obtained after the calcination of LZP at 580 °C for 18 h, and named 22.

2.2 Swelling of LZP

Swelling of the LZP was similar to the procedure reported in literature [7]. The swelling LZP was carried out at room temperature with 1.80 g of LZP, 7.20 g of distilled water, 35.00 g of an

aqueous solution of 29 wt% CTABr/OH with 51% of ionic exchange and 11.0 g of an aqueous solution of 40 wt% TPABr/OH with 45% of ionic exchange. The mixture was magnetically stirred for 18 h and the swollen LZP was separated by centrifugation (12000 rpm, 10 min). The washes were done with absolute ethanol (Sigma Aldrich) with a weight ratio of swollen LZP / ethanol = 0.8. at 25 °C with magnetic stirring (300 rpm) for 1 h and centrifuged. The repetitions were done with fresh ethanol and named according to the number of washes, E₁, E₂, E₃ E₄ and E₅.

2.4 Pillaring of swollen LZP

The pillaring procedure was carried out at 80 °C for 24 h with magnetically stirring under a nitrogen atmosphere and the weight ratio of swollen LZP / TEOS (Sigma Aldrich) was 0.2. The obtained material was calcined at 540 °C (rate 3 °C min⁻¹) under N₂ flow (1 mL s⁻¹) and synthetic air (1 mL s⁻¹) for 8 h. The pillared sample has the suffix “pil”.

2.5 Characterization

The XRD patterns of obtained materials were analyzed on PANalytical Cubix fast diffractometer, using Cu-K α 1 radiation and an X'Celerator detector in Bragg-Brentano geometry in the regions of $2\Theta = 2 - 30^\circ$. The XRD pattern in low-angle region of $2\Theta = 1 - 3^\circ$ were recorded on Bruker D2-Phaser using Cu-K α 1 radiation and Lynxeye detector in Bragg-Brentano geometry.

Nitrogen adsorption isotherms at -196 °C were measured with a Micromeritics ASAP 2010. Prior to analysis, 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 external surface area (S_{ext}) was estimated using the t-plot method. The total pore volume (V_{TP}) was obtained from the adsorbed amount of N₂ at a relative pressure of approximately 0.99. The pore size distribution (PSD) was obtained using BJH method with nitrogen adsorption branch data.

Elemental analyses were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian 715-ES after dissolution of samples in a HNO₃ / HF solution.

Thermogravimetric analyses (TGA / DTG) were determined by a Mettler-Toledo SDTA851E analyzer in air flux with a heating range of 10 °C min⁻¹.

Transmission electron microscopy analyses (TEM) were recorded on a Philips CM10 operating at 100 kV. Scanning electron microscopy (SEM) analyses were recorded on a JEOL JSM6300 at 30 kV using backscattered electron detector.

3. Results and discussion

Fig. 1 shows the XRD pattern of LZP and the swollen samples after five washes with ethanol. The main difference between LZP and swollen samples is the overlapping of (101) and (102) reflections to a broadband and the shift of (00 l) diffraction bands to low angles, which is characteristic of swollen samples [25]. In addition, the (002) reflection emerges after the second extraction (E₂) and indicates the long-range ordering of stacking of MWW lamellae. In contrast, the traditional procedure reports that it is necessary to perform 20 cycles of centrifugation and redispersion in fresh water to observe the emerging (002) reflection of the swollen material [16].

The slight shift of the (00 l) diffraction planes at high angles indicated a slight decrease of the d-spacing with the increase of washes. It was noted that the (003) peak did not disappear but was gradually overlapped by the intralamellar (100) diffraction plane after the second wash. Furthermore, all (100), (220) and (310) diffraction planes are characteristic of the intralamellar MWW zeolitic structure, which was maintained. The pH measurement of the starting swelling mixture was 13.60 and did not decrease after the ethanol washes.

The amount of organic content after each wash was monitored by TGA / DTG analysis and is shown in Fig. 2 (weight loss values for each event are in Table 1A, Appendix). In general, when the number of washes increases, the organic content decreases. The swollen samples E₁, E₂, E₃, E₄ and E₅ showed total weight loss values of 39, 39, 32, 31, 30 wt%, respectively. The first weight loss event (25 - 110 °C) was attributed to physically adsorbed water and ethanol, which decreased after swelling due to the hydrophobic surfactant chains of swelling agents. The second event (110 - 180 °C) is associated with the weakly interacted surfactant with the MWW structure or located outside of the interlamellar region. It was observed that the decrease of this peak occurred with the increase of washes. The weight loss values showed an abrupt decrease of the organic content after the second and third washes, from 9.39 to 3.79 wt%, respectively. This indicates a considerable removal of the weakly interacted surfactant.

The event between 180 - 340 °C is associated with the oxidation of swelling agents located in the interlamellar region and the HMI molecules in 12-ring hemicavities of the MWW surface. In addition, the weight loss values of swollen samples between the first and fifth washes range from 14.85 to 13.00 wt%, respectively. These results indicate that ethanol did not remove a considerable amount of strongly interacted surfactant between interlamellar regions with the increase of the washes. The weight loss event between 340 - 480 °C is associated with the oxidation of HMI molecules in the sinusoidal 10-ring channels of individual MWW lamellae. The events above 480 °C were associated with the residual organic molecules (surfactant and HMI) and water produced by the condensation of silanol groups present on the surface of the MWW lamellae [7]. Both events have similar values for all samples and indicate that only the weakly interacted surfactant molecules were considerably removed.

The XRD patterns in Fig. 1 showed the increase of (001) diffraction bands characteristic of long-range ordering of the lamellar structure after the second wash. In addition, TGA / DTG results in Fig. 2 demonstrated that weakly interacted surfactant was removed after the third wash. Thus, the E₃ sample was chosen to pillaring and its XRD pattern is shown in Fig. 3. The diffractogram showed the (001) diffraction planes of second and third order, which indicate a long-range ordering of the lamellar structure. In addition, the coalescence of (101) and (102) diffraction peaks into a broadband reflection was maintained and indicate that MWW lamellae were separated. The d-spacing of 4.6 nm indicate the interlamellar region of 2.1 nm (d-spacing subtracted of the thickness of an individual MWW lamella, 2.5 nm). The ICP results for E₃ and E₃-Pil samples showed the increase of the Si/Al ratio from 18 to 35, respectively, and confirm that silica pillars were stabilized after calcination.

The Fig.4 showed the nitrogen adsorption isotherms and PSD of E₃-pil and the tridimensional zeolite, 22. The E₃-pil showed a higher amount of nitrogen adsorbed at low pressures when compared to 22 sample. In addition, the pressures between p/p^0 0.1 - 0.4 indicate the capillary condensation phenomena in the mesopores after pillaring. The 22 sample showed a type-I isotherm which is characteristic of microporous materials where the high nitrogen capacity adsorbed occurred at pressures $p/p^0 < 0.1$. The Fig. 4 (image b) showed the *PSD* of synthesized materials and the E₃-pil sample showed pore regions between supermicropores and small mesopores (2 - 4 nm), which corroborates with the XRD results. The BET surface area of E₃-pil is 728 m² g⁻¹ when compared with 446 m² g⁻¹ for the 22 sample. In addition, the *S_{ext}* showed values of 373 m² g⁻¹ for the E₃-pil sample, which is higher than the 22 sample with 120 m² g⁻¹. These values indicate the high accessibility of the

SEM images of LZP and E₃-pil samples are shown in Fig. 5 (images a and b, respectively) and the crystals of E₃-pil are less smooth than LZP due to swelling and pillaring treatments. However, hexagonal flake-like crystals with 1.4 μm are observed for both samples and no morphology of other mesophases were observed. TEM analysis of the LZP and E₃-pil are shown in Fig. 5 (images c and d, respectively). The E₃-pil image showed more expanded MWW particle crystals when compared to the flat crystals of LZP, which attributed to the interlamellar expansion after swelling and pillaring procedures. The scheme in Fig. 6 summarizes the swollen, pillared MWW-type zeolite and the removal of the weakly interacted surfactant after ethanol-assisted washes.

4. Conclusions

An alternative procedure to obtain swollen and pillared MWW-type materials with long-range ordering of lamellar structure using ethanol as washing solvent was reported. It was demonstrated that (002) and (003) diffraction planes are obtained showing the high degree of ordering of lamellar stacking after the second wash. The thermogravimetric analyses showed that weakly interacted surfactants were substantially removed after the third wash. The pillared material maintained the high degree of lamellar stacking, with d-spacing of 4.6 nm, surface area of 728 m² g⁻¹ and pores sizes between 2 – 4 nm. These results confirm that washes of ethanol serve as an alternative route to the successive repetitions of washes with high centrifugation cycles commonly used to obtain MWW materials with high order degree of lamellar structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found in Appendix A

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Figure Captions

Fig. 1. XRD patterns of LZP and swollen materials after the washes with ethanol E₁, E₂, E₃, E₄, and E₅.

Fig. 2. TGA / DTG analyses of swollen materials after the washes with ethanol E₁, E₂, E₃, E₄, and E₅.

Fig. 3. XRD pattern of pillared sample E₃-pil.

Fig. 4. Nitrogen adsorption isotherms (a) and pore size distribution (b) of samples the E₃-pil and 22.

Fig. 5. SEM images of samples (a) LZP, (b) E₃-pil and TEM images of (c) LZP and (d) E₃-pil.

Fig. 6. Scheme of swollen MWW-type materials after ethanol-assisted washes and pillaring.