Microporous and Mesoporous Materials 275 (2019) 26–30

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

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

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ARTICLE INFO

Keywords:
Ethanol extraction
MWW
MCM-22
Swelling
Pillaring
Hierarchical zeolites

ABSTRACT

We studied the influence of the ethanol used as a washing solvent for obtaining swollen and pillared MWW topology zeolites with long-range ordering of lamellar structure. The diffractogram results showed that the increased number of washes increases the degree of order of the lamellar structure. Thermogravimetric results showed a considerable removal of the weakly interacting surfactant molecules after the third wash. The washes with ethanol did not remove the surfactant that strongly interacted with the MWW structure. The pillared material after the third wash showed a long-range ordering of the lamellar structure with the surface area of 728 $m^2 g^{-1}$, mesopore sizes of 2–4 nm and morphology characteristic of pillared MWW-type zeolites.

1. Introduction

Zeolites are a class of microporous crystalline materials formed by the tetrahedral (Si Al, P, Ti, Ge, Ga, Fe, Nb, etc.) units linked by oxygen atoms and widely used as catalysts, adsorbents, molecular sieving materials, ion-exchangers and supports [1,2]. According to the International Zeolite Association, there are more than 230 zeolite topologies, with most of them showing 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 for creation of open pore structures (pillared, exfoliated, disordered, desilicated, hybrid) with improved access for larger molecules compared to the microporous zeolite channels (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 sinusoidal 10-ring channels and 12-ring hemicavities on the external surface, and after its calcination of LZP, the silanol groups are condensed on the surface of the MWW lamellae and form internal supercavities by the union of hemicavities through 10-ring windows [5].

To obtain open lamellar pore structures and in particular the pillared-MWW materials, the individual MWW lamellae of the LZP are separated with a swelling procedure using cationic surfactants in high pH media [9]. The intercalation chemistry involves the deprotonation of the silanol groups ($\equiv Si{-}O^-$) on the surface of each MWW lamellae. The negatively charged groups on the surface of MWW lamella repel each other, and simultaneously, attract the cationic surfactant molecules that fill the interlamellar region [10]. Consecutively, a pillaring agent, such as tetraethylorthosilicate (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 the LZP of the MWW-type materials is still considered to be a complex procedure with a stoichiometry that is not completely defined and has a high cost and is time consuming [11,14,15]. These factors are still challenging for the large-scale implementation of lamellar zeolites with open pore architectures. Thus, several efforts have been focused on obtaining a better understanding of the transition between swollen and pillared MWW-type materials as well as the more economical and environmentally friendly routes for obtaining the MWW-type materials. The swelling procedure was studied using soft (25 °C) or aggressive (80 °C) treatments showing that structural integrity and long-range ordering of the 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

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https://doi.org/10.1016/j.micromeso.2018.08.010
Received 26 March 2018; Received in revised form 31 July 2018; Accepted 10 August 2018

procedures to obtain tunable properties such as surfactant accommodation between lamellae, the 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 it is possible to obtain swollen MWW-type LZP three times without compromising 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 interacting surfactant of the MWW structure. This procedure avoids the interaction of the excess of the surfactant with TEOS and the possible formation of the undesirable mesophases [18]. It was reported that this necessitates successive washes with water with a high number of centrifugation cycles from 10 to 40, at 10 000 rpm and 10 min for each cycle [16]. However, as mentioned above, the diminution of total stages to obtain swollen precursors synthesis is desirable and alternative routes to accelerate the synthesis of swollen materials with high degree of lamellar ordering still necessary.

The remove the surfactant from porous materials precursors using organic solvents are effective for this purpose. Furthermore, the ethanol is the most widely used organic solvent for extraction because it does not allow the complete remove of surfactant of the structure [19]. Although the economic impact of the use of ethanol can be seen negatively, the fact that it can be separated by simple solvent distillation for reuse opens up the possibility of its application. Indeed, the use of washing solvents for partial or total surfactant removal and reuse was reported for some porous materials such as MCM-41, SBA-15 and HMS [20–22]. In other cases, the remaining surfactant interacted with the inorganic structure served to adsorb molecules of specific interest [23,24]. To the best of our knowledge, there are no alternative procedures for the partial removal of a surfactant from swollen MWW-type zeolites in the current literature. Here, we explore the influence of the use of ethanol as a 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 the Si/Al = 25 M ratio similar to the report in the literature [25]. For the synthesis, 9.50 mmol of sodium hydroxide (NaOH, Sigma Aldrich) and 4.51 mmol of sodium aluminate ($NaAlO_{2,}$ Riedel de-Haën) were added to 4.51 mol distillated water under magnetic stirring. Then, 50.22 mmol of hexamethyleneimine (HMI (Sigma Aldrich) and 100 mmol of fumed silica (SiO_2, Aerosil 200, Degussa) were added to the mixture and stirred for 2 h. Then, the resulting gel was added to 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 was close to 7. The LZP was dried at 60 °C for 12 h. The tridimensional zeolite MCM-22 used as the reference was obtained after the calcination of LZP at 580 °C for 18 h and was named *3D* MCM-22.

2.2. Swelling of LZP

Swelling of the LZP was similar to the procedure reported in the 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 (12 000 rpm, 10 min) and named Sw. The washes were performed with absolute ethanol (Sigma Aldrich) with the weight ratio of swollen LZP/ethanol = 0.8. at 25 °C with magnetic stirring (300 rpm) for 1 h and centrifugation. The repetitions were done with fresh ethanol and named according to the number of washes, E_1, E_2, E_3 E_4 and $E_{5.}$

2.3. Pillaring of swollen LZP

The pillaring procedure was carried out at 80 °C for 24 h with magnetic stirring under 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 N_2 flow (1 mL s^{-1}) and synthetic air (1 mL s^{-1}) for 8 h. The pillared sample has the suffix "pil".

2.4. Characterization

The XRD patterns of obtained materials were analyzed with a PANalytical Cubix fast diffractometer using Cu-Kα1 radiation and an X'Celerator detector in the Bragg-Brentano geometry in the regions of $2\Theta = 2–30°$. The XRD pattern in the low-angle region of $2\theta = 1–30°$ were recorded with a Rigaku Ultima IV using Cu-Kα1 radiation.

Nitrogen adsorption isotherms at −196 °C were measured with a Micromeritics ASAP 2010. Prior to the 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 (*VTP*) was obtained from the adsorbed amount of N_2 at the relative pressure of approximately 0.99. The pore size distribution (*PSD*) was obtained using the BJH method with nitrogen adsorption branch data.

Elemental analyses were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian 715-ES instrument after the dissolution of the samples in a HNO_3/HF solution.

Thermogravimetric analyses (TGA/DTG) were determined by a Mettler-Toledo SDTA851E analyzer in air flux with the 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 with a JEOL JSM6300 at 30 kV using backscattered electron detector.

3. Results and discussion

Fig. 1 shows the XRD patterns of LZP, the swollen sample and after

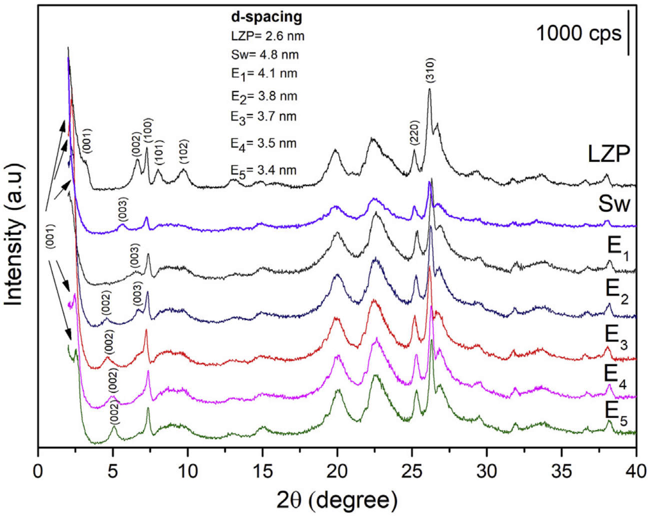

Fig. 1. XRD patterns of LZP and swollen material (Sw) and after the washes with ethanol, E_1, E_2, E_3, E_4, and E_5.