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Mechanistic study of zeolites recrystallization into micro-mesoporous materials

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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ABSTRACT

The mechanism of mordenite recrystallization has been studied using multinuclear MAS NMR, X-ray diffraction, IR spectroscopy, transmission electron microscopy, thermogravimetric analysis and nitrogen adsorption–desorption. The recrystallization procedure involved mixing of zeolite with alkali solution containing cetyltrimethylammonium bromide (CTAB) surfactant, heating the mixture in the autoclave to 423 K and hydrothermal treatment at 423 K. The intermediate products were recovered during each reaction step and thoroughly investigated. The results pointed to dissolution/re-assembling mechanism involving (i) fast ion exchange of protons with sodium cations and zeolite desilication, (ii) the diffusion of CTAB inside the pores and the ion exchange of sodium with CTA-cations and (iii) the formation of micelles and the condensation of siliceous species around micelles both in the intracrystalline mesopores formed during mordenite desilication and on the external surface of zeolite crystallites.

1. Introduction

Recrystallization of zeolites into hierarchical micro-mesoporous materials [1–11], which is also referred to as zeolites mesostructuring [12], pseudomorphic transformation [13,14] or desilication/re-assembly [14] attracts growing attention during the last years.

The recrystallization procedure involves treatment of a zeolite in alkali in the presence of surfactant and can be easily tuned by variation of alkalinity leading to materials with different levels of mesoporosity. It has been thoroughly studied over the large range of zeolites including MOR, MFI, FAU, BEA, FER, LTI, MAZ, MEL, MTW and has been demonstrated to be a versatile tool for the tailored synthesis of wide spectrum of micro-mesoporous materials, which have been reviewed recently [11].

The catalytic properties of the recrystallized materials have been studied in a wide range of reactions including alkylation of aromatics [6,15,16], dehydration of alcohols [17], isomerization [7,8], hydroconversion [3,4,9] and cracking [1,12] of hydrocarbons, disproportionation [10] and transalkylation [1] of alkylaromatics. It has been demonstrated that in most of the cases, recrystallized zeolites show superior catalytic activity, selectivity and life time with respect to parent zeolites and ordered mesoporous materials. However, the choice of the optimal recrystallized material depends on the type of the catalytic reaction and therefore each catalytic reaction requires the design of optimal material [11].

In spite of the fact, that zeolite recrystallization technique has been shown to be among the most advantageous and versatile methods for the preparation of micro-mesoporous materials with superior catalytic properties, the mechanism of recrystallization is not well understood. The detailed mechanistic information is not available and all the conclusions are based on several hypotheses presented so far in the literature.

Ivanova et al. proposed that zeolites recrystallization is based on desolution/re-assembly mechanism [1,8–11]. In this proposal, dissolution step involves partial destruction of zeolite and extraction of zeolitic fragments, which results in perforation of zeolite crystals by mesopores, or leads to its complete depolymerization, while re-assembling step includes assembling of the dissolved species around the micelles formed by surfactant and formation of mesoporous phase. Depending on the degree of zeolite dissolution, mesoporous phase was found either to cover zeolite surface, or to form zeolite/mesoporous phase composites, or to immerse completely the residual zeolite. Basing on that the recrystallized materials were classified into three groups: (i) mesoporous zeolite

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crystals coated with thin films of mesoporous materials; (ii) composite materials consisting of two co-crystallized phases, zeolitic and mesostructured; (iii) mesoporous materials containing small zeolitic fragments in the walls. These three groups of materials were denoted as RZEO-1, RZEO-2 and RZEO-3 [11].

Tsapatsis and Stein with co-workers [14] suggested desilication/re-assembly mechanism based on the concept of pseudomorphic transformation: a reaction in which chemical components change through dissolution and re-precipitation, while the shape of the solid material is preserved [18]. It was proposed that dissolved species formed during zeolite desilication and containing silicates, aluminosilicates and fragments of zeolite crystals can be re-deposited on parent zeolite structure by surfactant molecules via micelles formation under hydrothermal conditions.

The above two proposals are in fact similar. Slightly different proposal was expressed by Garcia-Martinez et al. [12]. The authors proposed surfactant-assisted crystal rearrangement mechanism. According to this mechanism, the Si–O–Si bonds break under basic reaction conditions and offer some flexibility to the crystalline structure, which rearranges to accommodate the surfactant micelles leading to intracrystalline mesostructures. The authors suggest that no desilication takes place, since no obvious changes in Si/Al was observed. However, they do not explain how the structure rearrangement takes place on the molecular level [12].

In this paper we aimed to clarify the mechanism of mordenite recrystallization at the molecular level by the combined application of various techniques including multinuclear MAS NMR, X-ray diffraction (XRD), IR spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and nitrogen adsorption–desorption. The recrystallization procedure used involves (i) mixing of zeolite with alkali solution containing CTAB surfactant, (ii) heating the mixture in the autoclave to 423 K and (iii) hydrothermal treatment at this temperature for selected periods of time. The intermediate products were recovered at each recrystallization step and thoroughly investigated by the above mentioned techniques.

2. Experimental

The commercially available dealuminated mordenite (MOR) with Si/Al = 48 supplied by Zeolyst was used as a starting material. To obtain recrystallized materials 2 g of parent MOR was mixed with 0.15 M solution of NaOH containing 3.1 g of CTAB. The mixture was placed into an autoclave and heated to 423 K. The hydrothermal treatment was performed during 10 h. The intermediate and final products were filtrated, washed thoroughly with approximately 2 L of hot distilled water (~363 K) and dried overnight at 383 K.

The products were analyzed both in as-synthesized and calcined forms. The calcination of the samples was carried out in a dry air flow at 823 K for 12 h.

The chemical composition of the samples was determined by ICP-MS and XRF. XRD data in the region of $5 < 2\theta < 60$ were obtained on a DRON-3M powder diffractometer using CuKa radiation. The diffraction data in the range $1 < 2\theta < 6$ were recorded on SAXSess diffractometer using CuKa radiation. TEM images were obtained using JEOL JEM 2010 electron microscope operating at 200 kV.

Sorption/desorption isotherms of nitrogen were measured at 77 K using an automated porosimeter (Micromeritics ASAP 2000). Micropore volumes (V_{micro}) were determined using *t*-plot method. The total sorbed volumes (V_{tot}), including adsorption in the micropores and mesopores and on the external surface, were calculated from the amount of nitrogen adsorbed at relative pressure p/p_0 of 0.95, before the onset of interparticle condensation.

TGA was performed on SDT Q 600 in an air flow of 6 L/h with a heating rate of 10 K/min.

MAS NMR spectra of the solids were recorded on a Bruker AVANCE II 400WB. The ^{1}H, ^{13}C, ^{29}Si, ^{23}Na and ^{27}Al chemical shifts are reported relative to TMS, $Na(H_2O)_6^+$ and $Al(H_2O)_6^{3+}$, respectively. The main parameters of the NMR spectra acquisition are given in Table 1.

3. Results and discussion

The synthetic procedure for zeolites recrystallization usually involves treatment of zeolite with Si/Al ratio in the range of 10–100 with 0.5–2.5 M alkali solutions containing long-chain alkylammonium surfactants such as CTAB [11]. Mixing of reactants is carried out in the temperature range of 298–353 K for 0.2–5 h and is followed by the hydrothermal treatment in an autoclave in the temperature range of 373–423 K.

The degree of recrystallization depends significantly on the alkalinity of the solution and on the order of alkali and surfactant addition [11]. Higher levels of recrystallization are achieved in the case of stepwise addition of alkali and surfactant. In the case of simultaneous addition of alkali and surfactant, more severe reaction conditions are required: higher alkali content, higher temperature and duration of treatment.

In this contribution, we have chosen the procedure involving simultaneous addition of alkali and surfactant and hydrothermal treatment at 423 K. The intermediate products were recovered during each reaction step: (1) after mixing of MOR with alkali and CTAB for 1, 5 and 20 min (samples denoted as RM-1M, RM-5M and RM-20M, respectively); (2) after heating the mixture in an autoclave for 2 h up to 423 K (sample assigned as RM-0H); (3) after hydrothermal treatment for 1, 5 and 10 h at 423 K (samples denoted as RM-1H, RM-5H and RM-10H, correspondingly).

The results obtained over the intermediate products are presented in Sections 3.1, 3.2 and 3.3.

3.1. Step 1: mixing of reactants

The analysis of the results obtained over the samples RM-1M, RM-5M and RM-20M points that the structure and morphology of the samples remain practically intact as confirmed by XRD and SEM data. The adsorption data point to slight changes in the porous structure (Table 2), in particular, small amount of mesopores with broad distribution of size is created due to the partial desilication.

On the contrary, significant differences are observed in the local structure of mordenite, as determined by multinuclear solid state NMR (Fig. 1).

The ^{27}Al MAS NMR spectrum of parent MOR (Fig. 1) reveals 2 peaks at ca. 55 and 0 ppm, corresponding to the tetrahedrally coordinated Al in the framework of MOR and to the octahedrally coordinated Al in the extraframework species, which were probably formed during dealumination of parent mordenite. Treatment of the zeolite with alkali solutions in the presence of CTAB results in the disappearance of the peak at ca. 0 ppm due to washing of the extraframework species out of the crystal. Besides that slight broadening and shifting of the peak at ca. 55 ppm is observed. The latter effect can be explained by the distortion of the tetrahedral coordination of Al due to the presence of Na^+ and CTA^+-cations [12].

The ^{29}Si MAS NMR spectrum of parent MOR (Fig. 1) shows an intense peak at ca. −112 ppm, corresponding to silicon atoms in Q^4, $Si(OSi)_4$ positions of mordenite framework [19,20] and two small peaks at ca. −106 and −103 ppm. The former is due to the presence of silicon atoms neighboring to Al (Q^4, $Si(OSi)_4OAl$) [19,20], while the latter corresponds to Q^3, $Si(OSi)_3OH$ defects in the mordenite framework. The ^{29}Si CP MAS NMR spectrum of MOR confirms this assignment. Treatment of the sample with alkali in the presence of CTAB results in the broadening of the Q^3 peak