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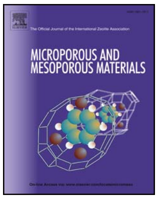

Structural investigations in pure-silica and Al-ZSM-12 with MTEA or TEA cations

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ABSTRACT

Two different quaternary ammonium cations, methyltriethyl- (MTEA) and tetraethylammonium cations (TEA) were used as templates in the synthesis of pure-silica as well as aluminosilicate ZSM-12 (MTW-type) frameworks. The distribution of the template cations in the 12-membered rings channels in the 1-dimensional framework topology was studied; thus the as-prepared products were characterized by means of X-ray powder diffraction, Raman, transmission FTIR, solid-state NMR spectroscopy, thermogravimetric and elemental analyses and SEM. It was shown that in pure-silica (PS) ZSM-12, TEA cations are well ordered - a superstructure with three-times longer *b* edge (in comparison to unit cell of empty framework) along the channel is formed, which can be seen by virtue of a few additional peaks in the X-ray powder pattern. Herein we describe that its aluminosilicate counterpart with TEA also contains ordered TEA cations and is isostructural to PS-ZSM-12. Conversely, in both pure-silica and aluminosilicate ZSM-12 frameworks with MTEA, the cations are disordered and no superstructure is formed.

1. Introduction

Zeolite ZSM-12 (MTW framework type) belongs to the family of 1-dimensional zeolites with 12-membered rings which run along the *b*-edge. Although not commonly used for industrial purposes, it shows potential for use as a catalyst at different processes in petrochemical industry, e.g. cracking, hydrocracking, different alkylations and isomerisations [1]. The fundamental properties of the framework comprise the following: unit cell parameters, $a = 25.552$, $b = 5.256$, $c = 12.117$ Å, $\beta = 109.312^\circ$, $V = 1535.78$ Å^3, space group $C2/m$ [2,3]. The framework topology was first determined by LaPierre and coworkers [4] using a combination of electron and X-ray diffraction with model building leading to $C2/m$ cell with parameters $a = 24.88(4)$, $b = 5.02(2)$, $c = 12.15(3)$ Å, $\beta = 107.7(1)^\circ$ and seven symmetrically independent silicon atoms, confirmed by the ^{29}Si NMR study of Trewella et al. [5]. Additional studies, especially combinations of complementary synchrotron XRPD and NMR, further confirmed the $C2/c$ framework symmetry. In this case, the unit cell is doubled along *c* axis, yielding $a = 24.8633(3)$, $b = 5.01238(7)$, $c = 24.3275(7)$ Å, $\beta = 107.7215(6)^\circ$ [6].

To date, ZSM-12 can be prepared in the presence of several different organic cations (organic structure directing agents, OSDA), most of which are quaternary ammonium cations. A few reports on OSDA-free synthesis of ZSM-12 are also available [7,8]. The most frequently used OSDA is the tetraethylammonium cation (TEA). We observed that the powder pattern of PS-ZSM-12 with TEA contains additional diffraction peaks which have been overlooked in the past [9]. These are not due to impurities, and additionally they disappear with the removal of the TEA from the framework. It was proven that additional diffraction peaks are due to ordering of TEA cations (*tt.tt* conformation) in the ZSM-12 channels along *b* axis and that leads to a formation of superstucture with a three times larger unit cell [9]. However, a few questions remain unanswered; firstly, does the inclusion of Al^{3+} in the zeolite framework affect the ordering of the TEA cations? If so, what is the highest concentration of Al^{3+} that enables the formation of the superstructure? On the other hand, methyltriethylammonium cations (MTEA) are of a similar size with similar physico-chemical characteristics as TEA and it also enables the formation of MTW framework [10]. The question here is, whether MTEA cations also order in the channels of ZSM-12 or not?

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Therefore, the aim of this study was to explore the presence of ordering of TEA and MTEA cations when trapped in the zeolite channels of pure-silica and aluminum-containing ZSM-12.

2. Experimental

2.1. Synthesis

Pure-silica ZSM-12 with MTEA was prepared according to a modified double-silica source method published by Mitra et al. [11]. The molar ratio between reactants was as follows: 1 Na_2SiO_3: 147 H_2O: 3.80 MTEAOH: 12.50 SiO_2. Initially, 0.325 g (2.67 mmol) of Na_2SiO_3 was dissolved in distilled water (1.75 g, 0.097 mol), followed by dropwise addition of 6.67 g of MTEAOH (20%, Sigma Aldrich) to the clear solution. The mixture was allowed to stir at room temperature for 0.5 h and then, 2.00 g of SiO_2 was added (Davisil, mesh size 35–60, 150 Å, Sigma Aldrich). After additional stirring for 3.5 h, the obtained highly alkaline gel was transferred to teflon-lined stainless steel autoclaves (~20 mL) and heated for 1–8 days at 150 °C under static conditions. When the reaction finished, the products were filtered off, washed with distilled water to neutral pH value and dried at 50 °C overnight.

Al-ZSM-12 with TEA or MTEA, respectively, were prepared by the modified synthetic route as published by Gopal et al. [12]. In case of TEA, the molar ratios between the reactants were x Na_2O: x Al_2O_3: 80 SiO_2: 12.7 TEAOH: 1040 H_2O, where $x = 0.25$, 0.50, 0.57, 0.67, 0.80, 1.00, 1.33 and 2.00 (representing Si: Al molar ratios of 160, 80, 70, 60, 50, 40, 30 and 20). In case of MTEA, the molar ratios were 1 Na_2O: 1 Al_2O_3: 80 SiO_2: 12.5 MTEAOH: 980 H_2O (*i.e.* Si: Al = 40). Initially, appropriate amounts of MTEAOH or TEAOH (35 wt. %, Sigma Aldrich) were diluted with distilled water, followed by the slow addition of $NaAlO_2$ (Alfa Aesar, technical grade). When the solid was dissolved, Ludox HS-40 (Sigma Aldrich) was added dropwise and stirred for a few minutes. The obtained gel with low viscosity was then transferred to teflon-lined stainless steel autoclaves and heated at 150 °C under static conditions for 3–8 days. The solid products were isolated from the highly basic reaction mixture, washed with distilled water to neutral pH value and dried at 50 °C overnight.

2.2. Characterization methods

X-ray powder diffraction data were collected using a PANalytical X'Pert PRO MPD diffractometer with reflection geometry and primary side Johansson type monochromator, with $CuK_{\alpha 1}$ wavelength (1.540596 Å). Rietveld refinement was performed with TOPAS Academic software [13] on the product obtained with a Si:Al ratio of 80 and heating time of 96 h. The crystal data, collection conditions and refinement parameters are presented in Table 1.

Table 1
The crystal data, collection conditions and refinement parameters for Al-ZSM-12 with TEA.

Crystal data	
Formula	$C_{64}H_{160}Al_{2.36}N_8O_{336}Si_{165.64}$
M_r	2783.63
Crystal system	monoclinic
Space group	*Cc*
a, b, c (Å)	25.36(2), 15.2124(10), 24.4980(16)
β (°)	108.444(6)
V (Å^3)	8921.8(12)
Z	1
μ (mm^{-1})	0.715
ρ (Mg m^{-3})	2.072
Specimen shape and colour	white powder
Data collection	
Diffractometer	PANalytical X'Pert PRO MPD
Radiation	$CuK_{\alpha 1}$, $\lambda = 1.540596$ Å
Temperature (K)	293(1)
Tension, current	45 kV, 40 mA
Detector	Full range, 128-channel
Specimen mounting	Flat plate
Data collection mode	Reflection
Scan method	Step
2θ (°)	$2\theta_{\min} = 5$, $2\theta_{\max} = 86$, $2\theta_{\text{step}} = 0.033$
Time per step (s)	500
Refinement data	
R-factors	$R_p = 6.950\%$, $R_{wp} = 9.442\%$, $R_{exp} = 1.928\%$, $R_{Bragg} = 4.066\%$
No. of profile points	2459
No. of reflections	3287
No. of structural parameters	6
No. of non-structural parameters	12
Background	Chebyshev polynomial, order 5
Profile	TCHZ-psevdo Voigt profile function (Thompson et al., 1987)

$$R_P = \frac{\sum_{i=1}^{n} |Y_i^{obs} - Y_i^{calc}|}{\sum_{i=1}^{n} Y_i^{obs}} \cdot 100\%; \qquad R_{wp} = \left[\frac{\sum_{i=1}^{n} w_i \cdot (Y_i^{obs} - Y_i^{calc})^2}{\sum_{i=1}^{n} w_i \cdot (Y_i^{obs})^2}\right]^{1/2} \cdot 100\%; \qquad R_{\exp} = \left[\frac{n-p}{\sum_{i=1}^{n} w_i \cdot (Y_i^{obs})^2}\right]^{1/2} \cdot 100\%;. R_{Bragg} = \frac{\sum_{j=1}^{m} I_j^{obs} - I_j^{calc}}{\sum_{j=1}^{m} I_j^{obs}} \cdot 100\%.$$

The compositional weight percentage of carbon, hydrogen and nitrogen were determined on Perkin Elmer 2400 CHN microanaliser by the Chemistry Department service at the University of Ljubljana. The weight per cent of silicon and aluminum in the products were estimated using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo Jarrell Ash, model Atomscan 25 with ultrasonic nebulizer Cetac, model U-6000 AT) at National Institute of Chemistry, Ljubljana.

Raman spectra were recorded on a Holoprobe Kaiser Optical spectrometer. The spectrometer makes use of a Nd:YAG laser source which operates at a wavelength of 532 nm (frequency doubled) with a typical power output of 60 mW. A CCD camera was used for signal detection through a pair of holographic notch filters. A 1.3″ objective lense was used to focus the laser light. The sample was first pressed into a disc-shaped, self-supporting wafer before measurements were performed with a collection time of 2 s per spectra. In order to improve the signal-to-noise statistics, 240 spectra were recorded and summed.

FTIR measurements were performed on self-supporting wafers of the as-prepared zeolite materials (0.01–0.02 g) using a Perkin Elmer 2000 spectrometer (25 scans were collected per measurement over a range of 4000–1300 cm^{-1} with a resolution of 4 cm^{-1}). The wafer was placed in an IR transmission cell equipped with CaF_2 windows. The cell was first evacuated to $2 \cdot 10^{-8}$ bar before the temperature was raised from 323 K to 573 K at 3 K/min and held for 2 h in order to dehydrate the sample.

Thermal analysis of the product (TG/DTG) was performed on a SDT 2960 Thermal Analysis System (TA Instruments, Inc.). The measurements were carried out under nitrogen flow with a heating rate of 10 °C/min up to 720 °C.

Solid-state ^{27}Al MAS, ^{1}H-^{29}Si CPMAS and ^{29}Si MAS NMR spectra were recorded on a 600 MHz (14.1 T) Varian VNMRS spectrometer using a Varian 3.2 mm double resonance MAS probe. Solid samples were spun at 10 kHz for ^{29}Si and 16 kHz for ^{27}Al MAS spectra. A single-pulse excitation with repetition delays of 0.5 s and 30 s, and 15,000 and 1500 scans accumulated for ^{27}Al and ^{29}Si nuclei was used, respectively. For the ^{1}H-^{29}Si CPMAS acquisition, a repetition delay of 5 s was adopted and 4000 scans were accumulated. The ^{27}Al spectra were referenced to $Al(NO_3)_3$, while the ^{29}Si spectra were referenced to 2,2-dimethyl-2-silanpentane-5-sulphonic acid (DSS), with a chemical shift of $\delta = 1.53$ ppm relative to tetramethylsilane (TMS).

The morphology of the samples was studied by Zeiss ULTRA 55 plus field-emmission scanning electron microscope (FE-SEM). A small quantity of powder sample was placed onto the sample holder and coated with gold to obtain appropriate conductivity.