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The disordered structure of silica zeolite EU-20b, obtained by topotactic condensation of the piperazinium containing layer silicate EU-19

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

Zeolite EU-20b was prepared by heating the piperazinium containing layer silicate EU-19 in air at 1000 °C. The microporous silica framework of EU-20b forms by topotactic condensation of the silicate layers of the crystalline precursor EU-19. According to the observed diffraction data, the EU-20b structure is closely related to the (orthorhombic) CAS zeolite framework type. However, the diffraction pattern revealed structural disorder of the material as indicated by the presence of sharp and broad reflections. In spite of the disorder, the XRD pattern of EU-20b can unambiguously be indexed based on a C-centered orthorhombic unit cell with lattice parameters $a_0 = 13.817(4)$ Å, $b_0 = 4.995(1)$ Å, $c_0 = 16.637(5)$ Å. The program DIFFaX was used to simulate diffraction diagrams of various stacking disordered silica-materials made up by layer-like building units. The best fit between simulated and observed patterns was obtained for a probability of about 88% CAS-type stacking and 12% NSI-type stacking. EU-20b is a small pore zeolite characterized by a one-dimensional pore system consisting of straight and non-intersecting 8-ring channels and has a very high framework density of ≈20.8 T/1000 Å^3. Although the pore volume of EU-20b is free of organic pore fillers due to the heating process at 1000 °C, nitrogen sorption experiments showed that there is no "free" access to the pore volume. Two effects might block access to the pores: According to ^{29}Si MAS NMR spectroscopy a few defects are probably present caused by incomplete or random condensation of the silanol groups and the elliptical pores are very small in one direction (2.3–2.5 Å) compared to N_2 (kinetic diameter 3.64 Å). Thus, EU-20b is formally porous by topology, but apparently non-porous to N_2.

Keywords: Zeolite; Layer silicate; EU-20; NU-6(2); Disorder; Structure; CAS; NSI; Topotactic condensation

1. Introduction

In the last few years, a high interest in the preparation of zeolite-type materials from layer-like silicate precursors has arisen. In the past, microporous materials of only two different zeolite framework types have been prepared accidentally from layer-like silicate precursors: a material having the type FER (Ferrierite) from PREFER [1,2], and several materials possessing the type MWW (MCM-22, ERB-1, PSH-3, ITQ-1, SSZ-25) from their respective layered precursor phases [3]. For the zeolite framework types see [4]. Recently however, we were able to synthesize two new microporous framework silicates by topotactic condensation of layered silicates:

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- a material of zeolite framework type RRO represented by RUB-41 [5] and
- a material of zeolite framework type RWR represented by RUB-24 [6].

In addition, a series of publications reported on the successful topotactic condensation of layered silicates to zeolite materials of framework types:

- CDO represented by MCM-65 [7], CDS-1 [8] and UZM-25 [9], and
- NSI represented by NU-6(2) [10]—a structure being closely related to framework type CAS.

EU-20 [11] is another material which had been suspected to have a zeolite-type framework formed by condensation of a layered silicate. EU-20 was first described by Blake et al. in 1988 [11] who obtained this material by heating EU-19 [12]. EU-19 is a layer silicate consisting of dense silicate layers and piperazinium ions as the interconnecting cations. The structure of EU-20, however, remained unsolved because only powder material, giving poor XRD data, was available. The presence of broad and less broad reflections in the XRD pattern are indicative of a disordered material.

To arrive at a better understanding of the structural changes occurring during the condensation of layered silicates we continued our work in this field by investigating the structure of EU-20b. EU-20b was obtained from a EU-19 type precursor and seems to be structurally closely related to EU-20 since the corresponding XRD diagrams are very similar. However, the diagrams of the investigated EU-20b and EU-20 as presented by Blake et al. [11] are not identical and, therefore, we decided to choose a slightly different name for our material.

2. Experimental

EU-20b was prepared by heating an EU-19 type precursor material in air at 1000 °C for 8 h. EU-19 is a layered piperazine silicate first described by Andrews et al. [12] and is closely related to MCM-69(p) [13]. The precursor material was synthesized from a synthesis mixture of composition $SiO_2:0.56C_4H_{10}N_2:0.56HF:7.7H_2O$. Piperazine was dissolved in a mixture of Ludox AS-40 and water at 40 °C. After cooling down, HF was added and the mixture was stirred by hand before transferring it to a Teflon-lined autoclave, which was then heated at 150 °C for 14 days under slow rotation (60 rpm). The solid product was recovered by filtration, extensively washed with water and dried at 100 °C. The precursor material contained some Dodecasil 3C crystals (zeolite framework type MTN) as a minor impurity. Dodecasil 3C is a typical product in the synthesis system SiO_2–H_2O–piperazine under hydrothermal conditions. Eu-19 was also synthesized by heating a mixture of the above composition at 135 °C for 15 days under rotation or at 175 °C for 18 days without rotation. Calcination of all these EU-19 samples at 1000 °C yielded EU-20b with XRD patterns essentially identical to each other (except for the noted impurity). This confirms the reproducibility of the synthesis of EU-20b, even when using EU-19 starting materials synthesized under different conditions.

Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2000 instrument. The surface area was calculated using the BET method and the micropore volume was calculated by the *t*-plot method and by the nitrogen uptake at $P/P_0 = 0.3$.

Scanning electron microscopy (SEM) investigations to study the morphology of the crystals and the homogeneity of the samples were performed using a LEO-1530 Gemini microscope.

The ^{29}Si-solid state MAS NMR (Bloch decay) experiments were performed with a Varian VXR 400SWB spectrometer using a Varian 7 mm probe spinning at 5.5 kHz. The data were recorded at 79.454 MHz resonance frequency with a 55.4° pulse of 4.0 μs and a recycle delay of 60 s. The ^{29}Si chemical shift is reported relative to TMS.

The density was determined by the pyknometer method.

Thermal properties were analyzed with a Bähr STA 503 Thermal Analyzer under air in the temperature range from RT to 1000 °C. The heating rate was 10 °C/min. DTA- and TG-signals were recorded simultaneously. In a different experiment the EU-20b material was heated in an oven at 1000 °C in air for 7 days.

Powder X-ray diffraction data were collected with a Siemens D5000 diffractometer in a modified Debye–Scherrer geometry with a capillary sample holder using Cu $K\alpha_1$ radiation from a primary monochromator. The intensity data sets of EU-20b and EU-19 were recorded in the range of 4–39.0° 2θ and 4–54.0° 2θ, respectively. A Rietveld refinement of the structure of the EU-19 type material was performed using the FullProf program system [14]. In situ high temperature XRD powder data were collected in an Anton Paar HTK10 camera installed in a Philips PW1820 diffractometer and the experiments were performed in air. The heating rate between recording plateaus was 10 °C/min. A thin film was deposited in a 1 mm thick Pt filament from a suspension of as-made EU-19 in acetone.

The geometry of the layer-like building unit used for the simulations with DIFFaX was optimized with the distance least squares refinement program DLS-76 [15].

Diffraction intensity calculations for EU-20b were performed with the DIFFaX program [16], using Version 1.801.

In order to check whether the EU-19-type material used here as a precursor has in fact the structure of