Microporous and Mesoporous Materials 237 (2017) 222–227

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Microporous pure-silica IZM-2

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ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form
16 September 2016
Accepted 21 September 2016
Available online 21 September 2016

Keywords:
Pure silica
IZM-2
Zeolite
Synthesis
Defects
Post treatment

ABSTRACT

Pure-silica IZM-2 was synthesized for the first time, and the concentration of sodium hydroxide used during synthesis affected the phase purity and size of crystals. Most of the micropores in calcined pure-silica IZM-2 that was synthesized in the presence of high concentrations of sodium hydroxide were inaccessible to N_2 adsorption; however, the micropores could be rendered accessible by applying either of two different post-synthetic treatments. Pure-silica IZM-2 could also be synthesized without sodium ions using the hydroxide version of the template. In this case, the micropores were accessible to N_2 directly after calcination. The size of pure-silica IZM-2 crystals obtained increased with the concentration of sodium hydroxide, with the highest concentrations giving spherical and micrometer-sized aggregates of pure-silica IZM-2 that consisted of intergrown particles (60–500 nm). The nature of the defects in pure-silica IZM-2 was studied with a combination of ^{1}H, and ^{29}Si solid-state NMR spectroscopy. As expected, direct-polarization ^{29}Si NMR spectroscopy showed that the number of non-condensed silica groups decreased upon calcination. Calcined samples also showed broader ^{29}Si NMR bands for the fully condensed silica moieties, which indicated a broader distribution of bond angles and/or bond lengths. The siloxy and silanol groups in calcined pure-silica IZM-2 were accessible to protonation as determined by ^{1}H NMR spectroscopy. We could not determine the structure of pure-silica IZM-2 in its aggregated form; however, further studies of the synthetic conditions could yield larger, non-aggregated crystals that would facilitate structural determination.

1. Introduction

Zeolites are crystalline microporous aluminum silicates, and they are being extensively used for catalysis, gas separation and ion exchange [1]. Pure-silica zeolites have enhanced thermal stability and hydrophobicity [2], which make them relevant for CO_2 removal from natural gas mixtures, flue gas, or mixtures with H_2 [3–8], and capture of volatile organic compounds [9]. Their potential as insulators with ultra-low dielectric constants for the semiconductor industry is also being investigated [10]; however, note that today's porous inorganic low-k materials do not withstand the processing conditions of this industry [11].

The frameworks of pure-silica zeolites consist solely of silicon covalently bonded with oxygen, and at least 41 polymorphs have been synthesized and studied [12]. Specific aspects of the nucleation and crystallization growth mechanisms for this class of compounds are known [13,14]. To better understand the mechanisms of crystallization is very important for the design of pure-silica zeolites and regular zeolites [15]. In addition, pure-silica zeolites are compositionally simple and often suitable model systems of zeolites [16].

Pure-silica zeolites are synthesized hydrothermally in either OH^--rich (pH > 10) or F^--rich media (neutral pH). The as-made pure-silica zeolites synthesized in OH^--rich media have more connectivity defects [17]. These defects are commonly siloxy-silanol pairs that balance the positive charge of organic templates and are located on the external surfaces as well as within the frameworks [18]. The number of defects are reduced by the condensation of silanol groups into fully-connected frameworks [19] or peroxy linkages [20,21], during calcination. For calcined pure-silica zeolites, the medium of synthesis is less relevant to the number of defects. Trzpit et al. showed similar numbers of defects in calcined silicalite-1 synthesized in a OH^--rich and a F^--rich medium [22].

Pure-silica and high-silica zeolite nanocrystals [23] can be used to manufacture membranes and thin films, which are desirable for application in catalysis, gas separation and low-k thin films

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http://dx.doi.org/10.1016/j.micromeso.2016.09.033
1387-1811/© 2016 Published by Elsevier Inc.

[24–27]. The IZM-2 zeolite is a high-silica zeolite that could be relevant for membranes if non-aggregated nanocrystals could be synthesized. Its structure is unknown, and it was first synthesized by A. Fecant and N. Bats [28]. This zeolite consists of intergrown nanocrystals with intercrystalline slit-shaped mesopores [29]. Previously, three of us reported on a post-treatment method, which etched and enlarged the inter-particle-based mesopores in the aggregated particles of IZM-2. The original crystallinity and framework composition was kept intact [30]. Here, we present a study of the synthesis of pure-silica IZM-2 and its defects.

2. Experimental

2.1. Zeolite synthesis and Na ion removal from framework

Pure-silica IZM-2 was synthesized by modifying the method used for the synthesis of IZM-2 [29]. Two silica sources were used, LUDOX® HS-40 colloidal silica and tetraethyl orthosilicate (TEOS), with molar ratios of: x Na_2O: 0.15 template: 1 SiO_2: 30 H_2O; x equals to 0, 0.03, 0.08 and 0.24. LUDOX-based samples were denoted as L0, L03, L08 and L24, and TEOS-based ones as T0, T03, T08 and T24. Typically, aliquots of a solution of sodium hydroxide (50 wt%) were diluted by adding 7.5 g of distilled water. To these solutions, 1.1 g of the organic template (1,6-bis(methylpiperidinium)hexyl dibromide) was added and dissolved, followed by an addition of 2.25 g of LUDOX. The mixtures were stirred on a multi position stirrer (IKA) at room temperature for 2 h and subsequently transferred into 23-ml-stainless autoclaves. The autoclaves were placed in a preheated oven at a temperature of 160 °C for 4 or 10 days. White powders formed and were recovered by centrifugation. The powders were washed with distilled water until the pH values of the eluates were neutral and subsequently dried at a temperature of 70 °C for 12 h. The organic template was removed by calcination at 550 °C for 6 h. The temperature was ramped from room temperature to the target temperature using a rate of 1.5 °C/min, and the full procedure took 12 h. When TEOS was used, ethanol was evaporated from the gels before they were transferred to autoclaves. For TEOS-derived gels, the autoclaves were kept for crystallization at a temperature of 180 °C for 7 or 10 days. When preparing L0 and T0, the counter ions of the template were ion-exchanged from Br^- to OH^- by using an Amberlite® IRN-78 resin. The OH^- concentration was determined by phenolphthalein titration. The OH^- concentration in the synthesis gels for L0 and T0 was kept identical to those of L03 and T03.

The Na^+ ions of the Na^+-rich L08 were removed or partly removed with two different approaches. First, the as-made L08 was treated three times with an aqueous solution of ammonium nitrate (0.5 mol/dm^3) at a temperature of 60 °C. The ammonium treated samples were calcined using the procedure described above. In the second method, already calcined L08 was subjected to an aqueous solution of HCl (0.1 mol/dm^3) at a temperature of 60 °C, and then centrifuged and washed with water. This procedure was repeated twice.

2.2. Characterization

Powder X-ray diffraction (PXRD) data was collected on a PANalytical X'Pert Pro diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-7401F microscope using an accelerating voltage of 2 kV and a working distance of 8 mm. Nitrogen sorption data were recorded with a Micromeritics ASAP 2020 instrument at a temperature of −196 °C on samples that had been degassed at a temperature of 350 °C for 6 h. Brunauer-Emmett-Teller (BET) surface areas were calculated from the adsorption data at relative pressures (p/p_0) of 0.05–0.15. The characteristic mesopore size was determined from the maximum of the pore size distribution, which was calculated in the Barrett-Joyner-Halenda (BJH) model using the N_2 desorption data. Micropore surface areas and volumes were determined using the t-plot method. Total pore volumes were determined from the N_2 uptake at $p/p_0 = 0.99$ by assuming a complete pore saturation. Elemental analysis was conducted by Medac Ltd. in the United Kingdom. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used for determining the Na^+ concentration with a Varian Vista MPX ICP-OES instrument and CHN analysis was performed on a Carlo Erba Flash 1112 elemental analyser. Thermogravimetric analysis was carried out with a Perkin Elmer TGA 7 instrument. Particle size distributions of colloidal dispersions were measured at room temperature by dynamic light scattering (DLS) with a Malvern Zetasizer Nano series instrument.

^{29}Si magic angle spinning (MAS) NMR spectra were recorded on a 9.4 T Bruker Avance-III spectrometer (Larmor frequency of 79.5 MHz) equipped with a 7 mm double-resonance MAS probe. Spectra were recorded at a MAS rate of 7 kHz. Tetramethylsilane was used to externally calibrate the chemical shift and to estimate the strength of the radio frequency (rf) pulse used for direct polarization (DP) experiments. For all DP experiments, a rf pulse with a 45° flip angle a repetition delay of 300 s were applied. For the cross polarization (CP) experiments, the repetition delays were set to 3 or 10 s, and cross-polarization times of 4 and 9 ms were used. ^1H spectra were recorded using a repetition delay of 15.5 s. A moderately wide exponential function was applied to the recorded free-induction decays prior to Fourier transformation. The spectra were normalized with respect to the mass of the sample when stated.

3. Results and discussion

Pure-silica IZM-2 was synthesized with different sodium hydroxide concentrations as well as without sodium hydroxide. Small colloidal silica particles (LUDOX) and larger TEOS-derived silica gels were used as silica sources. The compositions and some synthesis conditions are listed in Table 1. MTW and MFI are framework type codes [31].

The PXRD patterns of both as-made and calcined samples are shown in Fig. 1. L0, L03, and L08 consisted of pure-silica IZM-2. Sodium hydroxide significantly reduced the crystallization time needed to achieve IZM-2. The crystallization time for L03 and L08 was 4 days and that of L0 was 10 days. Similarly, alkali-metal ions have already been shown to accelerate the crystallization of pure-silica variations of the ZSM-12, SSZ-24 and ZSM-48 zeolites [32]. At high concentrations, however, the structure-directing action of the alkali-metal appears to compete with that of the template [33]. Such a competition was observed for the L24 sample, which was synthesized at the highest concentration of sodium hydroxide. In addition to pure-silica IZM-2, this sample had additional PXRD lines at 21.7° and 36.4°, which were attributed to a dense compound. The sodium hydroxide appeared to have started to compete with the organic templates and directed the crystallization towards other phases. Notably, the PXRD lines of the pure-silica IZM-2 in the L24-as-made sample were narrower than in the other LX-as-made samples. This difference suggests that the degree of crystallinity increased with the concentration of sodium hydroxide used in the synthesis. This increase could potentially allow for further optimizing of the synthesis conditions for the synthesis of large crystals of pure-silica IZM-2.

The PXRD patterns of the calcined samples, in Fig. 1b, had higher line intensities in the low-angle region as compared to the as-made samples due to enhanced X-ray contrast [34]. Interestingly, the