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A powerful structure-directing agent for the synthesis of nanosized Al- and high-silica zeolite Beta in alkaline medium

Olivier Larlus [a], Svetlana Mintova [b], Stephen T. Wilson [c], Richard R. Willis [c], Hayim Abrevaya [c], Thomas Bein [a,*]

[a] Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstrasse 5-13 (E), 81377 Munich, Germany
[b] Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen Cedex, France
[c] UOP Research Center, 50 East Algonquin Road, Des Plaines, IL 60017, USA

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ABSTRACT

Purely siliceous and Al-containing nano-zeolite Beta (BEA) crystals were synthesized using 4,4′-trimethylenebis(*N*-methyl, *N*-benzyl-piperidinium) cations as structure-directing agent (SDA). The influence of the synthesis parameters (synthesis time and temperature, heating source) as well as the chemical composition of the precursor gel on the nature of the product and its particle size was investigated. Purely siliceous nano-zeolite Beta with a particle size of around 140 nm and single domains of around 30 nm in size was synthesized with a high level of reproducibility and stabilized in colloidal suspension. Aluminium-containing Beta zeolite (Al-BEA) crystals were prepared either under conventional hydrothermal treatment or under microwave irradiation. Stable colloidal suspensions of Al-BEA particles with a size of 200 nm were obtained, consisting of single domains in the range of 5–15 nm, depending on the nature of the heating mode.

1. Introduction

Zeolite Beta (BEA) is a three-dimensional large-pore zeolite [1,2], synthesized for the first time by Wadlinger et al. [3]. Due to the silica-rich framework and facile access to the active sites in the pores, the use of zeolite Beta for catalytic reactions has been extensively investigated and reported in the literature. Based on its high hydrophobicity and low framework density [1] (15.1 T per 1000 Å^3), zeolite Beta is also an interesting candidate for the preparation of films with low dielectric constant or coatings for other advanced applications. In order to ensure a homogeneous coating of nanoscale material on semiconductor wafers during a spin-on process, it is desirable to synthesize the high-silica or pure silica zeolite Beta in the nanosize range.

Zeolite BEA is readily synthesized with a relatively wide range of silica to alumina ratios (SAR) from about 12 to 200 in the presence of the tetraethylammonium (TEA) cation as structure-directing agent (SDA) by working in alkaline media [4–9] or by using fluoride anions in near-neutral media [10,11]. Under the same synthesis conditions (use of fluoride anions in near-neutral media), the purely siliceous form of zeolite BEA (Si-BEA) was obtained. Purely siliceous BEA can be prepared with TEA cations [12–16] and other quaternary ammonium cations acting as SDA [17,18]. Under these conditions, the pure silica material shows a low defect content and, as a consequence, exhibits a high level of hydrophobicity. However, the use of fluoride anions in near-neutral media leads to the formation of large crystalline particles, often more than 10 μm in diameter [12–16]. Even the use of a two-step nucleation process or a combination of hydroxide and fluoride anions during the nucleation and growth did not lead to a significant decrease of the Si-BEA particle size [15]. Hydrophobic Al-free zeolite BEA with incorporation of titanium has also been synthesized either by using the fluoride route (working with TEA cations as SDA) [19] or in alkaline media using di(cyclohexylmethyl)-dimethylammonium cations as SDA [20]. The particle size reported in the latter case was over 1 μm. Small BEA particles having a high SAR have been produced by dry gel conversion or steam-assisted conversion using TEA cations as SDA [21–25]. Although very small crystals were obtained, a high level of aggregation of the BEA material was also observed.

The synthesis of Al-containing nanosized zeolite BEA (Al-BEA) via spontaneous nucleation is well known [26–30], using alkaline media and TEA cations acting as SDA. It turned out that the gel SAR influences both the product SAR and the particle size: for a high SAR in the gel, a higher SAR is found in the crystalline product and a larger particle size distribution is observed. In other words, the smallest accessible nanosized BEA particles exhibit a higher

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* Corresponding author. Tel.: +49 89 2180 77623; fax: +49 89 2180 77622.
E-mail address: bein@lmu.de (T. Bein).

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aluminium content, which can be a serious disadvantage if nanoscale hydrophobic zeolites are desired.

Only few recipes leading to the formation of pure siliceous nanosized zeolite BEA have been reported in the literature [31]. Here we report the synthesis of high-silica and purely siliceous nanosized zeolite BEA in alkaline media in the presence of 4,4′-trimethylenebis(*N*-methyl, *N*-benzyl-piperidinium) (denoted TMP) acting as SDA. TMP was already reported to be an SDA for the synthesis of BEA material, but no information on the features of the obtained product was provided [32]. Here we investigate the influence of the physical (temperature and time, conventional heating, or microwave irradiation) and chemical (composition of the precursor gel) parameters on the resulting nano-zeolite BEA morphologies. In addition, a method to stabilize the nanosized particles and to prevent their aggregation in colloidal suspensions is presented.

2. Experimental

2.1. Preparation of the 4,4′-trimethylenebis(N-methyl, N-benzyl-piperidinium) bromide salt (TMPBr$_2$)

The *TMPBr$_2$* was prepared by reaction of benzyl bromide (Sigma–Aldrich, 98%) with 4,4′-trimethylenebis(1-methylpiperidine) (Sigma–Aldrich, 98%), at a stoichiometric ratio of two benzyl bromide to one 4,4′-trimethylenebis(1-methylpiperidine), using acetone as solvent. The amount of 12.0 g (0.05 mol) of 4,4′-trimethylenebis(1-methylpiperidine) was dissolved in 40 g of acetone (0.69 mol) and cooled down in ice. In a second flask, 17.1 g of benzyl bromide (0.10 mol) were dissolved in 80 g of acetone (1.38 mol), and the obtained solution was also cooled down in ice. Both solutions were mixed and stirred together overnight at room temperature after complete melting of the ice. The milky product was purified by filtration and rinsed with acetone. This operation was repeated three times, and finally the product was dried in an oven at 60 °C in order to remove the last traces of acetone.

2.2. Preparation of the 4,4′-trimethylenebis(N-methyl, N-benzyl-piperidinium)hydroxide solution (TMP(OH)$_2$)

The *TMP(OH)$_2$* was obtained by an ion exchange using silver oxide. Typically, 9 g of the TMPBr$_2$ (0.0156 mol) SDA were dissolved in 25 g of water (1.39 mol). To the TMPBr$_2$ solution was added 3.6 g of silver oxide (0.0156 mol) and the exchange was performed 24 h at room temperature under stirring. After separation of the silver bromide formed in the TMP(OH)$_2$ solution by centrifugation, the concentration of the hydroxide solution was determined by titration with sulphuric acid (0.05 M). A dark yellow solution was obtained.

2.3. Preparation of the BEA precursor gels using TMP as structure-directing agent

The chemical and physical synthesis parameters for all samples are listed in Table 1. A typical preparation of purely siliceous BEA precursor gel consisted of mixing 14.45 g of double distilled water (0.80 mol) with 27.8 g of 20 wt.% TMP(OH)$_2$ solution (0.012 mol of TMP(OH)$_2$ and 1.24 mol of water) together. Next, 4.89 g of Cab-O-Sil M5 (0.0807 mol of silica, Cabot) was added to the solution and the system was stirred at room temperature for 2 h. Tetraethoxysilane (TEOS, 98%, Sigma–Aldrich) was also used as silica source. The EtOH obtained during the hydrolysis of TEOS was evaporated at room temperature overnight under stirring prior to the hydrothermal treatment, the concomitant water loss was compensated. The syntheses of purely siliceous zeolite BEA were performed using the following molar gel composition: 1 SiO$_2$:*x* TMP(OH)$_2$:25 H$_2$O, where *x* is in the range of 0.15–0.30.

The precursor gels were transferred into steel autoclaves with 20 mL Teflon liners, and the syntheses were performed under autogeneous conditions with conventional heating (CH) at 100 °C. Microwave irradiation (MW) was performed with a CEM-MARS 5 microwave oven, heating the gels (25 mL) to 90 or 100 °C with power in the range of 200–800 W. After hydrothermal (HT) treatment, the zeolite nanoparticles were purified by three-step centrifugation (19,000 rpm, 30 min) using water as a solvent.

For the Al-containing BEA precursor gel, aluminium tri-(sec-butoxide) was used as aluminium source, and its hydrolysis was achieved in the TMP(OH)$_2$ solution within an hour at room temperature. The silica source was then added to the latter solution and the combined solutions were stirred at room temperature for 2 h. The composition of the precursor gel was 1 SiO$_2$:0.01 Al$_2$O$_3$:0.25 TMP(OH)$_2$:16 H$_2$O. The gels were heated at 125 °C for 10 days in a conventional oven or for 28 h in a microwave oven.

2.4. Preparation of the BEA precursor gels using TEA cation as structure-directing agent

Al-containing nano-BEA zeolite was also prepared by using a conventional synthesis route in the presence of TEA cations acting as SDA. The reactants used were tetraethylammonium hydroxide (TEAOH) 35 wt.% (Fluka), aluminium tri-(sec-butoxide) as alumina source, and TEOS or Cab-O-Sil M5 as silica source. The alumina source was first dissolved at room temperature during 1 h in the TEAOH solution, followed by addition of the silica source. The ethanol released during the hydrolysis of the TEOS was evaporated at room temperature overnight prior to the synthesis. The precursor gels were aged overnight. A typical preparation consisted of mixing 15 g of water (0.83 mol) with 21.0 g of TEAOH 35% (0.05 mol of TEAOH and 0.76 mol of water). Next, 0.51 g of aluminium tri-(sec-butoxide) (0.002 mol) was added to the solution and the mixture was stirred for 1 h at room temperature, followed by the addition of 6.05 g of Cab-O-Sil (0.1 mol). The composition of the precursor gel was 1 SiO$_2$:0.01 Al$_2$O$_3$:0.50 TEAOH:16 H$_2$O. The gel was stirred and aged overnight. After pouring the precursor gels into steel autoclaves with 20 mL Teflon liners, the syntheses were performed under autogeneous conditions for 5 days at 140 °C. See also Table 1.

After the hydrothermal treatment, the zeolite nanoparticles were purified according to the procedure described above.

2.5. Characterization

The powder X-ray diffraction (XRD) patterns of zeolite samples extracted after each individual HT synthesis stage were collected in Debye–Scherrer geometry on a STOE STADI-P diffractometer equipped with a linear position sensitive detector employing monochromatic Cu Kα radiation. The mean particle size and the particle size distribution of the crystals stabilized in water, ethanol (EtOH), normal propanol (*n*-PrOH), or normal butanol (*n*-BuOH) suspensions were determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS instrument (scattering angle of 173°, laser wavelength of 632.8 nm, output power of 3 mW). Micrographs of the samples were taken with a Philips XL 30 LaB$_6$ scanning electron microscope (SEM). Transmission electron micrographs of the nanosized crystals were recorded using a JEOL JEM 2011 microscope operated at 200 kV. Prior to the TEM investigation, the zeolite suspensions were purified twice and finally redispersed in ethanol. The diluted zeolite–ethanol suspensions were deposited on carbon grids and dried at room temperature.