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Pure silica BETA colloidal zeolite assembled in thin films

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Received (in Cambridge, UK) 31st October 2002, Accepted 5th December 2002
First published as an Advance Article on the web 20th December 2002

Pure silica nanoscale zeolite BETA with monomodal particle size distribution was synthesized from a colloidal precursor solution and successfully applied for the preparation of hydrophobic ultrathin films on silicon wafers *via* spin coating.

Zeolite BETA is a large-pore microporous material characterized by three sets of mutually perpendicular channels with 12-membered ring apertures; these features make the material suitable for numerous applications such as heterogeneous catalysis, sensors, membranes, *etc*. BETA can be prepared from classical aluminosilicate gels with a wide range of Si/Al ratios.[1–3] The number of acid sites and the hydrophobicity of the microporous materials can be tuned by controlling the Si/Al ratio. One very important application of pure siliceous microporous zeolites exhibiting hydrophobicity is in the field of nanoscale layers with low dielectric constant (low-*k*) for microelectronics applications.[4–6] Several strategies have been applied for the formation of microporous films, and recently a very effective method was established for the preparation of ultra-thin pure siliceous MFI type films on two-dimensional supports *via* spin-coating of stable colloidal solutions.[4,5] By using organic additives during the synthesis procedure, colloidal solutions were prepared and used for the preparation of different nanosized colloidal molecular sieves.[7–13] Several microporous materials including MFI, LTA, FAU, BEA and LTL in the form of stable colloidal suspensions with narrow particle size distribution (100 nm) have been described in the literature. Interestingly, among all colloidal zeolites the pure silica forms were only reported for the MFI and MEL structure types.[4,5,8,12,14]

Pure silica zeolite BETA has been synthesized by Corma and coworkers, using TEA as a template and fluoride ions at near neutral pH.[15] In addition, BETA crystals were recently prepared *via* a solid–solid transformation method.[16] However, both methods and the resulting crystals are not appropriate for the preparation of thin films that could be used as low-*k* dielectric layers. The synthesis of large pore siliceous BETA zeolite in colloidal form is anticipated to permit a substantial improvement of zeolite film preparation and a decrease of the dielectric constant of the films compared with medium-pore MFI or MEL types zeolite.

In this communication we report the synthesis of pure siliceous hydrophobic zeolite BETA with monomodal particles size distribution from colloidal precursor solutions, and the preparation of ultra-thin films on silicon wafers *via* spin-coating of stable BETA/EtOH colloidal suspensions.

Nanosized BETA crystals were synthesized from a colloidal precursor solution having the following chemical composition: $SiO_2 : 0.2\ (TEA)_2O : 11.8\ H_2O$. The silica source for the preparation of the initial precursors was freshly freeze-dried colloidal silica Ludox SM 30 (30 wt%) and the alkali source was tetraethylammonium hydroxide (20 wt% in water). These components were mixed under vigorous stirring and aged on an orbital shaker at ambient temperature for 24 h prior to the further hydrothermal (HT) treatment at 100 °C for 11 days. The nanosized crystals resulting from the hydrothermal treatment of colloidal solutions were purified by separation from the mother-liquor by three steps of centrifugation (20000 rpm, 60 min). After each step the nano-particles were redispersed in doubly distilled water using an ultrasonic bath for 2 h. For the deposition of films the BETA crystals were redisperesed in ethanol (98%). Uniform films were prepared *via* spin-coating of BETA/EtOH coating solutions (solid content ~ 1.6 wt%) at an acceleration rate of 1500 rpm s^{-1} and a spinning rate of 3000 rpm for 30 s. Dynamic light scattering (DLS) was used to follow the crystal growth of pure siliceous BETA-type zeolite (ALV–NIBS/HPPS, scattering angle 173°, He–Ne laser with 3 mW output power at 632.8 nm wavelength). By applying a distribution function analysis (DFA), the particles were classified in logarithmic radius classes based on the Rayleigh–Debye model.[14] The ^{29}Si and ^{27}Al MAS NMR experiments were carried out with 4 mm ZrO_2 rotors in a commercial double resonance probe using a DSX advance impulse spectrometer (Bruker DSX avance 500). X-Ray diffraction (XRD) powder data of the freeze-dried BETA bulk samples were collected on a Scintag XDS 2000 instrument, while the structural evolution of zeolite films was studied with grazing incidence diffraction (GID) using synchrotron X-ray radiation (incident angle α_i = 0.1°). The scattering geometry for the grazing incidence diffraction is shown elsewhere.[17] Images of the nanosized zeolite particles were taken on a Philips XL 40 scanning electron microscope (SEM). The composition of the pure siliceous form of zeolite BETA was confirmed by ICP-AES chemical analysis.

A clear precursor solution, prepared as described above, was aged at room temp. on an orbital shaker and after a defined period of HT treatment was subjected to DLS measurements. The particles in the initial amorphous solution and the crystalline suspensions were classified in logarithmic classes and displayed as scattering intensity per unweighted particle size classes (Fig. 1). The presence of colloidal particles with a size of about 15 nm is detected in the precursor solution after an aging period of 24 h. In addition to these primary particles (~ 15 nm), larger ones with a mean radius of about 100 nm are present. The second population of particles is believed to be aggregates of primary particles existing in the pure silica source (mean radius of about 6 nm). The scattering intensity from the second generation of particles increases after HT treatment. The particle size distribution curves (see Fig. 1) demonstrate that the consumption of the small colloids is a time-dependent process,

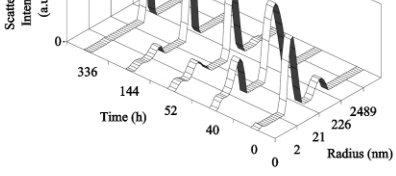

Fig. 1 DLS data of pure siliceous precursor solution resulting in zeolite BETA after different heating times at 100 °C. The DFA is displayed as scattering intensity per unweighted particle size classes.

DOI: 10.1039/b210767h

and after 46 h heating, the 100 nm fraction is already dominant in the system. However, the small fraction of particles of about 15 nm is still present in the system after 200 h HT treatment. The total consumption of the 15 nm particles and the associated formation of only one crystal-fraction with a radius of 100 nm and a narrow size distribution is shown for a sample heated for 340 h (Fig. 1). The XRD analysis of the purified and freeze-dried sample reveals that BETA-type molecular sieve was crystallized after 340 h (Fig. 2(a)), and with decreasing the fraction of 15 nm particles under heating of the solution from 30 to 200 h, the crystallinity of the sample increases. All Bragg reflections characteristic of zeolite BETA appear in this pattern and they are comparable with a BETA sample (Si/Al = 31) synthesized according to ref. 2 (Fig. 2(b)). Complementary ^{29}Si and ^{27}Al solid-state NMR investigations were performed with the freeze-dried pure silica zeolite BETA and the reference sample of zeolite BETA with Si/Al = 31. Both spectra contain two shifts at -102.0 and -109.9 ppm corresponding to the ^{3}Q and ^{4}Q types silicon species, respectively. On the other hand, tetrahedral aluminium species are found only in the BETA reference samples, where the chemical shift is observed at ~ 58 ppm. The pure silica zeolite BETA does not exhibit any single ^{27}Al resonance peaks, which confirms the pure silica form of the sample in addition to the results obtained by the ICP-AES chemical analysis.

The coating suspensions of small BETA crystals in ethanol were spin-coated on square-shaped Si wafers to form thin, quasi-continuous films. SEM top view images of the samples reveal that the suspensions of nanosized crystals cover the entire surface of the substrates (Fig. 3(a)). The BETA film contains close-packed zeolite particles that form a continuous multi-layer.

In order to evaluate the crystals constituting the films, XRD patterns were recorded at a constant incident angle $\alpha_i = 0.1°$ which corresponds to a penetration depth of about 8 nm. The Bragg intensity was collected with a position sensitive detector (PSD) placed perpendicular to the samples surface.[17] The XRD pattern obtained from the BETA film contains very intensive Bragg reflections with (*hkl*) values equal to (101), (205) and (302) (Fig. 3(b) and (c)). Grazing incidence diffraction using synchrotron X-ray radiation allows for an investigation of the very thin polycrystalline zeolite films, and the high intensity of the Bragg reflections permits to determine the average size of the individual zeolite particles forming the films. In this case, the preferred orientation of the crystals forming the BETA films is not of a great importance having in mind that this zeolite structure has three-dimensional channel systems with 12-member ring pore-openings.

In conclusion, the present paper reports on the preparation of pure siliceous zeolite BETA with monomodal particle size distribution in a colloidal form. The nanoscopic entities provided by the silica sol and the particle size distribution during the transformation from amorphous into crystalline pure siliceous BETA was studied by dynamic light scattering using the back scattering mode. The mean radius of the final BETA crystals is about 100 nm. These colloidal BETA crystals were used for the preparation of stable coating suspensions applied for the deposition of thin hydrophobic films on silicon wafers. The present method is suitable for several applications including sensor devices, and optical coatings. Owing to the high surface area, large pore volume, three-dimensional channel system and the hydrophobicity of pure siliceous zeolite BETA, this material is particularly interesting for the preparation of low-*k* dielectric layers.

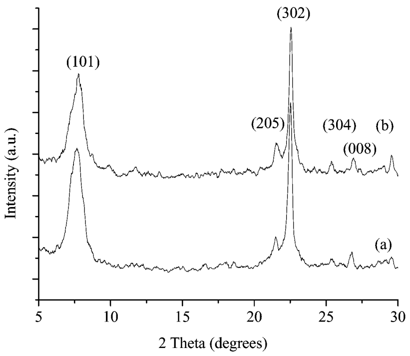

Fig. 2 Powder diffraction pattern of (a) pure siliceous zeolite BETA resulting from the precursor solution after 340 h of hydrothermal treatment at 100 °C, and (b) a reference sample of zeolite BETA (Si/Al = 31) synthesized according to ref. 2.

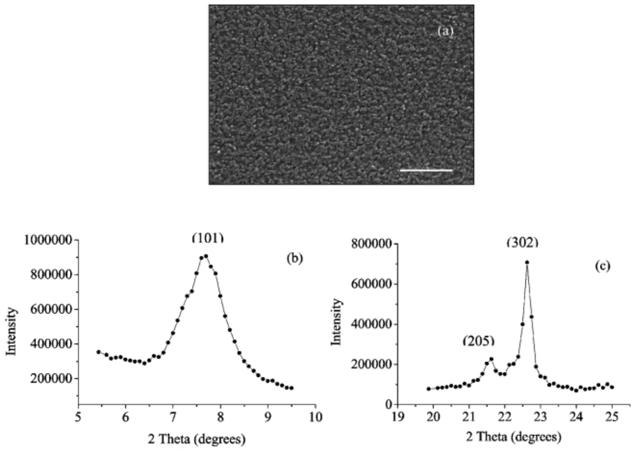

Fig. 3 (a) SEM image of zeolite BETA film deposited on a Si wafer *via* spin-coating (scale bar = 2 μm); Radial (2θ)-scans of BETA film deposited *via* spin-coating: (b) in the 2θ range 5–10°, (c) in the 2θ range 19–25° (angle of incidence: $\alpha_i = 0.1°$).

We thank the Bavarian–French Foundation, DFG and the ESRF-Grenoble for partial financial support.

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