Ultrathin oriented zeolite LTA films

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Ultrathin oriented films of zeolite LTA are prepared on single-crystal alumina supports by a method including adsorption of LTA seeds on the support followed by hydrothermal film crystallization.

Molecular sieve films have great potential for example as membranes and membrane reactors as well as in sensor applications. Supported films of molecular sieves are usually synthesized by direct crystallization of the zeolite on the support.[1] Most of the work reported concerns the preparation of MFI films[2–8] because of the simplicity of this system and only a few reports treating the preparation of other types of zeolite films have appeared in the literature.[9–12] Independent of zeolite type, these films generally have a thickness exceeding 1 μm. The flux through a membrane or the response time of a chemical sensor is greatly dependent upon the film thickness and hence thin films are preferable in both membrane and sensor applications. The performance of zeolite membranes and sensors is also influenced by the orientation of the zeolite crystals constituting the film. The orientation will affect the diffusion path through the membrane and the adsorption kinetics of a chemical sensor consisting of a supported zeolite film. Recently, a novel method was presented for the preparation of ultrathin films of silicalite-1 on various substrates.[13,14]

Here, we report on the first preparation of an ultrathin oriented zeolite LTA film on a single-crystal alumina(0001) wafer. LTA seeds were prepared by hydrothermal treatment at 63 °C for 63 h of a synthesis solution with the composition $0.22Na_2O:5.0SiO_2:Al_2O_3:8.0(TMA)_2O:400H_2O$. The synthesis solution was prepared by first dissolving aluminium isopropoxide (Sigma) and tetramethylammonium hydroxide pentahydrate (Sigma) in a sodium hydroxide solution at room temp. and then mixing this solution with a dilute silica sol (Bindzil 30/220, 31 mass% SiO_2 and 0.5 mass% Na_2O, Akzo Nobel AB). After synthesis, the seed sol was purified by repeated centrifugation and redispersion in an ammonia solution so as to maintain a pH exceeding 10.5. The sol was finally diluted to a solids content of 2.5 mass% (determined after drying at 100 °C) and adjusted to a pH of 10.7. A polished alumina(0001) wafer (10 × 10 × 0.5 mm, Coating & Crystal

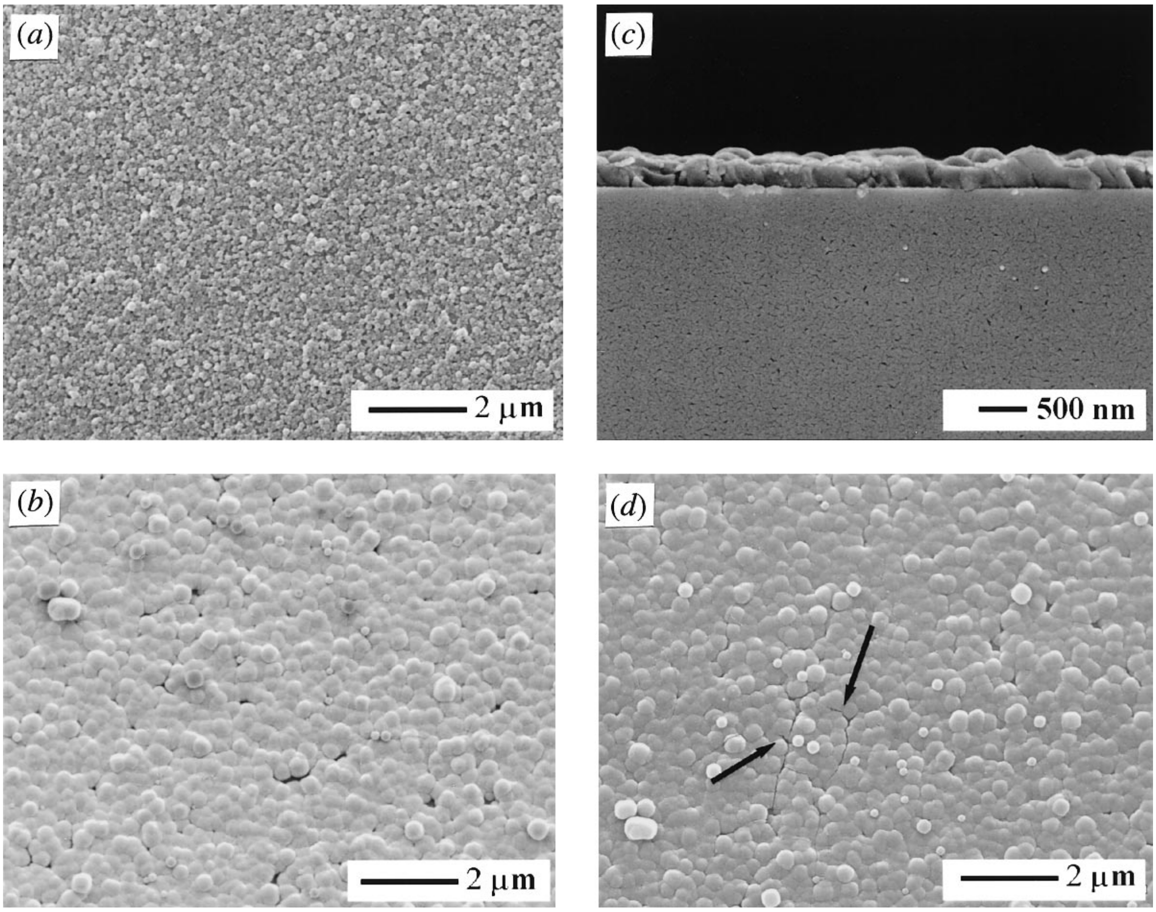

Fig. 1 SEM micrographs showing the adsorbed zeolite LTA seed crystals after three repeated adsorptions on the substrate surface (*a*), the top view of the film after calcination recorded at an accelerating voltage of 4 kV (*b*), the side view of the film after calcination (*c*) and the top view of the film after calcination recorded at an accelerating voltage of 20 kV with arrows indicating cracks (*d*)

Technology) was mounted vertically in a Teflon holder and treated in acetone in an ultrasonic bath for 5 min followed by rinsing with distilled water. The substrate was boiled for 5 min in a mixture of H_2O, H_2O_2 and NH_3 (5 : 1 : 1 v/v/v of H_2O, 30% H_2O_2 and 25% NH_3), rinsed with distilled water and boiled for 5 min in a mixture of H_2O, H_2O_2 and HCl (6 : 1 : 1 v/v/v of H_2O, 30% H_2O_2 and 37% HCl) and finally rinsed with water and a 0.1 M ammonia solution. After the rinsing procedure the wafer was immersed in a 0.4% solution of a cationic polymer (Berocell 6100, Akzo Nobel AB, repeating unit $[\mathrm{CH_2CHOHCH_2NMe_2}]^{+}{}_{n}$, M_w = 50 000 g mol^{-1}, pH 8.0) for 5 min to reverse the surface charge of the alumina wafer from a negative to a positive value. The charge reversed wafer was rinsed in a 0.1 M ammonia solution to remove excess polymer. The substrate was treated with the LTA seed sol for 5 min to adsorb seed crystals on the charge reversed alumina surface and rinsed in a 0.1 M ammonia solution to remove excess seed crystals. This sequence, charge reversal–adsorption of seeds, was repeated twice to improve the seed coverage on the surface. Film crystallization on the seeded substrate was effected by hydrothermal treatment at 100 °C for 6.3 h in a synthesis solution prepared in the same manner and with the same composition as that used for the synthesis of the seed crystals (*vide supra*). After completion of this treatment, the sample was rinsed with a 0.1 M ammonia solution and dried in air. Samples were calcined at 425 °C for 1 h in air, using a heating and cooling rate of 1 °C min^{-1}. Particle size analysis by dynamic light scattering (DLS) was performed on the seed sol and on synthesis solutions after synthesis with a Brookhaven Instruments ZetaPlus. Electron micrographs were recorded with a Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source. X-Ray diffraction (XRD) data were collected with a Siemens D5000 powder diffractometer equipped with a Göbels mirror, 12 cm soller slit and a secondary LiF monochromator when analysing the film. A primary soller slit and variable slits to keep the illuminated area constant were used when analysing powder samples.

The average crystal size in the LTA seed sol was determined by DLS to be 130 nm with a polydisperisty of 0.1. Fig. 1(*a*) shows a SEM micrograph of the adsorbed LTA seeds on the alumina support after the three adsorption steps. Approximately 80% of the support surface is covered by seeds. The coverage after one and two adsorption steps was approximately 40 and 65%, respectively. Fig. 1(*b*) and (*c*) show top- and side-view SEM micrographs of the calcined LTA film recorded with an accelerating voltage of 4 kV. The film is essentially continuous and free of cracks with a constant thickness of *ca.* 280 nm. Fig. 1(*d*) shows essentially the same area as in Fig. 1(*b*) but recorded with an accelerating voltage of 20 kV. A comparison between the two micrographs reveals that cracks have developed, most likely due to the bombardment of the film with 20 keV electrons in the SEM when recording the micrograph in Fig. 1(*d*). Fig. 2 shows X-ray diffraction patterns of freeze-dried seeds (*a*), the purified and freeze-dried product formed in the bulk of the synthesis solution (*b*) and the film after synthesis [(*c*) and (*d*)]. The powder patterns [(*a*) and (*b*)] were recorded using a θ–2θ scan whereas patterns (*c*) and (*d*) [(*d*) is an enlargement of (*c*)] of the film were recorded with a detector scan at a grazing incidence angle of 1°. From patterns (*a*) and (*b*) in Fig. 2 it is clear that both the seeds and the bulk product consist of well crystallized zeolite LTA. The Si/Al molar ratio of the bulk product was determined by EDS analysis to be 1.1. DLS measurements showed that the average size of the final crystals obtained in the bulk phase at 100 °C was *ca.* 330 nm, *i.e.* considerably larger than the 130 nm seed crystals formed at 63 °C. The difference in crystal size explains the narrower peaks in the diffractogram recorded for the bulk product compared with the peaks in the diffractogram from the seeds. The diffractograms (*c*) and (*d*), of the final film, show that the film consists of oriented zeolite LTA crystals. The only peaks visible in this pattern are those due to (*h*00) reflections or diffraction from planes with large *h* compared with *k* and *l* indicating that the (100) plane of all crystals in the film is essentially parallel to the substrate surface.

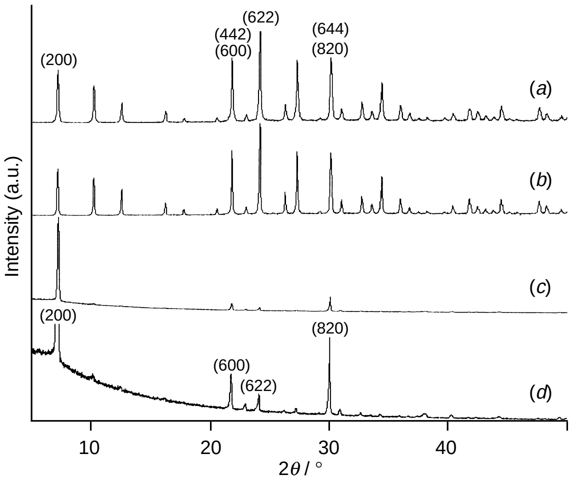

Fig. 2 X-Ray diffraction patterns of the freeze-dried seeds (*a*), the purified and freeze-dried product formed in the bulk of the synthesis solution (*b*) and the film after synthesis (*c*) and (*d*) [(*d*) is an enlargement of (*c*)]. None of the samples were calcined prior to X-ray diffraction analysis.

The results presented show that the seed film method[13] can be used to synthesize ultrathin, oriented zeolite LTA films in a simple and elegant manner.

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Footnote

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