

Seeded Synthesis of Very High Silica Zeolite A

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Microporous zeolite type materials are widely used in the chemical process industry. At present, there are 174 identified zeolite structure types, but only a few of them find industrial application. Thus, the development of new zeolitic materials that could lead to new or more efficient technological solutions is highly desirable. The continuous efforts in the preparation of new microporous solids are oriented in two directions: (i) synthesis of new structure types; and (ii) extension of the composition of known materials beyond known limits. In recent years, Corma and co-workers have made substantial contributions in both directions. Many new exciting structure types have been synthesized using the fluoride route and germanium as a costructuring agent.^{1–5} This approach led also to the synthesis of a silicogermanate counterpart of zeolite A (IM-11), a zeolite with a neutral LTA-type framework.^{6a} However, probably one of the most amazing discoveries was the all-silica LTA-type material named ITQ-29.^{6b,7} This breakthrough opens up routes for the extension of zeolite framework compositions beyond the limits postulated by the structure type.

Because of its excellent ion-exchange capacity and consequent use as a water-softener agent in modern-day washing powders, zeolite A boasts the greatest worldwide industrial tonnage of any zeolite. The LTA-type framework topology is known with the abundant presence of double four rings,⁷ which are the preferential place for aluminum atoms. The Si/Al ratio of the LTA-type framework is close to 1, and long-term efforts of the applied scientists did not bring a substantial increase. The replacement of sodium by the bulky tetramethylammonium (TMA) cation increased this ratio to about 2, which was not sufficient to change the hydrophilic

properties of the material and allow selective adsorption of organic molecules or catalytic applications.^{8,9} All-silica material with the LTA-type topology was synthesized by Corma et al. by supramolecular self-assembly of two organic moieties, which allowed them to overcome structural hindrance in the formation of double-four rings and made it possible to build the framework exclusively of SiO₄⁴⁻ tetrahedra.^{6b,c}

After the publication of the ITQ-29 synthesis in the patent^{6c} and open^{6b} literature, there appeared just one report devoted to its properties.¹⁰ Such low research activity about a material with exceptional importance from both industrial and academic points of view is most probably due to difficulties in its manufacturing. It should be mentioned that the synthesis of a new zeolitic material is often difficult to repeat because of a cryptic description or differences in the employed reagents. Certainly, the synthesis of an all-silica LTA-type material is very specific; two organic structure-directing agents are involved, as one of them forms a dimer that structures the large cage and the other one the sodalite unit.^{6b} It should also be mentioned that the material is synthesized in fluoride media at an extremely low water content (H₂O: SiO₂ = 2). Thus, any small deviation in the synthesis procedure might change the crystallization pathway and result in undesired products. The present paper reports on a simple and effective route providing high-quality LTA-type materials with Si/Al ratios ranging from 100 to 2400.

Our first attempt at synthesizing this material resulted in a mixture containing about 90% AST-type and 10% LTA-type zeolites. It is well-known that the nucleation under hydrothermal conditions can be induced by seeding, which was demonstrated for a number of zeolites, including the LTA-type.^{6c} Because all-silica LTA-type crystals were not available, we have employed zeolite A nanocrystals synthesized according to ref 11. The advantage of monodisperse nanocrystals is that they can be uniformly distributed in the gel and uniform nucleation can thus be induced. Furthermore, the chemical stability of the nanocrystals in the initial fluoride-rich system is expected to be higher in respect to the conventional Na–A crystals, first because of the higher Si/Al ratio (ca. 1.9) and second because of the tetramethylammonium (TMA⁺) cations stabilizing the sodalite cages. A series of experiments using different amounts of seeds (10, 5, and 1 wt % seeds with respect to the silica content)

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(12) The reactants used were tetraethylortosilicate (98 % Fluka), tetramethylammonium hydroxide (TMAOH·5H₂O, Aldrich), HF acid (40%, Carlo Erba), distilled water, and self-made 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3.2.1-ij]quinolinium iodide, which was transformed into its OH form by ion exchange (Amberlite IRA 400, Aldrich). After mixing of the reactants, the excess water was evaporated in a vacuum drier operating at 100 mbar pressure and 50 °C for at least 48 h. The syntheses were performed in Teflon-lined autoclaves at 135 °C for different periods of time.

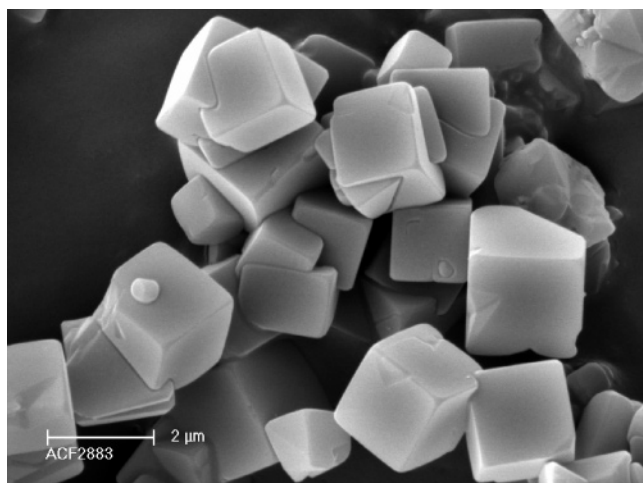


Figure 1. SEM micrograph of LTA-type crystals with Si/Al = 2400. Crystal size and morphology is representative for all synthesized samples.

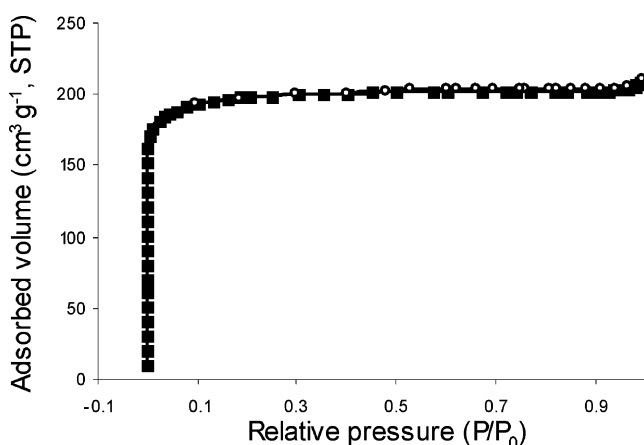


Figure 2. Adsorption/desorption isotherms of zeolite A crystals with Si/Al = 110.

and a gel with molar composition 1:0.25:0.25:0.5:4.5 SiO₂:ROH:TMAOH:HF:H₂O, where R is 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3.2.1-ij]quinolinium hydroxide, were performed.¹² The organic structure-directing agent (R) was prepared according to the procedure described in the Supporting Information of ref 6b. All syntheses yielded highly crystalline LTA-type material according to the XRD study (STOE Stadi-P) (see the Supporting Information). No indications of amorphous or other crystalline phases were found. The high purity of the materials was confirmed by the SEM (FEG Philips XL30) inspection of the solid. Only crystals with the typical cubic morphology of LTA-type material ranging between 1 and 3 μm were observed (Figure 1). The highly crystalline nature of the material was further proved by N₂ adsorption measurements (Micromeritics ASAP 2010). The adsorption/desorption isotherms of the calcined material are typical of microporous materials (type I), where the steep uptake at low relative pressure is followed by horizontal adsorption and desorption branches (Figure 2). The *S*_{BET} (ca. 690 m² g⁻¹) and micropore volume (0.26 cm³ g⁻¹) of the material are characteristic of a highly crystalline LTA-type material. The TG analysis showed that the weight loss between 25 and 180 °C, which corresponds to the water content in the as-synthesized materials, is below 0.5 wt %. The decomposition of the organic structure-directing agents

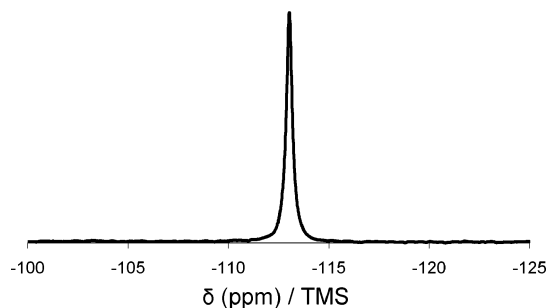


Figure 3. ²⁹Si MAS NMR spectrum of calcined LTA-type material with Si/Al = 2400.

(25.5 wt %) takes place in a very broad temperature range (180–700 °C; see the Supporting Information). After calcination at 600 °C for 8 h, the materials were white and showed high crystallinity. The framework Si/Al ratio of the obtained LTA-type materials determined by X-ray fluorescence (Philips MagiX) was found to be a function of the amount of seeds introduced in the initial system. Thus, LTA-type materials with Si/Al ratios of 110, 267, and 440 were obtained with 10, 5, and 1 wt % nanoseeds, respectively. These data clearly show that during the hydrothermal treatment, the seeds were dissolved and aluminum was incorporated in the growing crystals. This series of syntheses revealed also that the introduction of 1 wt % seeds is sufficient to promote the nucleation of siliceous LTA-type material. We considered 1 wt % seeds to be a reasonable amount and did not perform further experiments to decrease the seed content. All following syntheses were performed with 1 wt % seeds with respect to the silica content. Second- and third-generation crystals were active as seeds and LTA-type materials with aluminum content on the order of a few parts per million were thus synthesized. For instance, the Si/Al ratio of material synthesized with third-generation seeds was 2400. The XRD study did not detect any presence of crystalline or amorphous material in the solid (see the Supporting Information). This material was studied by ²⁹Si MAS NMR (MSL 300 Bruker). Only a sharp resonance at -113 ppm, characteristic of Q⁴ units was observed. The spectrum was carefully inspected for the presence of Q³ sites indicative of structural defects (Figure 3). No resonance in the range 95–100 ppm was found, which proved the defect-free nature of the synthesized LTA-type material.

The original synthesis of an all-silica LTA-type material was performed at 135 °C for 7 days.⁷ Our seeded syntheses were performed under the same conditions. However, the traces of dissolution observed on the 100 faces of some crystals suggest that the required crystallization time was exceeded. Zeolites are metastable phases and, under non-equilibrium conditions, they can be easily dissolved or transformed into more stable ones. Hence, the observed traces of dissolution are most probably due to relatively rapid crystal growth kinetics and thus reach nonequilibrium conditions in seeded systems. To determine the exact time required for seeded synthesis of all-silica LTA-type materials, we have studied the crystal growth kinetics in the presence of 1 wt % seeds (Si/Al = 440) that yielded LTA-type materials with Si/Al = 1500. As can be seen in Figure

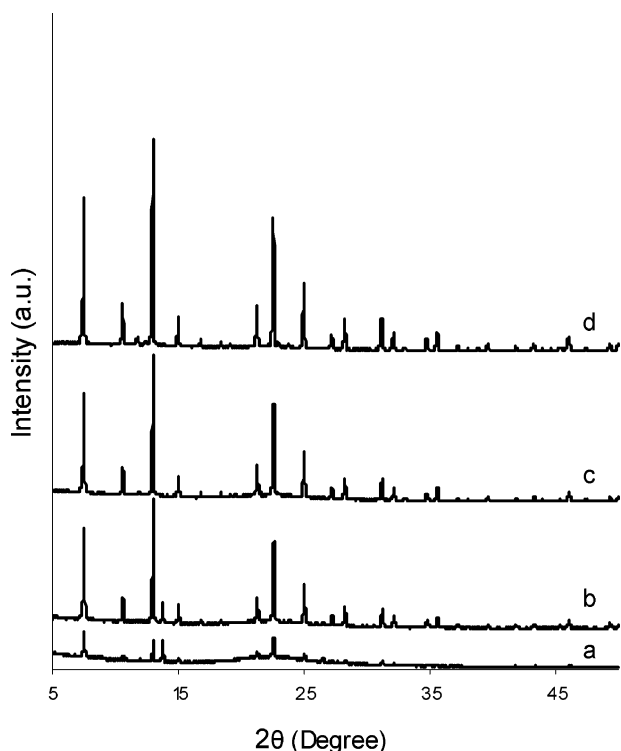


Figure 4. XRD patterns of the LTA-type samples (Si/Al = 1500) collected after (a) 6, (b) 14, (c) 18, and (d) 24 h of hydrothermal treatment at 135 °C.

4, after only 6 h of crystallization, the solid contains a distinguishable portion of crystalline LTA-type material. Further conversion of the amorphous into crystalline material was observed after 14 and 18 h of crystallization (parts b and c of Figure 4). An amorphous halo is still visible in the latter sample, whereas the 24 h material is fully crystalline according to the XRD study. The comparison of the surface area of 200 peaks of the 24 h solid and a reference sample (material synthesized with 10 wt % seeds) showed that the conversion of the seeded system is 85%. LTA-type material with about 95% crystallinity was obtained within 48 h. The crystal growth kinetics seems to slow down at this latter crystallization stage, most likely due to insufficient supply of nutrients. During this period, the nutrients are generally provided by the dissolution of larger or inert amorphous particles and smaller, less-stable crystallites (Ostwald ripening).

The above data are a sound proof that seeded syntheses substantially improve the crystal growth kinetics and lead to complete conversion of the amorphous precursor into all-silica LTA-type materials. On the other hand, without seeds, we obtained only about 10% LTA-type material using the same initial system. We consider as a fairly possible reason for the low LTA-type yield in the nonseeded system the presence of a small amount of iodine. As a matter of fact, the conversion of the organic template (R) into its OH form was about 95%. A series of experiments with an 84% OH form converted template supports this suggestion. Thus, the

latter provided a mixture of amorphous LTA- and AST-type materials, although 1 wt % seeds were added to the gel. After further OH exchange, the iodine content in the template was reduced below 5%, and pure LTA-type material was thus synthesized. It should also be mentioned that we have never reached a SiO₂:H₂O ratio equal to 2 as in the original recipe describing the synthesis of all-silica zeolite A.^{6b} The H₂O:SiO₂ molar ratio in our systems was between 4 and 5, which is, however, still in the range pointed out for the synthesis of germanosilicates with the LTA-type topology.^{6b}

Another question that needs to be addressed is the role of aluminum released during seed dissolution. Although the amounts are negligible, they might have an important function in the formation of first unit cells of LTA-type crystals. We observed the presence of 3–4% AST-type zeolite in sample with Si/Al = 1500 (parts c and d of Figure 4) that might be related to a substantial decrease of aluminum in the system. On the other hand, traces of AST-type were not found in the XRD pattern of the Si/Al = 2400 sample. Hence, we consider that the presence of aluminum is not an indispensable condition for the nucleation of LTA-type zeolite. The presence of AST-type contamination is more likely to be a result of the quality of the organic structure-directing agent used in some experiments or insufficient homogenization of initial reactants.

In the present study, we have reported on the seeded synthesis of zeolite ITQ-29. Besides having much faster crystal growth kinetics, the zeolite seeds ensured full conversion into all-silica LTA-type materials of systems that without seeding provided mainly AST-type zeolite and noncrystalline material. The study revealed that conventional Al-rich LTA-type crystals can be successfully employed as seeds. Aluminum-containing zeolite A seeds were dissolved during the crystallization, and Al was incorporated in the framework of the growing high-silica-content LTA-type crystals. Materials with Si/Al ratios of 110, 267, 440, 1500, and 2400 were thus synthesized. Strictly speaking these materials are not all-silica zeolites. However, the decrease in aluminum content much below one atom per unit cell makes them materials that possess all characteristics of all-silica zeolites.

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Supporting Information Available: (1) XRD pattern of LTA-type material with Si/Al = 110; (2) XRD pattern of LTA-type material with Si/Al = 2400; (3) TG/DTA curves of the LTA-type material with Si/Al ratio of 1500 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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