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Microscopic Investigation of Nanocrystalline Zeolite L Synthesized from Rice Husk Ash

Jia-Tian Wong, Eng-Poh Ng, † and Farook Adam ‡
School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

An investigation of aluminosilicate zeolite L (structure code LTL) nanocrystals converted from rice husk ash in template-free system is reported. Crystallization evolution of the zeolite L was monitored and followed by X-ray diffraction, high-resolution transmission electron microscopy, scanning electron microscopy, atomic absorption spectroscopy, and infrared spectroscopy techniques. It was found that fully crystalline zeolite L (Si/Al = 3.0) with square tablet morphology was nucleated at 4 h, and the crystals with a mean particle size of 210 nm was completely transformed from amorphous silica after 24 h of hydrothermal treatment.

I. Introduction

Zeolites with intricate micropores have been extensively studied for a long time as an important class of industrial porous materials in different areas of chemical industry, such as gas adsorption and separation, ion exchange, and shape selective catalysis. 1 Particularly, zeolites in nanometer scale (<1000 nm) have been fascinating the world of science due to their unique properties, namely small crystal size, large external surface area, and the ability to reduce intracrystalline diffusion pathway to the active sites. 2,3 As a result, they are more favorably used than micrometer-sized zeolites, especially in catalysis, biological applications, chemical sensors, semiconductors, electronic applications, etc. 4-9

Nanocrystals with narrow particle size distribution are generally obtained from colloidal clear solution system. 10,11 To obtain such homogeneous precursor solution system, abundant amount of tetraalkylammonium hydroxides (organic templates) and alkaline cations are employed. The crystallization process is then performed at moderate temperatures for several days to obtain crystalline nanosolids. The formulated recipes for the synthesis of nanocrystalline materials, however, are noneconomically viable and environmentally unfriendly due to the large consumption of very expensive organic template, long crystallization time, and low crystalline yield (<10%). 12,13 Furthermore, the organic agents need to be removed by calcination to open up the porosity, which make the synthesis to be industrially unfavorable. Hence, the need for alternative synthesis method for the preparation of microporous molecular sieves in nanometer scale is highly desirable and is becoming a major focus of research mainly in academia and probably, at a later stage in the industry.

Over the last few years, many synthetic strategies have been derived for the preparation of nanocrystalline zeolite materials in an attempt to replace the conventional templating approach, including centrifugation-assisted grinding, 14 seed-induced, 15,16 reversed microemulsion, 17,18 confined space, 19 and ionothermal syntheses. 20 Nanocrystalline zeolites prepared from organic template-free system using economical sources, such as organic waste rice husk ash (RHA) is an interesting alternative. The RHA is an agricultural waste material which contains 96%-98% of SiO₂ 21,22 It can therefore provide a good alternative source of highly active silica for the synthesis of different zeolite types, such as Y 23 beta, 22 ZSM-5, 24 and NaA 25 zeolites. Nevertheless, there are only several articles reported on zeolite synthesis (NaA and NaX) in nanometer scale (<500 nm) from RHA. 26,27 This approach, however, has not been reported so far for the synthesis of zeolite L in nanometer size, and thus an attention on this research is worth to be explored.

Zeolite L has a framework structure consisting of cancrinite (CAN) cages and hexagonal prisms (D6R), alternating to form columns that run parallel to the c-axis, forming a cylindrical crystal shape. 28 It is a 12-membered ring zeolite system with a large pore opening (0.71 nm) which is widely used in catalysis and host-guest chemistry. 29,30 Recently, it was reported that the morphology of the LTL crystals can be controlled by precursor gel composition, source of silica, seeding, time, and temperature of crystallization. 31,32

This work reports on the microscopic investigation of discrete nanosized zeolite L crystals (structure code LTL) synthesized using RHA 23 as the reactive silica source in template-free system. Unlike previous nanosized LTL synthesis techniques, 31,34 the LTL nanozeolites in our system are obtained under static hydrothermal condition instead of dynamic condition as reported by other researchers.

II. Experimental Procedure

The RHA was chosen as an alternative source of silica as it is abundantly available in Malaysia. The silica was extracted from rice husk using a previously reported method. 35 The starting composition of the mixture was 10SiO₂:Al₂O₃:4K₂O:100H₂O. Initially, the silicate solution was prepared by dissolving RHA (3.9275 g, 98.4% SiO₂) in 8 mL of KOH solution (3.7787 M) at 80°C for 2 h. The clear alumina solution obtained from dissolution of Al(OH)₃ in KOH solution (1.0452 g, 3.7787 M) was then introduced into the silicate solution under vigorous stirring. The solution was autoclaved and treated at 170°C up to 24 h. The resulting solids were then purified with distilled water and dried at 80°C overnight.

The crystallinity and purity of the molecular sieve samples were investigated by X-ray powder diffraction by a Siemens D500 diffractometer (Karlsruhe, Germany) using CuKα radiation (λ = 1.5406 Å). Information for the crystal size and morphology of the samples was obtained by transmission electron microscopy (TEM) using a Philips CM12 microscope (FEI, Eindhoven, the Netherlands) operated at 200 kV. Prior to the TEM investigation, the zeolite suspensions were purified twice and finally, dispersed in ethanol. The diluted zeolite-ethanol suspensions were deposited on carbon grids and dried at room temperature. Micrographs
of the samples were also taken with a Philips XL 30 LaB$_6$ scanning electron microscope (SEM). Elementary analyses were performed by atomic absorption spectroscopy (AAS) using Perkin-Elmer Analyst 200 (Perkin-Elmer Instruments, Waltham, MA). Infrared spectroscopy analysis of solid samples was performed using KBr pellet technique with a Nicolet IR 200 spectrometer (Perkin-Elmer Instruments, Norwalk, CT) (32 scans, 4 cm$^{-1}$).

III. Results and Discussion

The crystallization process of nanocrystalline LTL solids was monitored by XRD technique. The initial solid material at 0 h under synthesis conditions is completely amorphous, Fig. 1(a). The morphology of the sample is shown in Fig. 2(a). Electron micrograph was unable to detect the presence of crystalline phase, but reveal the presence of 1–2 μm large amorphous entities. After 4 h of heating, crystalline lattice fringes with 0.7 nm spacing were observed in amorphous solid with TEM, showing that nucleation has taken place, Fig. 2(b). However, the XRD analysis was still not able to detect the crystalline phase due to the very low degree of crystallinity of the sample, Fig. 1(b).

The crystalline phase can be clearly observed after 8 h by XRD technique, and the diffraction peaks become more intense after 12 h, Figs. 1(c)–(e). The X-ray diffraction intensity of the solid after 24 h remains constant upon further heating. A simulated powder X-ray diffraction pattern of zeolite L is compared and indicates that a pure crystalline zeolite L phase is obtained, Fig. 1(f). The diffraction peaks for the samples were significantly broadened, indicating small crystal size. The relative crystallinity was calculated based on the ratio of the areas of the three most intense Bragg diffraction peaks at 2θ of 5.55, 11.76, and 27.97° for each sample, in comparison with a reference sample and the results are summarized in Fig. 3. It can be seen that the degree of crystallinity increased abruptly at 4 h and about 60% crystallinity had been achieved for the sample heated for 8 h, while crystalline sample with 91% crystallinity was obtained after 24 h of hydrothermal treatment.

The crystal size distribution was obtained by measuring 100 nanoparticles based on SEM micrographs, Fig. 4. The results clearly show the crystal morphology and the size of the synthesized zeolite L sample is in the range of 50–400 nm, centered at 210 nm. As shown in the SEM images in Fig. 4, the nanocrystalline zeolite L particles are present as discrete zeolite nanocrystals.

Nanocrystalline zeolite L prepared from RHA has a unidimensional channel structure with tablet-like feature (shorter c-dimension) which is different from the conventional cylindrical-shaped zeolite L, Fig. 2(c). This morphology is desirable in catalysis industry as the intracrystalline path length for reactants and products during reaction are reduced resulting in better diffusion. Figure 2(d) shows the TEM micrograph recorded on the a- and b-directions of the crystal after 12 h. It can be seen that zeolite L has a hexagonal structure which is well in agreement with the literature. Comparison of the simulated and experimental high-resolution TEM images of zeolite L viewed down the pores along c-direction is also shown in inset of Fig. 2(d), and confirms the hexagonal framework of the structure. The pore diameter is ~ 0.70 nm which agrees well with the actual pore size of zeolite L.

Evidence for the chemical evolution of the system was shown by analyses of the solid entities of the system. The
solid was separated from mother liquor, purified and analyzed by atomic absorption spectroscopy. The changes in the Si/Al ratio in the solids over different heating time are given in Table I. Results indicated that the initial solid has a Si/Al ratio of 4.23 and the silica content is slightly lower than the precursor Al and Si solutions before mixing (Si/Al ratio = 5).

A further decrease of the ratio was observed in a period of time from 4 to 12 h by which the mass transformation of the amorphous into crystalline material has been taken place as revealed by XRD and TEM studies. The Si/Al ratio reached a constant value after 12 h and no changes in the ratio of the solid were observed after that stage. The Si/Al ratio of the final crystalline product was ~3.0. Complimentary FTIR spectroscopy study was performed for the solid samples to follow the crystallization kinetic process. No IR absorption bands at 476, 580, 611, 714, and 778 cm⁻¹ were detected for the initial sample, which confirms the amorphous nature of this solid, Fig. 5(a). These five characteristic bands start to appear after 4 h of hydrothermal treatment, showing the formation of LTL framework structure is taking place which agrees with the observed TEM images, Figs. 2(b) and 5(b). Meanwhile, a band at 870 cm⁻¹ corresponding to T–OH (T = Al, Si) was also observed and it can be due to the formation of T–OH bonds as a result of T–O–T bonds breaking during the reorganization process of initial amorphous entity. This band, however, disappeared after 8 h and three bands at 1031, 1105, and 1158 cm⁻¹ appeared showing that the T–OH bonds had undergone hydrolysis and condensation to form monomeric or oligomeric intermediate species, Fig. 5(c). The five characteristic bands for zeolite L become more profound as the solid was further heated indicating that a fully crystalline zeolite L had been obtained, Fig. 5(e).

IV. Conclusion

A detailed investigation of the birth of zeolite L (LTL) nanocrystals from amorphous RHA has been reported for the first time. Microscopy and spectroscopy analyses have shown that the nucleation takes place in the very early 4 h. The fast formation of LTL nanoparticles is suggested to be caused by the use of RHA as the reactive silica source in the precursor solution. Pure and well-defined LTL crystals are formed after 8 h and a fully crystalline sample with a mean crystal size of 210 nm is achieved after 24 h.

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References
