

Nanoscale Snapshots of Zeolite Nucleation on Quartz Substrate

Tatsuya Okubo, Tooru Nakazawa and Masayoshi Sadakata

Department of Chemical System Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

phone: int+81-3-5800-3807, fax: int+ 81-3-5800-3806, e-mail: okubo@chemsys.t.u-tokyo.ac.jp

Zeolite, Si-ZSM-5, nucleation on a quartz substrate is visualized in nanometer scale using a field emission scanning electron microscope (FE-SEM). The change in the morphology and the size of particles formed on a substrate surface are carefully studied in the course of the synthesis. The 10nm sized particles are formed, whose number is increased and size is enlarged during the early stage of the crystallization. These particles are aggregated on the substrate, followed by the formation of the crystal-shape materials of 50 nm in size.

Key words: Zeolite, Nucleation, Crystal Growth, FE-SEM, Quartz

1. INTRODUCTION

Zeolite is a class of aluminosilicate microporous crystals occluding angstrom scale spaces within, and has been widely used as adsorbents, ion exchangers and catalysts. However, the detailed mechanism of the synthesis, the nucleation and the crystal growth, has not been well understood. Accordingly, the present synthesis process strongly depends on the experiences through trial and error. Based on the recent developments of instrumental analyses, the nucleation and the growth mechanism is getting clearer in these years, especially for high silica zeolites.

Burkett and Davis¹⁻³ applied cross-polarization magic angle spinning solid-state nuclear magnetic resonance (CP MAS NMR) to the Si-ZSM-5 synthesis in order to understand the noncovalent interaction in between Si of silicate and H of organic structure directing agent (SDA). Prior to the development of long-range order detected by powder x-ray diffraction (XRD), preorganized inorganic-organic composite structure was built in liquid phase. Before the synthesis, the SDA (tetrapropylammonium cations, TPA) in the aqueous solution was hydrated by hydrophobic hydration. When the silicate was added to the SDA solution, water hydrated was replaced with more hydrophobic silicate, and the silicate was ordered around the SDA. This complex could be the precursor of the zeolite nucleation and growth. Small

angle x-ray scattering (SAXS)⁴⁻⁶ as well as light scattering⁷⁻¹⁰ was performed to understand the nucleation in the homogeneous liquid phase. Dokter et al.⁴ combined SAXS with wide angle x-ray scattering (WAXS) to monitor the early stage of the Si-ZSM-5 crystallization *in-situ*. The formation of the nanometer-sized primary silicate/TPA cluster (<3.2nm), as proposed by Burkett and Davis, was confirmed by SAXS. The long-range order was detected by WAXS at the same time, and the crystallization point was determined. Based on these results, a schematic view of the nucleation was provided. In the continued work de Moor et al.⁵ studied the influence of the synthesis condition on the nucleation in detail.

Okubo et al. applied field emission scanning electron microscopy (FE-SEM) to elucidate the morphological changes of CVD diamond¹¹, sol-gel derived titania¹² and zeolite L film^{13,14} in nanometer scale. Based on these backgrounds, we performed FE-SEM observation to visualize the early stage of Si-ZSM-5 synthesis. When microscopy is used for nucleation study in liquid phase, the difficult step is how to collect the nuclei dispersed in liquid. Therefore, we inserted quartz substrate in the synthesis solution to localize the nucleation stage on the two dimensional plane, and could successfully obtained the interesting snapshots of the Si-ZSM-5 nucleation in nanometer scale.

2. EXPERIMENTAL

Si-ZSM-5 was synthesized from clear solution with 1TPAOH : 4NaOH : 8SiO₂ : 2000H₂O molar composition. Tetraethyl orthosilicate (TEOS) was used as the silicon source. After the sodium hydroxide and TPAOH was dissolved in distilled water, TEOS was added under stirring at room temperature. After 60 min aging at room temperature under stirring, the single-phase transparent solution was prepared. An AT-cut quartz substrate with polished surfaces was placed in a Teflon®-lined autoclave with 23 ml inner volume (Parr 4749), and the solution 20 ml was filled. Prior to the synthesis the quartz was washed with distilled water in an ultrasonic bath for 3 minutes. The autoclave was transferred to a convection oven preheated at 448K. After prescribed duration, the autoclave was removed from the oven and cooled down rapidly in water. The substrate was washed with distilled water enough to remove the residual solution, and dried at 358K under atmosphere. The detailed procedure is published elsewhere¹⁵. The characterization was carried out by FE-SEM (Hitachi S-900) and x-ray diffraction (XRD, Mac Science MXP-3TA) equipped with Cu-K α radiation. Prior to the FE-SEM observation, the specimen was coated with Pt by magnetron sputtering in argon for a few seconds (Hitachi E-1030). The coating particle was < 1 nm, and there was no significant influence on the following pictures.

3. RESULTS AND DISCUSSION

According to the XRD patterns, the peaks due to Si-ZSM-5 were identified when synthesized for > 2 hours. For 2h and 6h syntheses, the peaks only due to (x00) and (0x0) are detected, which suggests the oriented growth of Si-ZSM-5 in the early stages under this synthesis condition. When synthesized for 12 hours, the XRD patterns were the same as that of the powder. The FE-SEM views of quartz substrate surface before and after 0.11 M NaOH aq etching at 448K are shown in Fig. 1. Before the etching, the micrometer-sized polishing scratches are observed. On the contrary,

the dissolution of the surface silicate by etching caused regular trigonal pit formation. In Fig. 2, snapshots along with the synthesis up to 2 hours are shown. After 0.5h, surface is not flat, but rugged in a few nanometer scale. In this stage no pit is observed, which shows the substrate surface is covered with a layer, most probably consisting of silicate/TPA¹⁻³ composites. In 1 hour, 10 nm-sized particles partly appear on the top. The number increases, and the size is enlarged during 1-1.5 h. After 2h synthesis, the particles start to aggregate each other, which means that the particles are mobile on the layer and sticky each other. It is noteworthy that faceted crystal-like particles as large as 50 nm are found in this stage. The 10 nm-sized particles are formed within the layer since some look embedded within the layer. The size found in the 1 h synthesis is in the same order as the one shown by Dokter et al. using SAXS⁴. Our FE-SEM work clearly visualizes the growth and the aggregation of nanoparticles, which is followed by the crystallization.

FE-SEM provides us with the morphological information in nanometer scale. Still the formation mechanism of 10 nm-sized particles on the top surface, driving force of their aggregation and the nutrient path for the particle growth (directly from liquid phase? or from surface coated layer?) are open for the discussion. The further characterization of the surface layer with different tools will elucidate these points.

4. CONCLUSION

We showed the nanoscale snapshots of the product on the substrate surface along with Si-ZSM-5 crystallization. The 10nm sized particles were formed within 0.5h, whose number increased and size was enlarged during 1-1.5 h. These particles aggregated, and then the crystal-like shaped particle appeared. The nucleation was visualized in nanometer scale.

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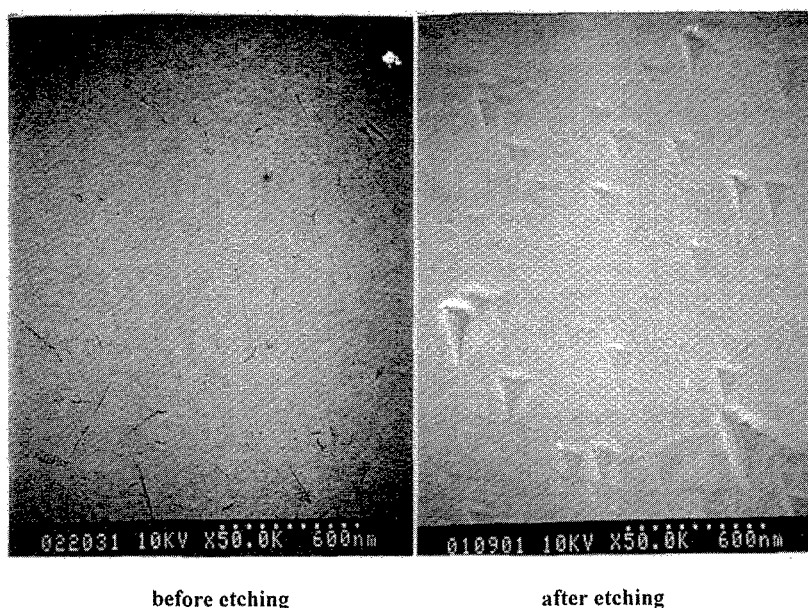


Fig. 1 FE-SEM pictures of quartz substrate surface before and after etching in 0.11 M NaOH solution at 448K for 1h.

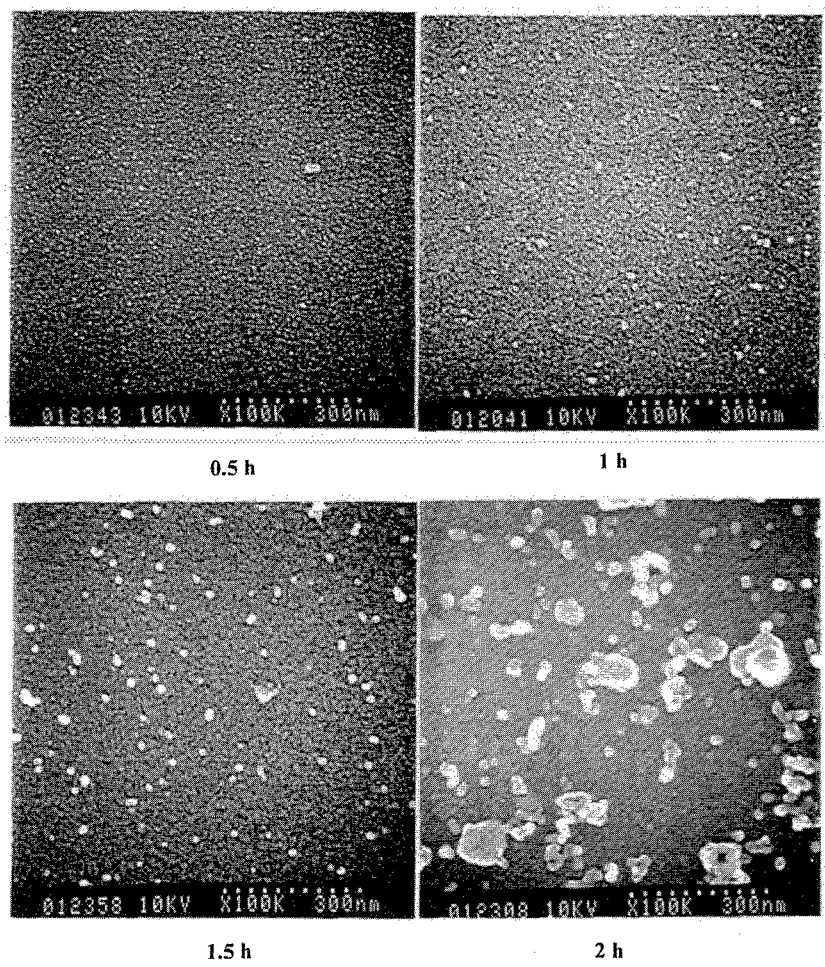


Fig. 2 FE-SEM pictures of synthesis products on quartz substrate surface.