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Template-Free Synthesis of ZSM-5 Type Zeolite Layers on Porous Alumina Disks

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ZSM-5 crystals were synthesized from template-free batches on macroporous α-alumina disks. The SiO_2/Al_2O_3 ratio of the synthesis gel influenced the crystal morphology, surface coverage and intergrowth among the crystals. Prismatic ZSM-5 crystals covered the disk surface when the SiO_2/Al_2O_3 ratio of the batch was higher than 100, whereas spherical polycrystalline particles of ZSM-5 were obtained from batches with a SiO_2/Al_2O_3 ratio of 80. Mordenite type zeolite was formed on the disk surface due to the incorporation of alumina dissolved from the disk when the time of crystallization was extended. The effects of silica source and seeding of the support surface with 0.3 and 2 μm ZSM-5 crystals on the morphology of zeolite layer were also investigated. The purity, surface coverage and SiO_2/Al_2O_3 ratio of ZSM-5 crystals increased in the order of silica sol containing methanol, silica sol, and silicic acid. Seeding decreased the length of prismatic ZSM-5 crystals from 45 μm 10 μm and increased the surface coverage.

Key Words: ZSM-5, template-free synthesis, zeolite layer, zeolite membrane.

Introduction

Zeolites, with their uniform pore structure and high thermal and chemical stability, are considered good candidates for membrane fabrication. Zeolite membranes were usually synthesized by direct contact of a support material, such as alumina or stainless steel, with a reactive synthesis mixture.[1−4]

Considerable effort has been devoted to prepare ZSM-5 type membranes because of their potential in the separation of light hydrocarbons. The syntheses were usually performed in the presence of an organic structure directing cation, typically tetrapropylammonium (TPA^+).[1−5] These cations trapped in the zeolite pores during crystal growth are later removed by calcination at 400-500 °C. However, calcination may cause the development of microcracks on the membrane surface due to the thermomechanical incompatibility between ZSM-5 crystals and the support material.[6−8] Template-free synthesis of ZSM-5 can be an alternative to the template containing synthesis to eliminate calcination.

Mintova et al.[9] synthesized ZSM-5 layers on non-porous quartz substrates from template-free batches. Prior to the synthesis, the quartz surface was covered by silicalite seed crystals to promote crystallization.

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Hedlund et al.[10] prepared template-free ZSM-5 membranes in a similar manner on porous alumina supports covered with seed crystals. These membranes showed selectivities for H_2/i-C_4H_{10} as high as membranes synthesized from template including batches. The permeation of molecules larger than the ZSM-5 pores, such as m-xylene, also showed that membranes contained non-zeolitic pores. Few studies were later reported concerning the synthesis of ZSM-5 membranes from template-free batches.[11−15] All those studies were performed using seeded supports.

The crystallization of ZSM-5 powder from template-free batches requires more defined synthesis conditions than the crystallization of ZSM-5 from batches containing a template molecule.[16,17] Template-free ZSM-5 was crystallized from batches with SiO_2/Al_2O_3 ratios of 40 to 70 and Na_2O/SiO_2 ratios of 0.13 to 0.20. The batches having compositions outside these ranges usually resulted in impurity phases such as mordenite[13] or analcime[16] type zeolites, quartz,[19] and unreacted amorphous solid.[20]

In the present study, ZSM-5 crystals were grown on porous α-Al_2O_3 disks from template-free batches with and without seeding. The effects of the nature of the silica source and the SiO_2/Al_2O_3 ratio of the batch on the purity and morphology of crystals were investigated.

Experimental Methods

Preparation of substrates

Home-made α-Al_2O_3 disks, which were used as support, were prepared with a diameter of 21 mm and thickness of 1 mm. Disks were made by pressing about 0.8 g of α-Al_2O_3 powder (Riedel de Haen) under 128 MPa. A small amount of sodium silicate solution (Merck) was added to the alumina powder as binder. The green disks were dried overnight at ambient conditions and sintered at 1200 °C for 22 h. Sintered α-Al_2O_3 disks consisted of 5.5% by weight dry sodium silicate.

The sintered disks had void volume of 0.20 cm^3/g and average pore diameter of 1.6 μm, which were measured by Micromeritics Pore Sizer 9310 mercury porosimeter. Before the synthesis of zeolite layer, both sides of the disks were polished by sandpaper and washed with distilled water in an ultrasonic bath for 5 min; this procedure was repeated 3 times. The polished disks were dried at room temperature.

Synthesis of template-free ZSM-5 layers without seeding

The gel composition, 6.5 $Na_2O:Al_2O_3:80SiO_2:3196H_2O$, reported by Grose and Flanigen[21] for the synthesis of template-free powder of ZSM-5 was used to prepare the zeolite layers. The synthesis gel was prepared using 3 silica sources: silicic acid (Merck), silica sol (Ludox HS40, Aldrich), and silica sol containing 15% methanol by weight (Merck). The other reactants were $Al(OH)_3$, NaOH, and distilled water. The crystallization was carried out at 200 °C for 24 h to 172 h in stainless steel autoclaves with PTFE cup inserts. The capacity of a PTFE cup was about 35 mL and 85% of this volume was filled with the synthesis gel. Two alumina disks, one at the top and the other at the bottom, were vertically placed in a PTFE cup by PTFE holders. After crystallization, the disks were washed with distilled water and dried at room temperature.

Synthesis of template-free ZSM-5 layers with seeding

The disk surfaces were covered with silicalite seed crystals before crystallization. Silicalite with an average size of 0.3 μm and 2 μm was synthesized from a batch with a molar composition of 6.5 $Na_2O:30SiO_2:6.9TPABr:$

$1136H_2O$ at 100 °C for 72 h and at 200 °C for 24 h, respectively.[22] The crystals were calcined at 500 °C for 10 h and were used to prepare the seed suspension, which had a concentration of 0.3% by weight for 0.3 μm and of 0.2% by weight for 2 μm crystals.

For seed coating, an alumina disk was slowly dipped into the seed suspension and kept for 10 min, and then slowly removed. The disk was dried at 50 °C for 30 min. Dipping was repeated 5 times. The seed deposited disks were kept at 250 °C for 2.5 h to fix the seed crystals onto the alumina surface.[23] The synthesis on seeded disks was performed by following the same procedure applied for the synthesis of template-free ZSM-5 layers on the bare disks.

Characterization of zeolite layers

The crystalline phases formed on the support surface were determined by X-ray diffractometer (Philips PW 1840) using Ni filtered CuKα-radiation. Scanning electron microscopy (JEOL JSM-330) was used to examine the morphology of the zeolite layer. The chemical analysis of the layer was performed by energy dispersive X-ray spectrophotometer (EDX, Norton Instruments Series II).

Results and Discussion

Effect of alumina content of batch on the morphology of crystals

Batches having SiO_2/Al_2O_3 ratios between 80 and infinity (Al_2O_3-free) were prepared to synthesize template-free ZSM-5 layers by using Ludox HS-40 as the silica source. The SiO_2/Al_2O_3 ratios were adjusted by increasing the alumina content of the gel. Table 1 shows the crystallization conditions as well as the crystalline phases that appeared on the alumina disk surface after specified times of crystallization. The only crystalline phase that formed on the disk surfaces was ZSM-5 except for the batch with a SiO_2/Al_2O_3 ratio of 80, which yielded mordenite in addition to ZSM-5 when no seeds were used.

Table 1. Synthesis conditions of template-free ZSM-5 layers and the crystalline phases formed on α-Al_2O_3 disks.

Code	SiO_2/Al_2O_3 ratio in batch	Silica source	Synthesis time (h)	Seed size[1]	Phases formed[2]
D1	80	Silicic acid	96	-	ZSM-5+MOR (minor)
D2	80	C.S.[3]	96	-	ZSM-5
D3	80	Ludox	96	-	ZSM-5+MOR (minor)
D4	100	Ludox	96	-	ZSM-5
D5	160	Ludox	72	-	ZSM-5
D6	∞	Ludox	72	-	ZSM-5
D7	∞	Ludox	168	-	MOR+ZSM-5 (minor)
D8	80	Ludox	96	0.3	ZSM-5
D9	80	Ludox	96	2	ZSM-5

[1]D1-D7 synthesized without seeds
[2]MOR: mordenite type zeolite
[3]Colloidal silica containing 15% methanol

Figure 1 shows the SEM images of disk surfaces prepared from batches with different SiO_2/Al_2O_3 ratios. The surface of sample D6 that was synthesized from the alumina-free batch was extensively covered by ZSM-5 crystals of prismatic shape with an average length of 8 μm and an aspect ratio of 5. Although the coverage was very high, the cross-section image of the disk (not given) showed that the interaction between the ZSM-5 crystals and the alumina disk is weak. Most of the crystals detached from the surface after the disk was treated in an ultrasonic bath for 5 min.

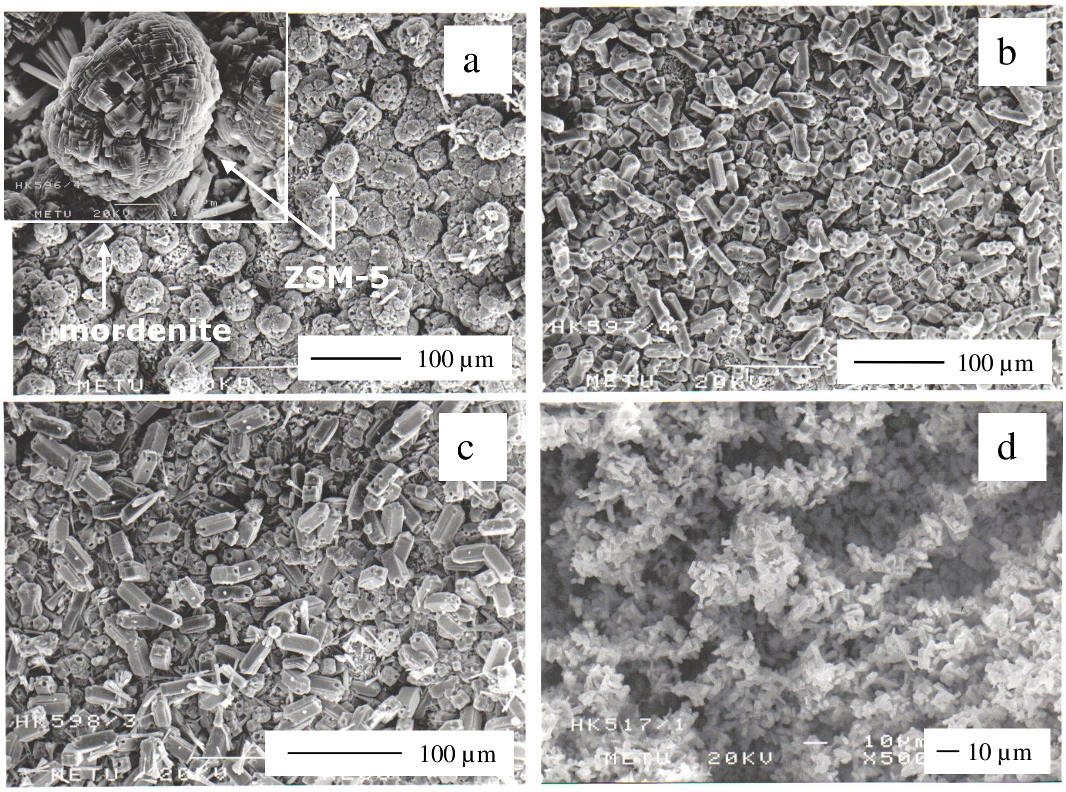

Figure 1. SEM image of template-free synthesized ZSM-5 layers on α-alumina disk surface with a SiO_2/Al_2O_3 ratio of (a) 80, D3 (b) 100, D4, (c) 160, D5, (d) ∞, D6.

The surfaces of samples produced from batches D4 and D5 were extensively covered by ZSM-5 crystals (Figure 1b and c). Although the intergrowth among the crystals was still low, the interaction between the ZSM-5 layer and the alumina disk increased. The crystals on samples D4 and D5 had the typical prismatic shape of ZSM-5, which was similar to the shape of ZSM-5 crystals obtained from the alumina-free batch. However, the crystals were significantly larger than the crystals obtained from the alumina-free batch. The average crystal size on both D4 and D5 was 20 x 45 μm. The alumina addition to the synthesis gel did not change the crystal shape significantly; however, the particle size considerably increased as the SiO_2/Al_2O_3 ratio of batch decreased to 100. Upon a further decrease in the SiO_2/Al_2O_3 ratio of the batch to 80, large spherical particles, consisting of smaller cube-like ZSM-5 crystals, formed with a diameter of approximately 40 μm as shown on the image of sample D3 (Figure 1d).

Persson et al.[28] showed that the crystal size increases with increasing alumina concentration in the synthesis of submicron ZSM-5 crystals from clear solutions. Similarly, Yan et al.[29] showed that addition of alumina to the synthesis medium increases the size of particles covering the alumina support during the synthesis of ZSM-5 membranes from template-containing batches. The larger crystals formed from batches with SiO_2/Al_2O_3 ratios of 100 and 160 can be attributed to the higher alumina concentration of batch compared to the alumina-free batch.

The holes seen on the ZSM-5 crystals, which usually appeared at the crystal edges (Figure 1b and c), are probably because of the dissolution of the ZSM-5 crystals. The metastable nature of ZSM-5 may cause the dissolution of crystals and recrystallization into a more stable phase.[24] On the other hand, Shiralkar and Clearfield[17] attributed the dissolution of the ZSM-5 crystals synthesized without templates to the excess sodium trapped in the zeolite pores during the synthesis.

The alumina-free batch yielded pure ZSM-5 layer after 72 h of crystallization (sample D6), whereas the powder that formed in the bulk solution and settled during the crystallization was pure quartz. Extending the crystallization time to 168 h resulted in the complete coverage of surface with mordenite (sample D7) as shown in Figure 2a. Although no ZSM-5 crystals can be detected from the surface image, the cross-section image (Figure 2b) showed that there are some ZSM-5 crystals among the mordenite crystals. The SiO_2/Al_2O_3 ratio of crystals on the surface was 28.4 and 8.8 after 72 and 168 h of crystallization, respectively. Note that the alumina surface was covered by aluminum-containing zeolites, either mordenite or ZSM-5, although the synthesis had been performed with an alumina-free batch. The formation of alumina-containing zeolites from an alumina-free batch suggests the partial dissolution of the support material and incorporation of dissolved aluminum into the crystallization medium.

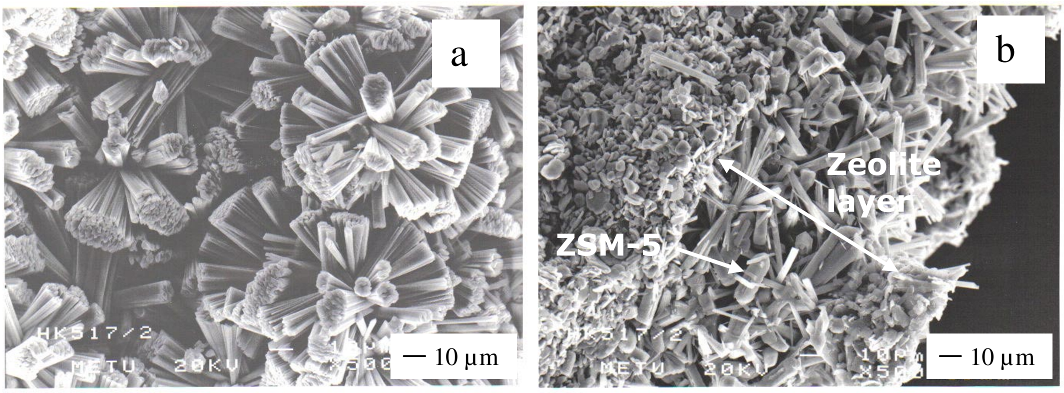

Figure 2. Surface (a) and cross-section (b) SEM images of ZSM-5 layers synthesized from alumina-free batch D7 for 168 h.

Geus et al.[6] prepared zeolite films on various supports including porous α-alumina, zirconia and clay from the same template containing gel. ZSM-5 crystals were seen only on clay and insoluble zirconia support while alumina-rich analcime type zeolite phase was formed on α-alumina support that was leached during crystallization. Similarly, Pan et al.[12] and Lassinantti et al.[25] observed dissolution of alumina support and incorporation of leached aluminum into the zeolite layer during the synthesis of template-free ZSM-5 membranes. The gel that was presumed to be formed on the disk surface[7,23] is enriched in aluminum as a result of leaching such that an aluminum-rich zeolite like analcime may form on the membrane surface. ZSM-5 and mordenite type zeolites were formed on the disk surface, whereas the settled powder was quartz since the aluminum concentration is likely to be the highest around the alumina support and its pores, while the bulk of crystallization solution was rich in silica.

Effect of the nature of the silica source on the morphology of crystals

Figure 3 shows the XRD patterns of disk surfaces after 96 h of crystallization in template-free gels that were prepared using different silica sources. The peaks that belong to the alumina disk are marked with an asterisk. Silicic acid (D1) and silica sol containing methanol (D2) yielded only ZSM-5 as the crystalline phase on the disk surface; however, the template-free synthesis of ZSM-5 in powder form using the same silica sources had yielded ZSM-5 with quartz.[26] The ZSM-5 (sample D3) synthesized from Ludox, which is a silica sol without methanol, contained mordenite as minor phase, the peaks of which are marked with arrows on Figure 3. Strong XRD peak intensities for samples D2 and D3 indicated that a larger amount of ZSM-5 crystal was deposited on the disk surface compared to sample D1. However, the hump centered at around 23° Bragg angle on the background reflections[27] of all samples also suggests the presence of amorphous gel residue on the substrate surface.

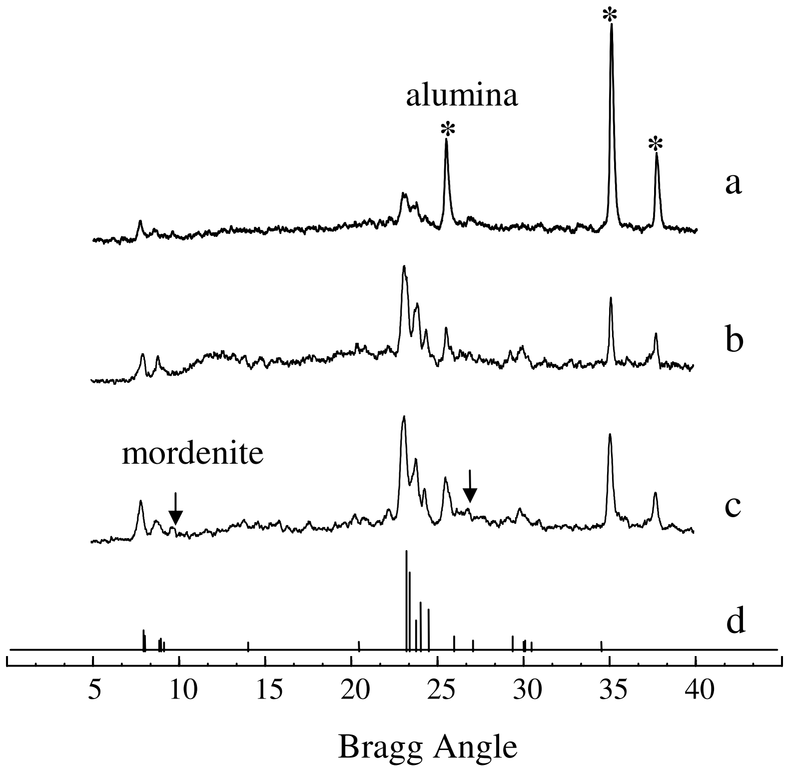

Figure 3. XRD patterns of template-free synthesized ZSM-5 layers on α-alumina disk surface with (a) silicic acid, D1, (b) silica sol with methanol, D2, (c) Ludox, D3, (d) pattern of ZSM-5 from ICDD PDF No: 42-0023.

Figure 4 shows the SEM images of disk surfaces. The disk surface was fully covered by ZSM-5 crystals in sample D2 and partly covered in sample D3 (Figure 1a); however, few crystal deposits were seen on the surface of sample D1. The crystals on sample D2 had a morphology resembling the typical prismatic shape of ZSM-5. The large spherical particles on the image of D3 are ZSM-5 particles. The particles on D1 and D3 are the agglomerates of cube-like ZSM-5 crystals. The size of agglomerates is around 20 μm on D1 and 40 μm on D3. The minor mordenite phase, which was detected by XRD on sample D3, could also be seen as needle-like bunches in Figure 1a.

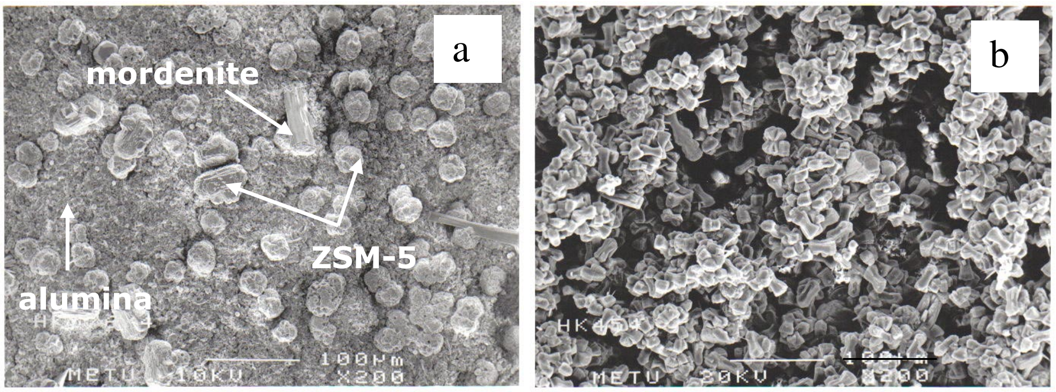

Figure 4. SEM images of template-free synthesized ZSM-5 layers on α-alumina disk surface with (a) silicic acid, D1, (b) silica sol with methanol, D2.

Dai et al.[18] showed that silica sources having small particles favored the formation of ZSM-5 more than the silica sources having large particles. Kalıpcılar and Çulfaz[26] studied the effect of the nature of the silica source and the presence of organic stabilizing agents in the silica source on the crystallization of template-free ZSM-5 in powder. The methanol present in the silica sol promoted the crystallization. Silica sol that does not contain an organic stabilizing agent or silicic acid yielded ZSM-5 with quartz as minor phase. The nature of the silica source is significant for product purity in template-free synthesis of ZSM-5.

The chemical analysis of ZSM-5 particles on the disk surface is shown in Table 2. Samples D1 and D2 have SiO_2/Al_2O_3 ratios of 18.6 and 19.2, and Na_2O/Al_2O_3 ratios of 0.4 and 0.6, respectively. The SiO_2/Al_2O_3 ratio of the samples was similar but much lower than the SiO_2/Al_2O_3 ratio of the synthesis gel, which was 80. Although any type of zeolite containing aluminum within its framework needs a cation to compensate for the negative electrical charge of the framework, the Na_2O/Al_2O_3 ratio of these samples was lower than one, probably due to the contribution of alumina substrate to the chemical analysis. The SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios of crystals on D3 were measured as 33.3 and 1.4, respectively. The presence of amorphous solid on the surface or the excess sodium that remained in the crystal pores are possible reasons for the high Na_2O/Al_2O_3 ratio.[17]

Table 2. Surface composition of the alumina disk surface performed by EDX.

Code	Silica source	SiO_2/Al_2O_3 ratio	Na_2O/Al_2O_3 ratio
D1	Silicic acid	18.6	0.4
D2	Silica sol with methanol	33.2	1.4
D3	Ludox	19.2	0.6

Effect of seeding on layer properties

Template-free synthesis of ZSM-5 without seed crystals showed that ZSM-5 crystals usually formed with a low degree of intergrowth, probably due to the low number of nuclei that formed on the surface. ZSM-5 seed crystals were embedded in the disk surface in order to increase the number of nucleation sites on the surface and to promote crystallization on the surface. The seeding technique was often used for the production of zeolite membranes both from template containing batches[1] and from template-free batches.[9–15] The synthesis conditions for seeded synthesis of ZSM-5 layers are also given in Table 1.

The SEM image of the disk surface after seed coating showed that the submicron seed crystals were mainly deposited on the alumina particles but did not fill the large support pores, whereas the larger seed particles were randomly distributed on the surface (Figure 5).

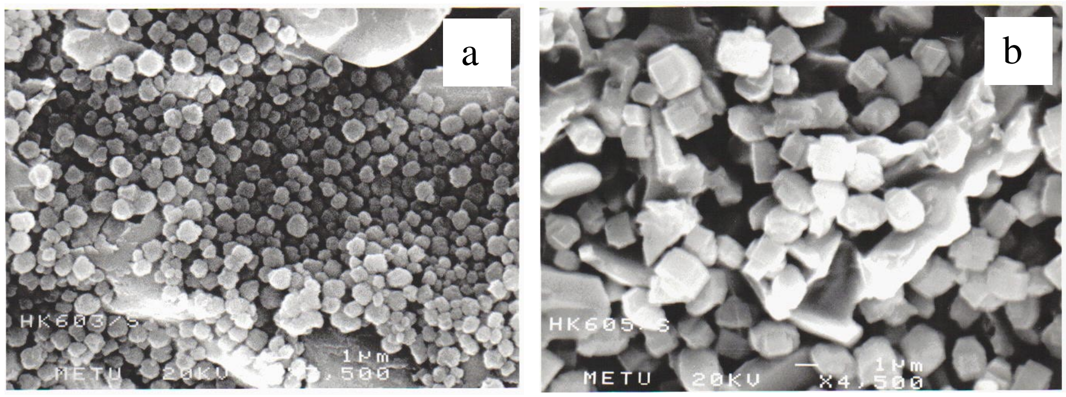

Figure 5. SEM images of α-alumina disk surfaces covered with silicalite seed crystals (a) 0.3 μm (b) 2 μm.

Figure 6 shows the SEM image of disks crystallized for 72 h using seed crystals. The disk surfaces were fully covered by ZSM-5 crystals. The surface coverage was significantly higher than the surface coverage of the samples synthesized on unseeded disks. The ZSM-5 crystals synthesized with submicron seed crystals (Figure 6a) were of prismatic shape and exhibited a narrow particle size distribution with a typical size of 2 by 10 μm. The crystals were much smaller than those produced on the unseeded alumina disks. When the micron size seed crystals were used for synthesis (Figure 6b), the crystals exhibited a cube-like morphology with an average size of 4-5 μm.

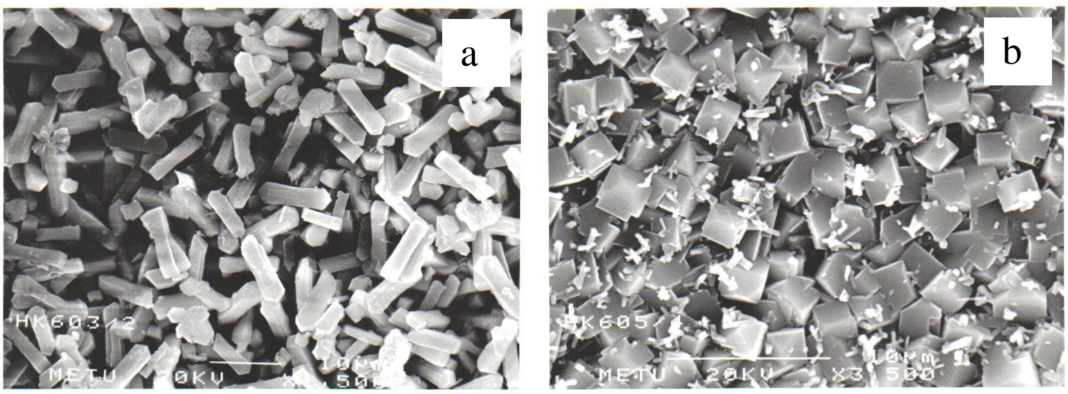

Figure 6. SEM images of template-free synthesized ZSM-5 layers from a batch with a SiO_2/Al_2O_3 ratio of 80 on α-alumina disk surface coated with seed particles, (a) 0.3 μm, D8 and (b) 2 μm, D9.

Conclusion

ZSM-5 crystals were synthesized on seeded and unseeded macroporous α-Al_2O_3 disks from template-free batches prepared using silicic acid, silica sol, and silica sol containing methanol as stabilizer with different SiO_2/Al_2O_3 ratios. The nature of the silica source influenced the purity, surface coverage, and morphology. ZSM-5 crystals fully covered the substrate surface when silica sol containing methanol was used as silica source. ZSM-5 crystals on the α-Al_2O_3 disks dissolved at long crystallization times, and mordenite crystals were formed due to the aluminum leached from the disk. Seed coating on the substrate surface before crystallization decreased the crystal size and increased the surface coverage.

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