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Synthesis of Fibrous Zeolite and its Applications

Yong Gun Shul, Kyeong Taek Jung, and Du Soung Kim*

Dept. of Chem. Eng., Yonsei. Univ., 120-749, Seoul, Korea
*Daelim Eng. Co. Ltd., Yeoidodong Yeongdungpogu, 150-010, Seoul, KOREA

Fibrous zeolite has been prepared from titanium silicalite (TS-1) particles with less than 150 nm in diameter. The formation of fibrous titanium silicalite (FTS-1) zeolite was mainly affected by the particle size of TS-1 zeolite. FTS-1 is formed by both the capillary force and the dehydroxylation among the TS-1 particles during the drying and evaporation process of the dispersed TS-1 particles in aqueous solution. The average length and the aspect ratio (= length/diameter) of FTS-1 are 2.2 mm and 50~70, respectively. The obtained FTS-1 shows two dimensionally aligned surface. After calcination at 750°C, FTS-1 still exhibited characteristics of MFI-type structure with orthorhombic symmetry. This method of FTS-1 formation may suggest a novel method for the preparation of various types of zeolite. Up to now, fibrous ZSM-5 (FZSM-5) was also obtained using nano sized ZSM-5 crystals.
Key words: Fibrous zeolite, Morphological change, FTS-1, FZSM-5, Nano sized zeolite, Capillary force.

1. Introduction

Zeolite are crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T= Si, Al), and that each apical oxygen atom is shared between two adjacent tetrahedra. They enable us to use molecular sieves to recognize, discriminates, and organize molecules with precision that can be less than 1Å because of the close connection between the microscopic structure and the macroscopic property.[1-3] Nowadays, this area of zeolite is still expanding, and resulting in the discovery of synthetic zeolite with new topologies and new catalytic, sorption, and separation properties. Up to now, hundreds of molecular sieves, corresponding to the nearly 75 structures, are known.[4] However, most of those researches on zeolites have been limited primarily to the synthesis of zeolite with new structure or to the reaction using pelletized or granular forms of zeolite. For further advanced application such as novel optical, electronic and magnetic materials, zeolite requires the morphological change in various forms. Figure 1 shows the statistical status of studies on the morphological changes of zeolite such as fiber, film, and monolith from 1988 to 1996. It shows re-

markable increase in the number of studies at the beginning of 1990. It is safe to assume morphological change of zeolite will continue to expand strongly, and the interest in this field will grow.

2. Why fibrous form of zeolite?

For the practical utilization of zeolite in commercial packed bed reactor system, zeolite powders are usually converted to relatively large particulate forms by granulation or pelleting processes. In these cases, diffusion rate of reactants as well as products into the zeolite pellet are usually reduced as the diameter of the pellet increased, and the selectivity of products is also changed. In recent years, many studies on the morphological design of zeolite such as fiber, film, and monolith have been reported (Fig. 1). To overcome the disadvantages of zeolite pellet or powders, zeolite membrane have been made by in-situ crystallization of zeolite on substrates or by incorporating the zeolite crystals in polymeric matrix such as silicone rubber or in a glassy silica matrix.[5-16] The monolithic zeolite has been also prepared by coating zeolite particles on the preshaped monolith for the fuel com-
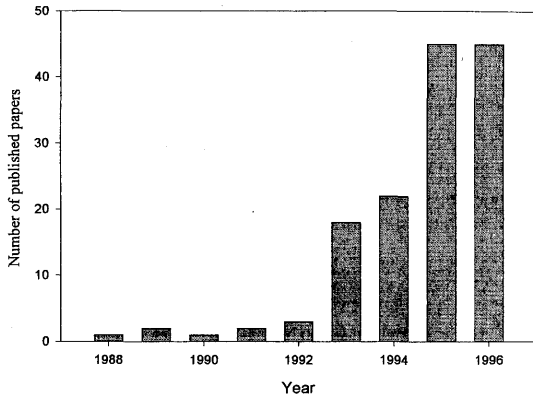
Fig. 1 Number of published papers related to zeolite fiber, film, and monolith.

bustion.[17-25] Fibrous zeolite is highly desirable for the practical use because it can provide high diffusion rate with low pressure drop in the reactor. Also fiber type of zeolite can be directly used as a reinforcement material and as a matrix of various shapes and sizes.[26-29] At present, most of composite fibers containing zeolite have been made by in-situ crystallization onto the mullite, carbon, and alumina fiber under hydrothermal conditions. As an alternative method, the zeolite crystals were incorporated into the polymeric matrix. In this incorporation method, zeolite particles were thoroughly mixed with polymer precursors and spined out to make a composite fiber containing zeolite. When the zeolite is embedded within the polymer or ceramic matrix, the zeolite content is relatively low (<10wt%) and/or the effective surface substantially decreases because the zeolite surface could not be fully utilized. In this sense, zeolite fiber made up of the crystal themselves may be more effective than composite ones and provide a new opportunity in advances application of zeolite.

3. Synthesis of fibrous zeolite
3.1 Synthesis of nano sized zeolite

TS-1 zeolite was prepared by the similar method given in a literature.[30,31] To obtain nano sized crystals, TS-1 zeolite was crystallized at 80°C under atmospheric pressure for 50~200 hours.[31] Tetraethyl orthosilicate,

titanium butoxide, and 20% aqueous tetrapropylammonium hydroxide solution were used for Si and Ti precursors, and template, respectively. The composition of initial reaction mixture in terms of molar ratios is as follows;

Ti : Si : H_2O : TPAOH : isopropanol
= 0.03~0.05 : 1 : 25 : 0.32 : 0.77

The clear mixture was heated in polypropylene bottle submerged in a silicone oil-bath preheated at 80°C with stirring under reflux condition. During the crystallization of TS-1 zeolite, the particle size of TS-1 was monitored by using the dynamic light scattering (DLS) method. To obtain a TS-1 solid phase, extracted mother solution was centrifuged with a 15,000 rpm.

3.2 Synthesis of fibrous zeolite

After separating the nano sized TS-1 particle, the TS-1 particles were redispersed in de-ionized water with the concentration of 0.01 ~50.0 wt%. The dispersed solution was transferred to glass test tube and dried at drying oven at 100°C to form FTS-1. To modify the morphology of TS-1 aggregates, TS-1 particles were redispersed in de-ionized water with the low solid concentration (<2.0 wt%) after obtaining nano size TS-1 particles. Under this condition TS-1 particles were easily redispersed in de-ionized water. The TS-1 particles showed no precipitation due to homogeneous redispersion of nano sized TS-1 particles in aqueous phase. As the drying of the dispersed solution containing TS-1 particles proceeded in the glass test tube at 100°C, the motion of nano sized particles become unstable and more restricted. Those particles adsorbed on the inner surface of glass test tube to make a particle-particle contact. At this condition attractive force is greater than the repulsive force among the particles. Then the fibrous titanium silicalite (FTS-1) started to grow from upside to downward as the drying was progressed. Figure 2 shows an optical microphotograph of a fibrous TS-1 obtained. Average length and the aspect ratio (length/ diameter) of FTS-1 were 2.5 mm and 50~70, respectively. Figure 3 shows SEM images of

(a)
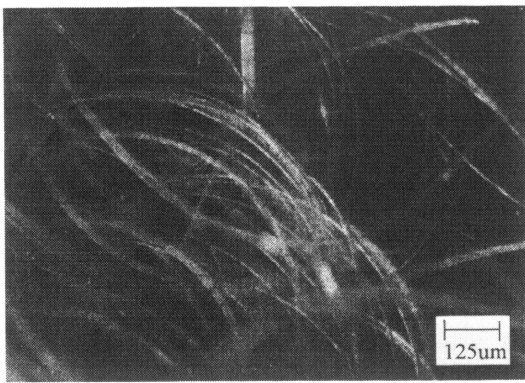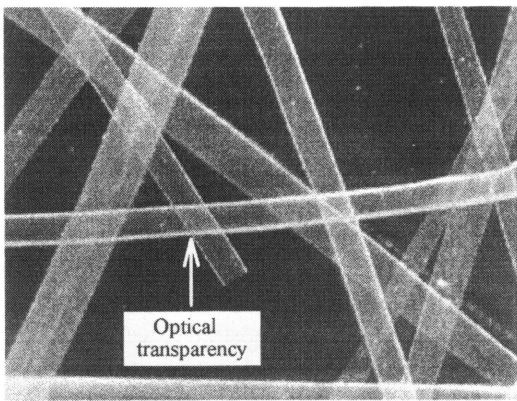
(b) ×135

Fig. 2　Optical microphotograph of fibrous titanium silicalite (FTS-1).

(a)

(b)

the surface of FTS-1 and the change of the surface morphology with calcination temperature. As shown in the photograph (Fig. 3a), TS-1 particles form highly ordered state. Therefore, we named it two-dimensionally aligned aggregates in contrasting to three dimensional aggregates. When we compare the photograph (Fig. 3a) with the image or TS-1 particles separated by centrifugation (Fig. 3c), it proves the importance of proper redispersion and alignment of particles by suitable treatment. Here we used moderate drying condition in glass test tube. Fig. 3b shows that the change of FTS-1 surface morphology with calcination at 750°C. No crack or breakage of the fibrous structure of the zeolite was found after heat treatment (Fig. 3b). As the increase of calcination temperature, the surface of FTS-
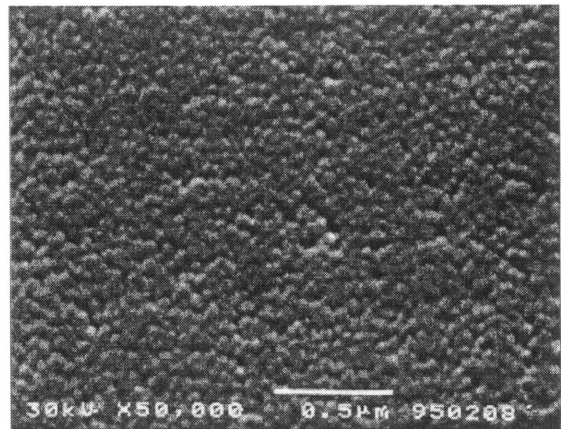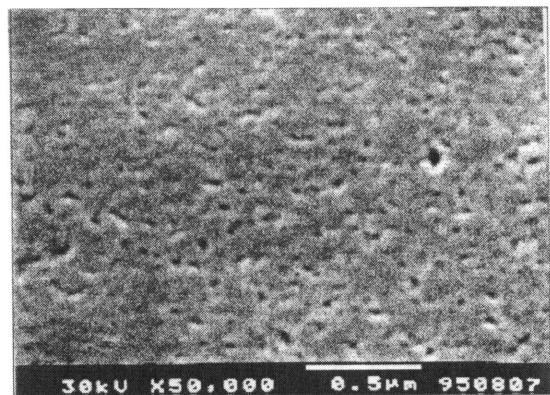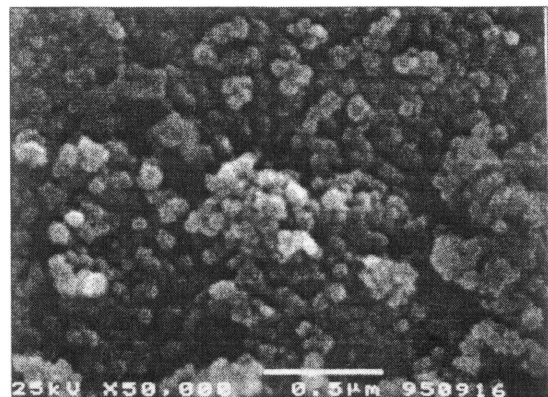
(c)

Fig. 3　SEM images of the surface of (a) FTS-1, (b) calcined sample (a) at 750°C and (c) TS-1 powder (1 cm=0.3 μm).

1 become smooth due to the sintering of TS-1 particles and many holes are found by the decomposition of remaining organic materials. This is similar to the sintering behavior of the oxide materials at high temperature[32] and polymer film formation of colloidal particles by particle coalescence with heat treatment.[33] In colloid system, polymer particles which are contacted each other were coalescenced and showed clear film surface with heat treatment. It shows the decreasing the grains-boundary upon heating like as sintering behavior of metal oxides and polymer film formation of colloid particles. We believe that this kind of structural reinforcement can be utilized for retaining its structure of FTS-1.

To know the effecting parameters on the formation of fibrous zeolite, we changed the particle size, TS-1 solid content, Si/Ti ratio, and surface charge of TS-1 particles.

3.3 Effecting parameters
3.3.1 Particle size of TS-1 zeolite

To confirm the effect of particle size on the formation of FTS-1, different size of TS-1 particles were prepared and then dispersed in de-ionized water at the concentration of 0.5 wt%. When the size of TS-1 particle is less than 150 nm, we could obtain FTS-1. However, when the particle size of TS-1 is greater than the critical size, the particles were precipitated and formed 3-dimensional aggregate on the bottom of the glass test tube as shown in Fig. 3c. It may be due to the increased contribution of gravitational force acting on the particles before the formation of FTS-1 on the glass wall, and it demonstrates the importance of nano size of TS-1 for the formation of FTS-1.

The nano sized TS-1 zeolite particles show high surface reactivity. When the TS-1 particles disperse in de-ionized water, the behavior of TS-1 particles in de-ionized water may be similar to the particles behavior in colloidal system. Owing to the Brownian motion of nano sized particles, TS-1 particles were well dispersed in the aqueous solution and behaved like as TS-1 colloidal solution. However, TS-1 particles have a tendency to form aggregate by
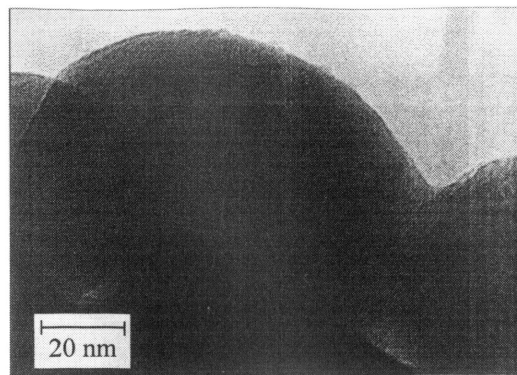

Fig. 4 Transmission electron micrograph of the TS-1 nano particles.

disturbing the stable equilibrium conditions. Drying process is critical to manifest the morphological modification of TS-1 particles (Fig. 4). This is quite similar to the sintering of solid particles observed in the liquid-phase sintering process.[34] This result shows that the nano sized TS-1 particles have the high surface reactivity and form aggregates like as colloidal particles when the repulsion force is reduced in the liquid medium.

3.3.2 TS-1 solid content

Figure 5 shows the change of the aspect ratio (=length/diameter) with increasing the TS-1 solid content. When the TS-1 solid content is neither lower than 0.01 wt% nor higher than 20 wt%, FTS-1 was not formed. At the 5 wt% solid content, the yellowish color on the FTS-1 appeared after drying at 100°C due to the remaining TPAOH on FTS-1. The increase of TS-1 solid content results in
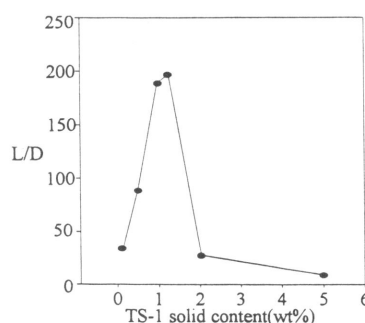

Fig. 5 Change of aspect ratio with TS-1 solid content.

the random aggregation of TS-1 particle. As increasing the TS-1 solid content from 0.02 wt% to 5.0 wt%, the aspect ratio increased from 30 to 200 and the aspect ratio of FTS-1 exhibited the maximum value at 1.5 wt% and dropped rapidly with increasing the TS-1 contents. These results suggest that the solid content of TS-1 greatly affects the formation of FTS-1.

3.3.3 Si/Ti ratio

To investigate the effect of molar Si/Ti ratio on the formation of FTS-1, the Si/Ti ratio was changed from 5 to ∞ and nano TS-1 having different Si/Ti ratio was prepared by atmospheric synthesis. When the TS-1 has the Si/Ti ratio of 10～∞, FTS-1 was formed. This result suggests that Si/Ti ratio is not critical for the formation of FTS-1.

3.3.4 Surface charge of TS-1 particles

3.3.4.1 Effect of washing

TS-1 particles should contain organic template (TPAOH) after centrifugation from mother solution. To change the surface charge of TS-1 particles, TPAOH attached onto the TS-1 particles was removed by washing with de-ionized water. The washed sample turned out to form powder type aggregates (hereafter referred as 'PTS-1') after the drying process. It shows that TS-1 particles are randomly aggregated each other to form large secondary particles with $10 \mu m$ in size as shown in Fig. 3c. Contrary to the image of surface of FTS-1 as shown in Fig. 3a, PTS-1 may form namely 3-dimensional aggregates from the washed TS-1 particles. This fact suggests the importance of surface charge of TS-1 particles for the formation of FTS-1. To investigate the effect of washing step on the dispersion state of TS-1 particle, the size of TS-1 particles was measured by dynamic light scattering (DLS) before and after the washing. Comparing with the initial size of TS-1 particle (70–80 nm), the size of washed TS-1 particle increased to 140–200 nm. The pH of the TS-1 dispersed solution decreased from 8.1 to 7.2 after washing. These results suggest that the surface properties of TS-1 particle could be changed by the washing step. Therefore, it can be assumed

that adsorbed TPAOH on the TS-1 surface is an important factor for the formation of FTS-1. To measure the amount of free and bonded TPAOH in TS-1 particles, DTA was carried out. PTS-1 sample shows no peak at 315°C which was assigned to loosely occluded TPAOH or free TPAOH in TS-1 zeolite. Free TPAOH may be mostly distributed on the surface of TS-1 crystal. These facts implied that the adsorbed TPAOH on the surface of TS-1 affects the surface charge of TS-1 particle and plays an important role in the formation of FTS-1.

3.3.4.2 Effect of solvents

The surface charge of TS-1 zeolite particles was also changed by dispersing TS-1 particles into various solvents. When TS-1 particles were dispersed in polar solvents such as formaldehyde (HCHO) and n-propanol (C_3H_7OH), TS-1 particles were also well dispersed and formed FTS-1 after drying at 100°C. However, TS-1 particles were not dispersed in non polar solvent (n-hexane) and only formed PTS-1. It clearly shows the importance of solvent polarity for the formation of FTS-1. Solvents with high polarity (formaldehyde > water > n-propanol > methanol) seem to promote the formation of FTS-1.

All these data show the importance of surface charge on TS-1 particles and suitable drying condition to form FTS-1.

4. Characteristics

4.1 Optical transparency

From the nano range ceramic particles, R. Daganis suggested that fairly transparent ceramic disk could be obtained because these samples do not scatter much light due to the size.[35] In inorganic-organic composite system, H. Schmidt also suggested that high transparent property could be obtained by using nano-scaled metals or ceramics as inorganic materials.[36] In our case, transparent property of zeolite fiber result from the use of nano-sized TS-1 zeolite (Fig. 2b). The size of TS-1 particles (80 nm) are below the wavelength of visible light (400–700 nm) and there are no secondary larger pores, which make zeolite fiber opaque, due to the dense packing of parti-

cles (Fig. 3a). Therefore, the zeolite fiber does not scatter much light and shows transparency.

5. Formation mechanism

Formation of FTS-1 was mainly affected by the factors such as TS-1 particle size, the surface charge of TS-1 and solid content of TS-1. From these results, it can be assumed several steps for the formation of FTS-1: (I) preparation and dispersion of nano TS-1 particle in an aqueous solution; (II) aggregation and deposition of nano particles; (III) 2-dimensional aggregation and suitable removal of liquid from solid-liquid interface; (IV) FTS-1 formation from the 2-dimensional aggregates during the drying step; and (V) reinforcement of FTS-1 by the condensation of TS-1 particles upon thermal treatment. Nanosize is necessary condition to minimize the force of gravitation acting on the TS-1 particle. When nano TS-1 particles dispersed in aqueous solution, TS-1 particles show that contribution of gravitational force is less dominant than that Brownian motion at room temperature. Upon heating the dispersed TS-1 solution, TS-1 particles are aggregated each other due to the reduced repulsive forces among TS-1 particles and start to grow near the solid (glass test tube)-liquid (dispersed TS-1 solution) interface to form aggregate by the strong hydrogen bonding from hydroxyl bond interactions between TS-1 particles.

As the drying of the dispersed TS-1 solution progressed, particles are partially immersed in a liquid on the top of the solid-liquid boundary. When menisci form around the protruding tops of hydrophilic particles in the nucleus, an intensive water influx carries the suspended TS-1 particles towards the nucleus due to the action of capillary force between particles. Namely, successive 2-dimensional growth and multi layer stacking of TS-1 particles could be occurred by water flux caused by the evaporation of water. In this moment, we could find a highly densified particles on the glass wall surface as a TS-1 film.

As the drying of the TS-1 film progressed, it start to crack vertically from the top to bottom on the surface of glass test tube. It may be due to the stress difference between the horizontal and vertical direction in the TS-1 film as observed in inorganic film.[37] At the final stage of drying, the capillary force could be substituted by the hydrogen bonding and/or chemical bonding. It is manifested by the hydroxyl group on the surface of TS-1 particles due to the decrease of bond length between TS-1 nano particles. TPAOH is known to accelerate the condensation reaction in the TS-1 zeolite.[38] More condensation reaction of surface hydroxyl groups is expected upon heating the sample on FTS-1. The use of ^{29}Si CP/MAS n.m.r. technique makes it possible to follow the condensation change of hydroxyl groups on the silicon atoms which are located on the surface of TS-1 particles. The ratio of ^{29}Si MAS n.m.r. peak area of -102 ppm to -113 ppm are ahown in Fig. 6. Peak at about -102 ppm and -113 ppm in ^{29}Si MAS n.m.r. spectra can be assign to defect hydroxyl groups, $Si(3Si)OH(Q_3)$ and $Si(4Si)$ (Q_4), respectively.[39,40] In FTS-1 and heat treated FTS-1 at high temperature, we can expect the decreasing the concentration of surface hydroxyl group by condensation reaction and reinforcing the fibrous framework by the more condensation reaction of surface hydroxyl group on TS-1 particles. The peak area ratio (Q_3/Q_4) of TS-1 particles dried at 100°C shows higher than that of FTS-1, which shows the higher concentration of hydroxyl
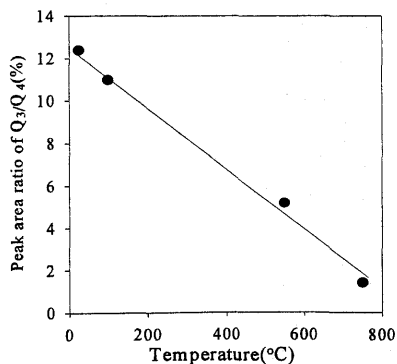

Fig. 6 Changes of peak area ratio of ^{29}Si MAS n.m.r., $Q_3 (-102 \text{ppm})/Q_4 (-113 \text{ppm}) \times 100$, with temperature.

group in TS-1 particles before forming FTS-1. The decrease of peak area ratio suggests the loss of hydroxyl group concentration upon drying and heating process as mentioned in mechanism (V). After heating the FTS-1 at 750°C, the decrease of Q_3 (hydroxyl groups of TS-1) may come from sintering behavior of TS-1 particles in FTS-1 structure. This result coincides with the surface smoothing of FTS-1 with calcination temperature and particle merging as discussed in the Fig. 3 and 4, respectively. In this kind of structure reinforcement of TS-1 particles can maintain the fibrous TS-1 morphology up to 750°C.

These results suggest that the formation mechanism of FTS-1 is also applicable to the other types of crystalline zeolite providing one can prepare nano range zeolite.

Recently, fibrous ZSM-5 zeolite was also obtained by using nano sized ZSM-5 particles. Their property and reaction will be reported soon.

Acknowledgment

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