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Synthesis of oriented zeolite MFI films by solid-state transformation

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Oriented zeolite MFI films were synthesized by solid-state transformation using tetrapropylammonium hydroxide (TPAOH) as a template and a silica–alumina sol as a silica–alumina source. Three factors in the preparation processes were found to be the keys to obtaining an oriented MFI film: the stirring time after adding TPAOH to a silica–alumina sol solution, the drying temperature of the coated film and the heating temperature of the dried film in an autoclave. XRD patterns of the films showed only reflections ascribed to (0*k*0) faces, indicating that the films were oriented. SEM analysis of the films in the drying and heating processes showed that oriented crystals were grown in two stages. In the first stage, oriented MFI crystals grew to an average size of 1.4 μm, which was the same as the size of the gel particles in the dried film; after interruption of growth for 2 h, oriented crystals grew again in the second stage to a size of 3.0 μm.

1. Introduction

There is much interest in zeolite films, not only because of their high performances with respect to ion exchange, solid acidity and transport of gases owing to their uniform-size micro pores, but also on account of their superior thermal, mechanical and structural stabilities as inorganic materials.[1–8] There are many reports in the literature concerning films obtained by hydrothermal processes.[1–13] Recently, film preparation processes based on solid-state transformation, including a vapor-phase transport method, have been developed.[14–19] Among the many types of zeolite film, MFI ones have been studied extensively and synthesized by hydrothermal[6–13] and solid-state transformation methods.[14–16,18,19]

Oriented zeolite films are promising materials for application as separation membranes and chemical sensors.[1–5,19–24] However, most of the films have been prepared by hydrothermal processes,[20–24] and there is only one report of oriented film synthesis by solid-state transformation.[19] In the latter case, oriented MFI films were obtained by vapor-phase transport, and X-ray diffraction (XRD) patterns of the films showed (*h*00) and (0*k*0) faces of MFI, indicating that these crystal faces were oriented parallel to the substrate. The dense and uniform dry gel film prepared by this process has been reported to lead to the formation of preferentially oriented MFI crystals.[19] However, the main factors affecting the formation of oriented films remain unclear.

This paper describes oriented MFI films synthesized by solid-state transformation using tetrapropylammonium hydroxide (TPAOH) as a template and a silica–alumina sol as a silica–alumina source. It also discusses three factors in the process that are the keys to obtaining oriented MFI films. The results of this study indicate that oriented crystals grow in two stages in the synthesis process by solid-state transformation.

2. Experimental

2.1 Synthesis of MFI films on silicon substrates

To a solution of tetraethoxysilane (26.0 g) and aluminium *sec*-butoxide (0.61 g) in 99.5% ethanol (220 ml), a mixture of H_2O (4.52 g) and 60% HNO_3 (3.44 g) was added and stirred for 20 min to obtain a silica–alumina sol. The sol (0.5 g; Si: 3.0×10^{-4} mol) was diluted with 99.5% ethanol (9.5 g) for use in MFI film synthesis.

Tetrapropylammonium (TPAOH) hydroxide (22.5 wt%; 0.14 g, 1.5×10^{-4} mol) was added to the diluted silica–alumina sol (10 g; Si: 3.0×10^{-4} mol) and the mixed solution was stirred for 0.5–5 min at room temperature. The mixed sol (0.025 ml) was coated on a silicon [111] wafer substrate (1.0 × 1.0 cm), and subsequently the coated film was dried in saturated water vapor at 13, 20, 27 and 35 °C for 24 h. The dried film was then heated in an autoclave to which H_2O (0.2 ml) was also introduced separately at 130–170 °C for 24–72 h to synthesize the MFI films.

2.2 Withdrawal of gel particles from the film

The gel films dried in the saturated water vapor were placed in 99.5% ethanol (10 ml) and treated ultrasonically to disperse the gel particles in the solution.

2.3 Measurements

The crystal phases of the films were determined with a Rigaku RAD-2 X-ray diffractometer (XRD) using graphite–filtered CuKα radiation. The surface morphology of the films was evaluated with a Hitachi S-800 scanning electron microscope (SEM). The diameter of the gel particles peeled off from the dried gel films was measured with a Plus N4 Dynamic Light Scattering (DLS) spectrometer.

3. Results and discussion

3.1 Factors affecting the formation of oriented MFI films

Both oriented and non-oriented MFI films were synthesized on silicon wafer substrates by solid-state transformation processes. By carefully changing the preparation conditions, it was found that three factors in the processes were crucial for obtaining oriented MFI films. The first was the stirring time after the addition of TPAOH to the silica–alumina sol, the second was the drying temperature of the coated film, and the third was the heating temperature of the dried gel film in an autoclave.

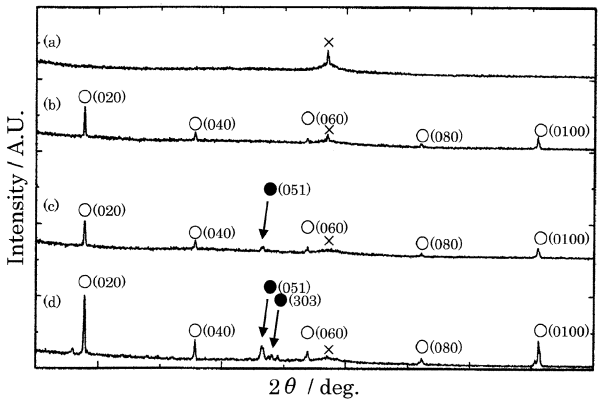

Fig. 1 XRD patterns of MFI films synthesized on silicon substrates as a function of stirring time: a, b, c and d denote stirring time of 0.5, 1, 3 and 5 min, respectively. The ×, ○ and ● symbols denote reflections of the silicon substrate, (0*k*0) face of MFI and other faces of MFI, respectively.

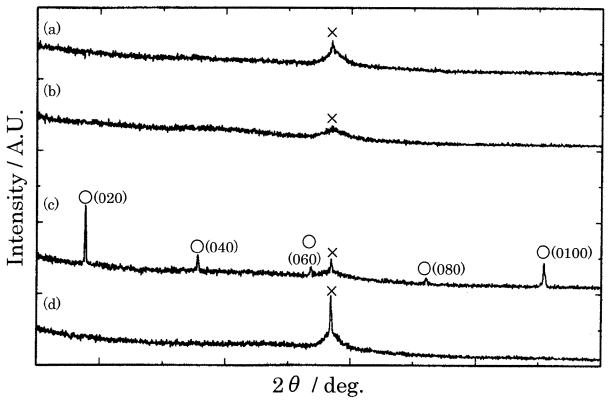

Fig. 2 XRD patterns of MFI films synthesized after drying at 13 °C (a), 20 °C (b), 27 °C (c) and 35 °C (d). The × and ○ symbols denote reflections of the silicon substrate and (0*k*0) face of MFI, respectively.

The stirring time after adding TPAOH to the sol was varied over a range from 0.5 to 5 min while the other two factors were kept constant as will be described later. The orientation of the MFI films was evaluated by their XRD patterns.

Fig. 1 shows the XRD patterns of the MFI films as a function of the stirring time. At a stirring time of 0.5 min (Fig. 1a), no XRD reflection is observed except for that of the silicon substrate (×), indicating that MFI crystals were not formed. For the sol solution that was stirred for 1 min after the addition of TPAOH, the XRD pattern of the film obtained (Fig. 1b) shows reflections (○) only at 8.5, 17.5, 26.5, 35.5 and 45.5° ascribed to the (020), (040), (060), (080) and (0 10 0) faces of MFI crystals, respectively, and no reflections attributed to the other faces of MFI crystals. These results indicate that the MFI crystals in the film were completely oriented and that their (0*k*0) faces were are parallel to the silicon substrate plane. At stirring times of 3 min (Fig. 1c) and 5 min (Fig. 1d), the XRD patterns of the films show not only MFI (0*k*0) reflections (○) but also other MFI ones (●), indicating that the films contained a large amount of oriented and a small amount of non-oriented crystals.

The degree of orientation of MFI crystals in the film is defined here as the value obtained by dividing the area of the (020) reflection by that of the (051) reflection. This definition has been adopted because the intensity of the (020) and (051) reflections is large in oriented films and non-oriented films, respectively. The degree of orientation shows ∞ when all the (0*k*0) faces of the crystals are parallel to the substrate plane, or oriented completely, and the value decreases when non-oriented faces increase. The degrees of orientation in Figs. 1b, c and d are ∞, 3.5 and 2.0, respectively.

These results indicate that only the stirring time of 1 min led to an MFI crystal orientation of ∞, whereas the other cases resulted in no MFI crystals or in non-oriented ones.

The drying temperature in saturated water vapor is another key factor in the formation of oriented films. Oriented films were obtained when the coated films were dried in saturated water vapor, but non-oriented ones formed when the films were dried in air without any humidity control. The drying temperature in saturated water vapor was varied in a range from 13 °C to 35 °C for 24 h , while the other two factors were kept at optimal values, to evaluate the effect of temperature on crystal orientation. Fig. 2 shows the XRD patterns of the films synthesized after drying the coated ones at temperatures from 13–35 °C. Only a temperature of 27 °C led to an oriented MFI film with an orientation degree of ∞, whereas the other temperatures resulted in no MFI reflections, indicating that no MFI crystals detectable by XRD were synthesized.

The heating temperature of the dried films is the third key factor in the formation of oriented MFI films. The heating temperature was varied in the range from 130 °C to 170 °C, while the heating time was set at 24 h and the other two factors were kept at optimal values. The XRD patterns of the resultant films are shown in Fig. 3. A completely oriented MFI film was obtained only at a heating temperature of 150 °C, whereas no MFI crystals were obtained at a temperature of 130 °C and partly oriented MFI ones with (0*k*0) and other reflections formed at 170 °C.

The experimental conditions in hydrothermal syntheses are important to synthesize the oriented crystals. Wang and Yan described how OH^-/Si and Na^+/TPA^+ ratios play a critical role in synthesizing crystal oriented; *b*-oriented films were formed at $0.5 \geq OH^-/Si > 0.2$.[25] Gouzinis and Tsapatsis pointed out the importance of the crystallization time in preparing the oriented films.[26]

On the basis of these XRD data, completely oriented MFI films were synthesized when the three key factors were controlled as follows: the stirring time to one min, the drying temperature to 27 °C and the heating temperature to 150 °C.

A scanning electron micrograph (SEM) image of an oriented film prepared under the optimum conditions is shown in Fig. 4. Only crystals with *ac* faces parallel to the substrate plane, which coincides with the XRD data, are observed.

3.2 Orientation processes

To clarify the formation process of the oriented MFI films, SEM observations were carried out to examine the effects of the heating time on the dried films and the effects of the heating

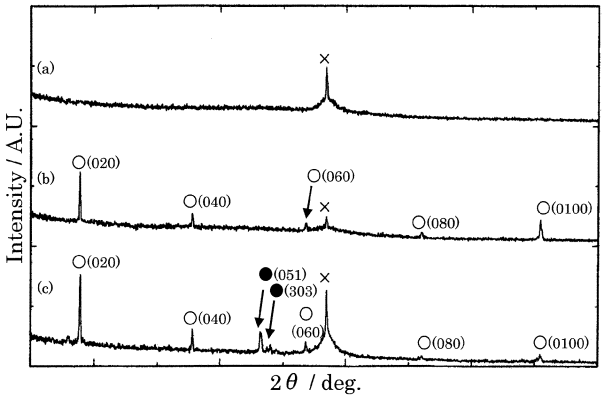

Fig. 3 XRD patterns of MFI films obtained by heating at 130 °C (a), 150 °C (b) and 170 °C (c). The ×, ○ and ● symbols denote reflections of the silicon substrate, (0*k*0) face of MFI and other faces of MFI, respectively.

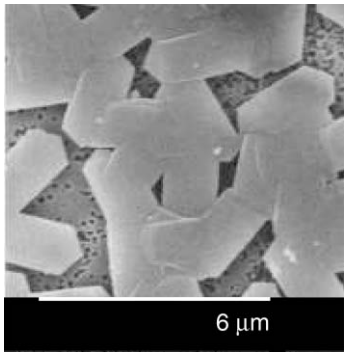

Fig. 4 SEM image of an oriented MFI film obtained under optimum preparation conditions.

temperature on the coated films in a range of 1 to 24 h and 20 to 35 °C, respectively. The size of the gel particles obtained by peeling the dried films was also evaluated.

Fig. 5 shows SEM images of the films prepared by varying the heating time from 1 to 8 h under optimum preparation conditions, and Fig. 6 shows the average crystal size as a function of heating time from 1 to 24 h. At a heating time of 1 h (Fig. 5a), no crystals are observed. However, at a heating time of 2 h (Fig. 5b), cubic crystals about 0.5 μm in size are seen, although only one crystal is shown in the figure. MFI crystals with *ac* faces parallel to the substrate and with a size of 1.2 μm were obtained after heating for 3 h (Fig. 5c). For almost all of the crystals, one edge of the *ac* face appears clearly, while

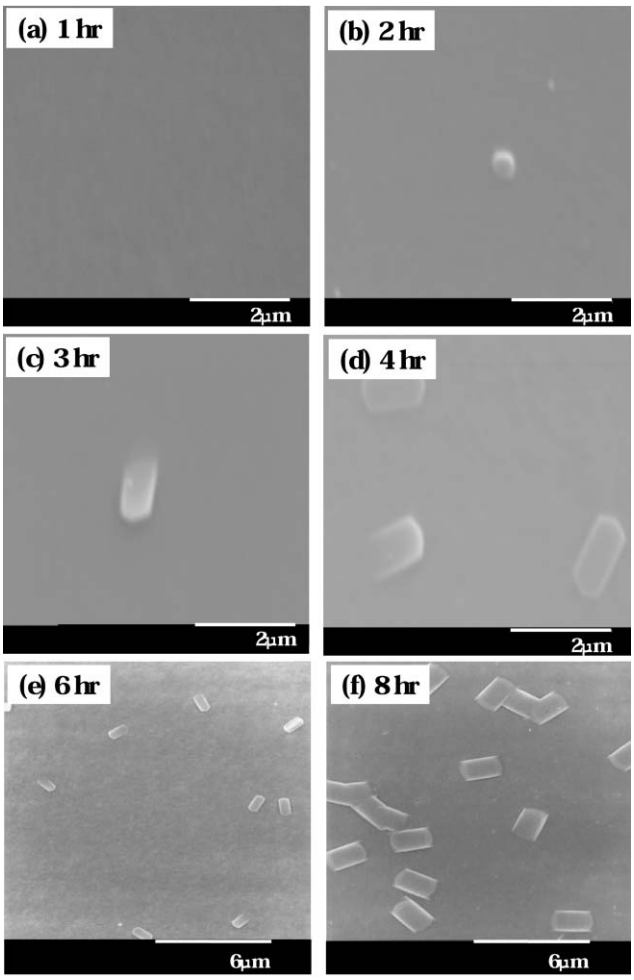

Fig. 5 SEM images of oriented MFI films prepared by varying the heating time in the range from 1 to 8 h in an autoclave while the other two key factors were kept at optimal values throughout the solid-state transformation process.

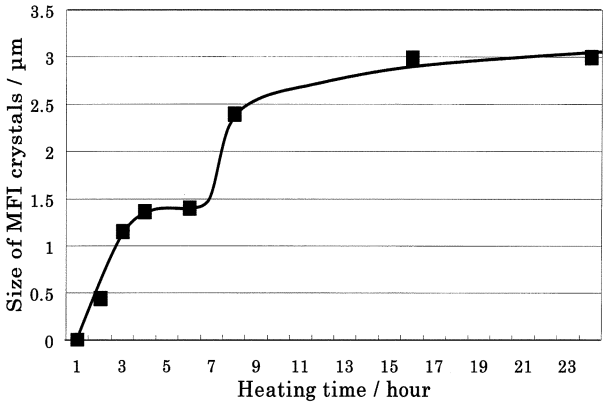

Fig. 6 Heating time-dependence of the average size of MFI crystals in an oriented film obtained though solid-state transformation under optimum preparation conditions.

the other edge is blurred, being buried under the gel. Fig. 5d (heating time of 4 h) shows oriented crystals about 1.4 μm in size with both edges clear and some crystals with a clear edge and a blurred one. The crystal size shows an almost constant value of 1.4 μm for heating times from 4 to 6 h (Fig. 5d and e), increases again at a heating time of 8 h (Fig. 5f) and grows to 3.0 μm at 24 h (Fig. 6).

SEM observation of a coated film that was dried at 20 °C and then heated for 6 h in an autoclave showed no crystals. However, after heating the film for 8 h and 16 h, a few cubic and non-oriented crystals were observed. However, no crystals were observed at a drying temperature of 35 °C.

These SEM images and the crystal size data indicate that the oriented MFI crystals grew in two stages: in the first stage, small cubic crystals grew to elongated and oriented MFI crystals with a size of 1.4 μm. After an interruption during which the crystal size did not change, in the second stage, the crystals grew to 3.0 μm after being heating for 24 h.

Because the drying temperature of the coated films was one of the key factors in the synthesis of oriented films, the size of the gel particles in the dried films was measured for three drying temperatures using DLS equipment. When the drying temperature was 27 °C, the average gel sphere size was 1.4 μm, whereas at 20 °C and 35 °C the sizes were 1.1 and 1.8 μm, respectively. These results indicate that the gel particle size became larger as the drying temperature increased. The size of 1.4 μm at a drying temperature of 27 °C was same as the crystal size in the first crystal growth stage. This value was a key factor in obtaining oriented films.

Several researchers have reported on the nucleation and crystal growth mechanism of MFI crystals and films formed by hydrothermal synthesis.[10,12,19,22,23] In the solution of the reaction mixture, primary gel particles on a nanometre scale aggregate to a size of about 10 nm. Nucleation occurs in the primary particles or the aggregates, resulting in smaller crystals of about 50 nm.[9,10] Nakazawa *et al.*[12] observed the early stages of MFI film formation in a nanometre scale using a field emission scanning electron microscope (FE-SEM) and reported there are two crystallization routes. After formation of a gel layer on a substrate, nucleation occurs in one route within the gel layer and crystals grow out of the layer; in the other route, gel particles in the layer aggregate and crystallization occurs at the aggregates. Koegler *et al.*[11] described the nucleation and oriented crystal growth of Si-MFI. They observed the nucleation and crystal growth on large silica gel particles by SEM and proposed a growth model. Initially, zeolite nucleation occurs on the surface of a particle and the nucleus grows rapidly in the plane of the surface, yielding a very flat crystallite, the morphology of which is cubic. Subsequently, growth proceeds from the surface into the gel particle, changing the shape of the crystallite from cubic to

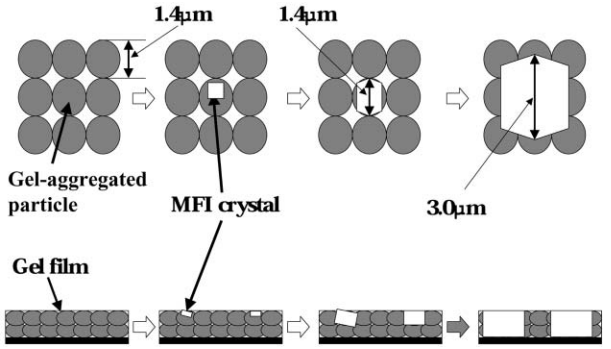

Fig. 7 A growth model of an oriented MFI film on a silicon wafer.

pyramidal. Finally, the crystal detaches from the gel particle and develops faces in the rounded *c*-direction (elongated cubic form) in the diluted medium. They also proposed a model for nucleation and crystal growth in an oriented MFI film based on SEM observation of crystallization on a gel particle. After a silica gel layer forms on the substrate, nucleation occurs on the gel film surface. The nuclei themselves already have a preferred orientation and grow in their preferred directions, the *a*- and *c*-directions, in the plane of the interface with the cubic crystals. The crystals consume the gel, thereby sinking into the substrate surface, resulting in the preferred orientation in which *ac* faces are parallel to the substrate.

Yan *et al.*[22] observed FE-SEM images of oriented Si-MFI films grown in a hydrothermal process. They reported that small cubic crystals are embedded in a gel layer composed of aggregated globular gels.

A few studies have also been reported concerning nucleation and crystal growth of zeolite[27] and the film orientation process[19] by solid-state transformation. Kikuchi *et al.*[19] synthesized zeolite films by a vapor-phase transport method and found the preferential orientations of MFI films. They proposed that the dense and uniform morphology of the dry gel films facilitated crystal growth with preferential orientations.

On the basis of the foregoing observations, the oriented MFI crystals by the solid-state transformation are presumed to form as follows and their growth model is illustrated in Fig. 7. In the first growth stage a crystal nucleus forms at the surface of a gel aggregate composed of small primary gel particles in a dried film as illustrated in Fig. 5b. The nucleus grows to a small cubic MFI crystal (as Fig. 5c and d) by consuming the silica–alumina nutrient in the gel-aggregated particle, resulting in an elongated and oriented MFI crystal (see Fig. 5e). Because all the nutrients in the sphere have been consumed, crystal growth is then interrupted for a while. In the second stage, the crystal begins to grow again when the silica–alumina source is supplied from particles around the crystal. In the case of a drying temperature of 27 °C, a small cubic MFI crystal grows to 1.4 μm, since the gel particle is large enough to supply sufficient silica–alumina nutrient to all the faces of the crystal as shown in Fig. 6. In this condition, the crystal grows in its preferred directions, *a*- and *c*-directions, to become an elongated and oriented one. After growth interruption, the crystal grows again to a large one, while maintaining its orientation, by being provided with silica–alumina nutrient from surrounding particles.

On the other hand, in the case of a drying temperature of 20 °C, a nucleus grows to a small cubic crystal. Since the gel particles in a dried film are small, insufficient silica–alumina nutrient is supplied to the MFI crystal faces. Thus, the faces cannot grow in their preferred directions, resulting in non-oriented crystals. At a drying temperature of 35 °C, no crystals were observed by SEM examination, although the gel particle size was large enough for crystal growth. The reason why MFI nucleation did not occur is unknown.

4. Conclusion

Oriented MFI films were synthesized by the solid-transformation process using TPAOH as a template and a silica–alumina sol solution as a silica–alumina source. Three key factors were found to be crucial for obtaining the films: the stirring time after the addition of TPAOH, the drying temperature of the coated film, and the heating temperature of the dried film. The optimum conditions were found to be a stirring time of one min, a drying temperature of 27 °C and a heating temperature of 150 °C. Observations of SEM images of the oriented MFI crystals and measurements of the gel particle size in the dried films revealed that the oriented crystals were grown in two stages. In the first stage, a cubic crystal formed and grew to an oriented MFI crystal of 1.4 μm in size. After growth was interrupted for 2 h, the oriented crystal grew again to 3.0 μm in the second stage.

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