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Stability of FSM-16 in a Highly Moist and Aquatic Condition

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The stability of a mesoporous material, FSM-16, against water vapor and water was investigated using an X-ray diffractometer with a relative humidity and temperature controlling unit. Under high relative humidity, the peaks for FSM-16 became smaller than the initial one from 60% of the relative humidity (RH) during an increase of the relative humidity from 10 to 95%, and the peak height was a minimum from 80 to 95% RH. However, the peaks for FSM-16 increased and returned back to the initial ones at 20% RH, while the relative humidity decreased. In soaked FSM-16 in water at 95% RH, the peaks for FSM-16 diminished owing to water. However, the peaks for FSM-16 appeared again, while water evaporated, and the peak heights were almost the same as the initial ones at 20% RH. However, the peak heights were about 25% lower than the initial ones after soaking FSM-16 in water for a long term. It might be supposed that the particles of FSM-16 on a sample holder were rearranged due to the pouring water, or that some of the mesopores for FSM-16 collapsed due to water.

It has been expected that mesoporous silicate materials, typified by FSM-16 and MCM-41 etc., are utilized as an adsorbent, a molecular-sieve material and a catalyst, etc.[1–5] On the other hand, it has been pointed out that the structure of those mesoporous silicate materials is collapsed by water molecule, because silicate, of which the wall of a mesopore is composed, dissolves in water. Therefore, it has been said that mesoporous materials have a difficulty to be handled in water, that is to say that the mesoporous material may be inapplicable to an adsorbent or a catalyst etc. of which the effect is taken in water.

Moreover, it is known that a mesoporous material can easily adsorb water molecules, such as water vapor.[6,7] Especially, a mesoporous material rapidly adsorbed water molecules at more than 60% relative humidity. For that reason, it is also expected that a mesporous material can be used as the material for removing water vapor from air. Therefore, it is necessary to investigate the change of the structure of mesoporous materials against water.

FSM-16 is a kind of mesoporous material. FSM-16 is synthesized from kanemite by the intercalation of a surfactant between silicate layers.[8] The stability of FSM-16 against water molecules was investigated under high relative humidity for 20 h and in water from 20 to 120 h in situ by XRD with a relative humidity and temperature-controlling unit. Also, the utility of FSM-16 as an adsorbent was discussed.

Experimental

FSM-16 was synthesized according to Inagaki et al. (1996).[8] Sodium silicate was dried at 70 °C in an oven for a few days and δ-$Na_2Si_2O_5$ was obtained due to the heating the sodium silicate at 700 °C for 6 h under an elevating ratio of the temperature of 2 °C per minute. Kanemite was obtained from δ-$Na_2Si_2O_5$, which was stirred in an aqueous solution for 3 h at room temperature. Kanemite was filtered and washed by deionized water 3 times. About 5 g of wet kanemite was added into 0.1 mmol/L of a hexadecyltrimethylammonium bromide solution. The temperature and pH were adjusted at 65 °C and 11 by 1 mol/L of NaOH, respectively. The mixture was stirred for 12 h. After the temperature of the mixture decreased to room temperature, the pH of the solution was gently adjusted at about 8.5, and the mixture was stirred for 3 h. The product was filtered and washed by deionized water 5 times. After drying the product in an oven at 50 °C, it was heated at 550 °C for 6 h. Both the elevating and falling ratio of the temperature in a furnace were 1 °C per minute. The product was measured by XRD and TEM observations to confirm FSM-16. A TEM image of FSM-16 is shown in Fig. 1. The pore size of FSM-16 was about 3 to 4 nm. FSM-16 shows a hexagonal structure. It is said that the space group of FSM-16 is hexagonal (*p*6*m*).[9]

The stability of FSM-16 to the relative humidity was investigated by an X-ray diffractometer (Rigaku, RINT2100S) with a relative humidity and temperature-controllable unit (XRD).[10] A schematic illustration of the relative humidity unit on the XRD with a temperature and humidity controllable function is shown in Fig. 2. Dry N_2 gas is branched off in two ways. The N_2 gas of one way passes through a boiler and a helical-type refrigerator. The gas is saturated by water vapor at a particular temperature (T3). Also,

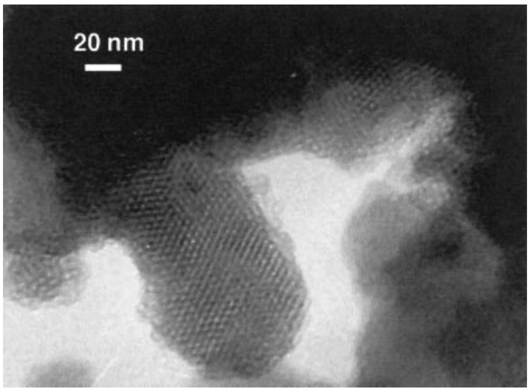

Fig. 1. TEM image of FSM-16. Small whitish dots or lines are the pore. The scale bar is 20 nm.

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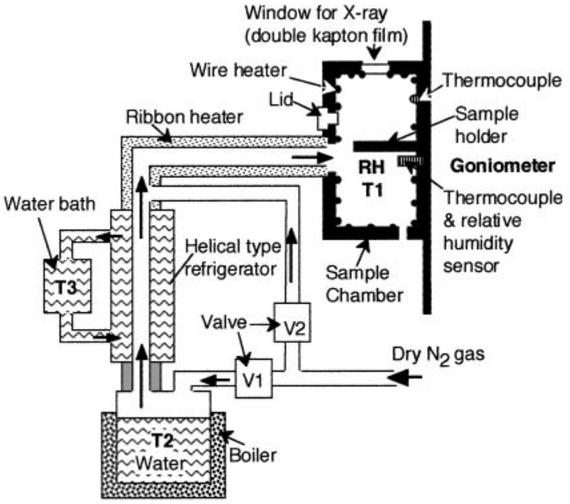

Fig. 2. The schematic illustration of XRD with a relative humidity and temperature controllable unit (modified in Hashizume et al., 1996[10]).

the saturated gas by water vapor is mixed with dry N_2 gas in another way. The two gases are mixed well while they reach the sample chamber. Gas at a certain relative humidity enters the sample chamber. The relative humidity is monitored by a relative humidity sensor and fed back to a computer that operates valves V1 and V2. The relative humidity can be held or changed by a computer that operates the two valves. Moreover, the temperature in the sample chamber is also monitored by two thermocouples, and a wire heater is controlled by the computer because the temperatures of the two thermocouples are the same. FSM-16 on the sample holder for an XRD measurement was placed in the sample chamber to control the relative humidity and temperature attached to the XRD. In this work, T1, T2, and T3 in Fig. 2 were set at 30, 48, and 50 °C. The initial relative humidity was set up at 10%. The relative humidity was raised every 10%. An XRD measurement was carried out after each relative humidity was held for 30 min. After a measurement at 90% of the relative humidity (RH), the relative humidity was raised to 95%; it was held for 30 min and the sample was measured by XRD. The 95% RH was held for about 20 h. The XRD measurement was performed about every 2 h. Thereafter, the relative humidity fell to 90%. It fell by 10% from 90% to 10% RH. An XRD measurement was also made after each relative humidity was held for 30 min.

The effect on water against FSM-16 was investigated as follows. The procedure for elevating the relative humidity until 95% was the same as that mentioned above. After the relative humidity reached 95% and the sample was measured by XRD, water was gently poured into the sample holder with FSM-16 through a window (diameter of 5 mm) on a lid of the sample chamber (Fig. 2). FSM-16 was fully soaked by water. The relative humidity and temperature hardly changed during the addition of water. The relative humidity was elevated at 97–98% after the XRD measurement of the sample with water at 95% RH because of the delay of an evaporation of water in the sample holder. The sample was measured by XRD after holding the relative humidity for 30 min. The relative humidity was held at 97–98% for about 20 h and the FSM-16 with water was measured by XRD about every 2 h. After 20 h, the relative humidity fell to 95% and the sample was measured after holding for 30 min. Thereafter, the relative humidity fell from 90 to 10% in 10% steps. Each relative humidity was held for 30 min and the sample was measured by XRD. In the case that FSM-16 was soaked in water for a long time (i.e., 75 and 120 h), the elevation of the relative humidity and the measurement of the sample by XRD were the same as in the above procedure. After that, the relative humidity was raised to 97–98% RH and the sample was measured by XRD every 3 h after water was poured into the sample at 95% RH. Also, water was poured every 24 h to prevent the sample from drying. After holding the relative humidity for the purpose duration, both the fall of the relative humidity and the XRD measurement were performed in the same way as the procedure mentioned above.

On all of the conditions of the XRD measurement, an X-ray was used Cu Kα radiation, and the X-ray was generated at 50 kV and 20 mA. The XRD patterns were obtained from 1.5° to 40° 2θ.

Results and Discussion

The changes in the X-ray powder diffraction patterns at each relative humidity without the addition of water are shown in Fig. 3. The patters from 10–50% RH were not changed at all. The peaks (i.e., 100, 110, 200, and 210) became smaller from 60% RH and became the smallest at 80% RH. They did not change at 90 and 95% RH; that is, they were the same as those at 80% RH. Further, they were changless while holding the relative humidity at 95% for 20 h. During the process of dropping the relative humidity, the peaks (i.e., 100, 110, 200, and 210) from 90 to 70% RH were almost the same as those under the condition of 95%. However, the heights of the peaks began to increase from 60% RH. They were almost the same as the initial ones at 20% RH.

Figures 4–6 show the behavior of the pattern for FSM-16 by XRD during the addition of water. The patterns are the same as those in Fig. 3 while the relative humidity was elevated from 10 to 95% RH. After the addition of water at 95% RH, all of the peaks in the pattern disappeared. During 97 or 98% holding,

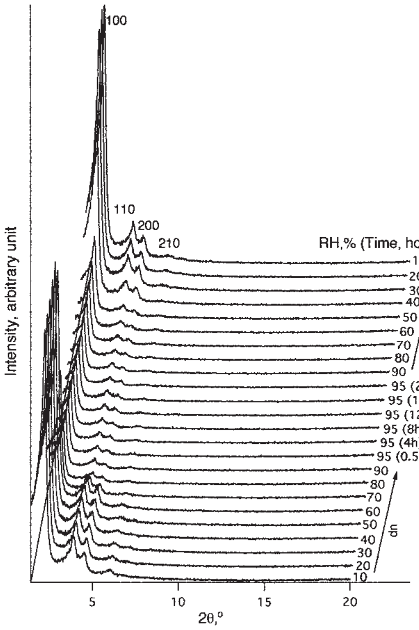

Fig. 3. XRD patterns for FSM-16 taken at increasing (10–95%) relative humidity (RH), holding at 95% RH in every 4 h and decreasing (95–10%) relative humidity.

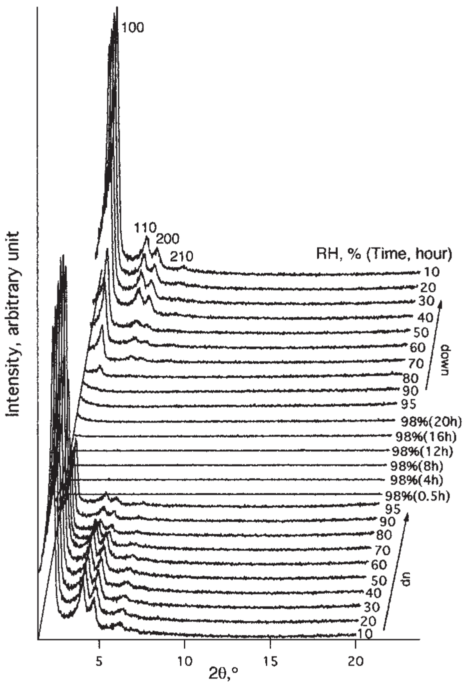

Fig. 4. XRD patterns for FSM-16 taken at increasing (10–95%) relative humidity (RH), holding at 98% RH in every 4 h and decreasing (95–10%) relative humidity. Water was poured in the sample at 95% RH after the measurement at 95% RH. Relative humidity made increased to 98% RH. The relative humidity was hold for 20 h.

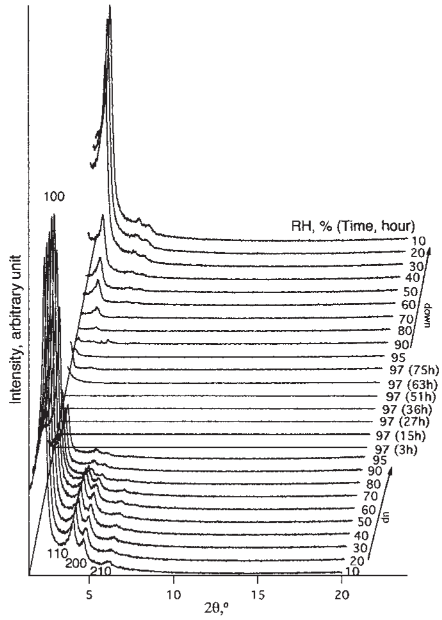

Fig. 5. XRD patterns for FSM-16 taken at increasing (10–95%) relative humidity (RH), holding at 97% RH in the initial 3 h and in every 12 h and decreasing (95–10%) relative humidity. Water was poured in the sample at 95% RH after the measurement at 95% RH. Relative humidity made increased to 97% RH. The relative humidity was hold for 75 h.

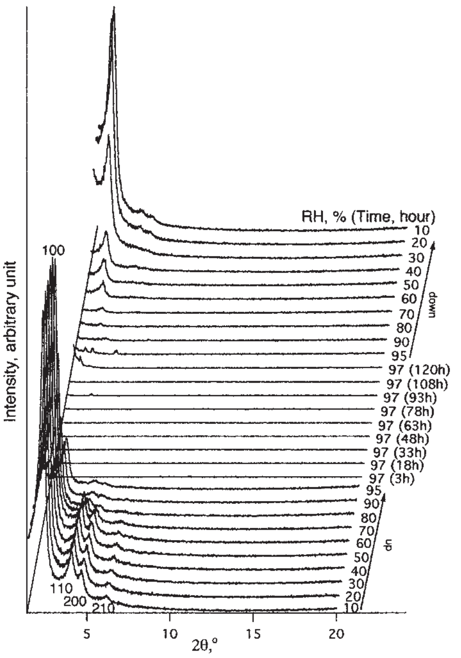

Fig. 6. XRD patterns for FSM-16 taken at increasing (10–95%) relative humidity (RH), holding at 97% RH in the initial 3 h, every 15 h, and the last 120 h and decreasing (95–10%) relative humidity. Water was poured in the sample at 95% RH after the measurement at 95% RH. Relative humidity made increased to 97% RH. The relative humidity was hold for 120 h.

no peaks appeared. A peak of 100 for FSM-16 was revealed at 80% RH during a descent of the relative humidity. All of the peaks for FSM-16 clearly appeared again, while the relative humidity was furthermore decreased. In the case of 20 h holding in water, they were almost the same as those of the initial one at 20% RH, as shown in Fig. 4. However, the height of the 100 peak after drying up was about 15% smaller than the initial one at 10% RH. Under the condition of duration times of 75 and 120 h in water (Figs. 5 and 6), respectively, the peaks for FSM-16 showed almost the same behavior as those of Fig. 3 with increasing relative humidity. After adding water, all of peaks were not identified as being the same as that of Fig. 4, though noises sometimes appeared in the pattern. After holding for 75 and 120 h, 100 of the peak for FSM-16 appeared again at 80% RH, and the peaks of FSM-16 were clearly measured while decreasing the relative humidity. Then, the peak of 100 almost returned to the initial one at 20% RH. However, the 100 peak height was about 25% smaller than the initial one under both conditions for duration times of 75 and 120 h, and the 110, 200, and 210 peaks were not as clear as those for 20 h holding, when the sample was dried up again. Those phenomena, which represent the decrease in the peak height in 100 and unclearness of the peaks of 110, 200, and 210, may happen due to modifications (e.g., the roughness) of the plane of the sample on the sample holder by which the X-ray was reflected, because of the rearrangement of the particles of FSM-16 to pour water every 24 h, or due to a modicum of the collapse of the mesoporous structure in FSM-16.

The peaks of FSM-16 changed to the only variation of the

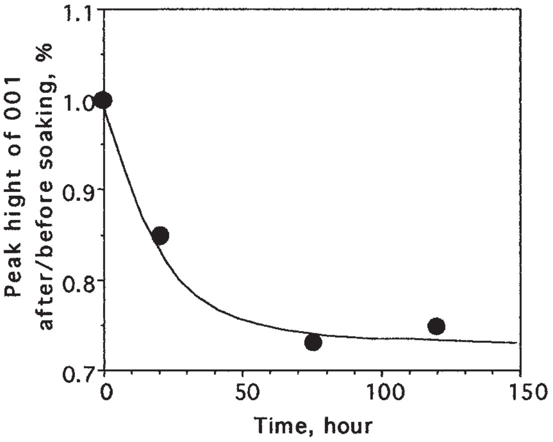

Fig. 7. Relationship between change of peak height of 001 and the soaking time. The ratio of the peak height of 001 in drying up after soaking in water/the initial peak height of 001 was shown.

relative humidity, as shown in Fig. 3. However, the peaks of FSM-16 almost returned to the initial ones due to drying. This means that the wall of FSM-16 would seldom collapse due to the water molecules. Inagaki and Fukushima (1995) as well as Fukushima (1996) showed that the rapid adsorption of water vapor occurred due to the capillary condensation by FSM-16.[6,7] The rapid adsorption of water started at 60% RH and about 75 wt % of water vapor was adsorbed in the pore of FSM-16 at 90% RH. The relative humidity (i.e., 60% RH) at which the peaks for FSM-16 became small in Fig. 3 was almost consistent with the relative humidity of the rapid adsorption of water vapor. At 95% RH, water would be almost filled in the pore for FSM-16. It was considered that decreasing the peaks of FSM-16 according to the increase in the relative humidity was caused by inserting water molecules into the pore for FSM-16. The change in the peaks of FSM-16 would occur becasue the X-ray was absorbed or scattered as water molecules filled the pores.

In the case of pouring water, the peaks for FSM-16 were smaller than the initial ones after drying up. Figure 7 shows the decreasing ratio for the peak height of 100 against the term in soaking FSM-16 in water. During the short term, the 100 peak decreased by about 25%. After that, it seemed that the peak height would be hardly changed. If the decrease in the peak height depended on the collapse of mesopores for FSM-16, the collapse of the structure of FSM-16 would be established at about a 25% decrease.

In conclusion, the mesoporous structure for FSM-16 did not collapse at a high relative humidity. The height of the peaks of FSM-16 were smaller at a relative high humidity greater than the initial ones, and all of the peaks of FSM-16 returned to the same as the initial ones owing to the drying up of FSM-16. The change in the peaks for FSM-16 was expected to result in the scattering of the X-ray due to a filling of water in the mesopores of FSM-16 by the insertion of water molecules. Therefore, FSM-16 did not collapse under a high relative humidity. In the case of adding water at a high relative humidity, the peaks of FSM-16 were smaller than the initial ones after drying up the FSM-16. The rearrangement of the particles of FSM-16 by pouring water to keep a wet condition may occur. Or a small amount of mesopores may be collapsed by water molecules for the dissolution of silica into water. Even if FSM-16 had collapsed, the destruction of the structure of FSM-16 will be a maximum of 25% for about 5 days, and the surface area of FSM-16 would still be sufficiently wide. FSM-16 can be utilized as an adsorbent.

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