Ion Exchange and Thermal Stability of MCM-41

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Mesoporous molecular sieve MCM-41 with a Si/Al ratio of 39 was obtained by hydrothermal synthesis with a gel composition of 6 SiO2:0.1 Al2O3:1 hexadecyltrimethylammonium chloride:0.25 dodecyltrimethylammonium bromide:0.25 tetrapropylammonium bromide:0.15 (NH4)2O:1.5 Na2O:300 H2O. The MCM-41 sample incorporating aluminum (AlMCM-41) was calcined in O2 flow at 813 K and subsequently ion exchanged with Na+, K+, Ca2+, and Y3+. The ion exchange levels have been increased as high as 0.41 Na/Al, 0.36 K/Al, 0.37 Ca/Al and 0.39 Y/Al, respectively. Hydrothermal stability of the ion exchanged AlMCM-41 materials has been investigated with X-ray powder diffraction pattern, BET specific surface area, and magic-angle spinning 27Al NMR spectroscopy, after the samples were heated for 2 h at various temperatures in O2 flow saturated with water vapor at room temperature. The hydrothermal stability of the AlMCM-41 has been found to extend to the following temperatures depending on ion exchange: Y3+ (1170 K) ≈ Ca2+ > Na+ (1070 K) ≈ as calcined AlMCM-41 > pure-silica MCM-41 (980 K).

Introduction

In 1992, the discovery of a new family of mesoporous molecular sieves designated MCM-41 has been reported by researchers at the Mobil Corporation.1,2 The MCM-41 material possesses a uniform hexagonal array of linear channels constructed with a silica matrix like a honeycomb. The novelty in synthesis of the MCM-41 is the use of surfactant micelles, around which silicates polymerize hydrothermally to form the matrix structure. The surfactant can be removed by calcination at temperatures around 800 K. The channel diameter can be tailored within the range of 1.6–10 nm by the choice of the surfactant. Thus, the MCM-41 has dramatically extended the domain of the pore sizes of molecular sieves from the pore sizes of conventional zeolites (≤1.3 nm). Due to the large channel diameters, the MCM-41 materials attract much attention as a new host for large molecules as well as a new catalytic material.3-9

Thermal stability is one of the most important physical properties to investigate for applications of MCM-41. Chen et al.10 reported that pure-silica MCM-41 could be heated to 1123 K in dry air or 1073 K in air with 8 Torr of water vapor before structural collapse began. However, the MCM-41 consisting of pure-silica framework is of limited use for applications as catalysts and adsorbents, due to lack of acid sites and ion exchange capacity. Aluminum can be incorporated within framework of the MCM-41 during synthesis, but studies11-13 using magic-angle spinning (MAS) 27Al NMR spectroscopy show that the aluminum-containing MCM-41 (AlMCM-41) is readily dealuminated upon calcination. Corma et al.14 reported that calcined AlMCM-41 exhibited an acidity of medium strength comparable to that of a USY zeolite. However, it was not clear whether the acidity was due to Brunsted acidic protons that were ion exchanged to framework alumina sites for charge compensation as in zeolites or the acidity could be attributed to the formation of extraframework aluminum. Except that there was a report of copper ion exchange for the inclusion of a conducting polymer,15 little was reported on ion exchange behavior of AlMCM-41 before the present work. Moreover, there was no systematic report on thermal and hydrothermal stability of AlMCM-41.

Recent studies on the structure of MCM-41 have indicated that mesoporous channels were uniformly arranged like zeolite pores, but the channel wall seemed to have a local atomic structure similar to that of amorphous silica.10 From such a similarity of the MCM-41 wall to amorphous silica, ion exchange capacity of the AlMCM-41 may be assumed to be very small, compared with a crystalline aluminosilicate zeolite, e.g., ZSM-5, containing same amount of aluminum. Nevertheless, Wu and Beidb reported exchange of copper into AlMCM-41 for the synthesis of polyaniline inside the channel of the copper exchanged AlMCM-41. More recently, Ryoo and Kim15 have reported that the textural uniformity and thermal stability of MCM-41 were markedly improved by repeating pH adjustment to about 11 during hydrothermal reaction of sodium silicate and hexadecyltrimethylammonium (HTA) chloride. High-quality MCM-41 materials thus synthesized were calcined like conventional zeolites in air using a muffle furnace at 773 K, but the calcination caused no significant line broadening for the XRD pattern. The lattice contraction upon calcination was also negligible, contrary to large lattice contractions as much as 25% upon calcination in other studies.10,11 Furthermore, when yttrium was ion exchanged onto an AlMCM-41 sample synthesized likewise with repeating pH adjustment, the AlMCM-41 could be heated to 1173 K in O2 flow with water vapor before structure collapsed seriously.

In the present investigation, we have extended our previous work on AlMCM-41 in order to clarify the ion exchange capacity of high-quality AlMCM-41 materials and dependence of the hydrothermal stability on the ion exchange. The ion exchanged AlMCM-41 has been investigated by 129Xe NMR spectroscopy, in order to probe the presence of the ions inside the AlMCM-41 channel. The effect of the ion exchange on the hydrothermal stability has been investigated using XRD pattern, BET surface area, and MAS 27Al NMR spectrum as a function of heating temperatures in O2 flow with water vapor saturated at room temperature.
Experimental Section

MCM-41 Synthesis Procedure. A pure-silica MCM-41 has been synthesized following a procedure of Ryoo and Kim. A clear solution of sodium silicate with a Na/Si ratio of 0.5 was prepared by combining 46.9 g of 1.00 M aqueous NaOH solution with 14.3 g of a colloidal silica. The resulting gel mixture had a molar composition of 6 SiO$_2$:0.1 Al$_2$O$_3$:1 HTACl:0.25 DTABr:0.25 H$_2$O. The sodium silicate solution was dropwise added to the surfactant source with vigorous stirring. The resulting silicate or aluminosilicate gel mixture had a molar composition of 6 SiO$_2$:0.4 wt % Al$_2$O$_3$:0.4 wt % Na$_2$O:60.1 wt % H$_2$O, and the mixture was stirred for 2 h at 353 K. After cooling to room temperature, the gel mixture was heated to 370 K for 1 day. The HTA-silicate mixture was then cooled to room temperature. Subsequently, pH of the reaction mixture was adjusted to 12.2 by dropwise addition of 15.0 wt % acetic acid with vigorous stirring. The precipitation mixture was adjusted to pH 10.2 and maintained for 1 day. The precipitated product, MCM-41, was filtered, washed with doubly distilled water, and dried at 370 K. The product yield was 90%, based on silica recovery.

For the synthesis of AlMCM-41, a surfactant source was obtained by dissolving 1.20 g of dodecytrimethylammonium (DTA) bromide (Aldrich) and 1.04 g of tetrapropylammonium (TPA) bromide (Aldrich) in a mixture of 20.0 g of 25 wt % aqueous solution of HTACl, 0.29 g of 28 wt % aqueous NH$_3$ solution, and 10.0 g of doubly distilled water. Alumina source was a solution of 0.43 g of sodium aluminate (Baker Analyzed Reagent) dissolved in 5.0 g of doubly distilled water. Silica source was 61.2 g of the same sodium silicate solution that was used for pure-silica MCM-41. The silicate solution was dropwise added to the surfactant source with vigorous stirring at room temperature. After the resulting surfactant—silicate gel mixture was stirred for 1 h at room temperature, the sodium aluminate solution was dropwise added with vigorous stirring. The resulting surfactant—aluminosilicate gel mixture had a molar composition of 6 SiO$_2$:0.1 Al$_2$O$_3$:1 HTACl:0.25 DTABr:0.25 TPABr:0.15 (NH$_3$)$_2$O:1.5 Na$_2$O:300 H$_2$O. The gel mixture was stirred for 30 min more before heating in oven at 370 K for 1 day. The remainder of the synthesis procedure (i.e., heating and pH adjustment) except for the product washing and calcination was the same as for the above pure-silica MCM-41. After washing with doubly distilled water and drying at 370 K, the product was slurried in an ethanol—hydrochloric acid mixture (0.1 mol of HCl/L of ethanol) for 1 h under reflux conditions. Subsequently, the product was washed with ethanol at room temperature and dried at 370 K. Calcination of the product was carried out in O$_2$ flow (1 L g$^{-1}$ min$^{-1}$) while the sample was heated to 813 K over 10 h and maintained at this temperature for 10 h. Elemental analysis for the Si/Al ratio was performed with inductively coupled plasma (ICP) emission spectroscopy (Shimadzu, ICPS-1000III). The Si/Al ratio was 39. The product yield was 92%, considering the silica recovery. This sample with a Si/Al ratio of 39 was used for the characterization of ion exchange capacity and hydrothermal stability of AlMCM-41 in the present work.

Ion Exchange. Ion exchange of the AlMCM-41 was carried out with aqueous solutions of NaNO$_3$ (4.2 $\times$ 10$^{-4}$ M), KNO$_3$ (4.2 $\times$ 10$^{-4}$ M), Ca(NO$_3$)$_2$, Y(NO$_3$)$_3$·5H$_2$O (2.1 $\times$ 10$^{-4}$ M), and pH of the exchange solutions was between 6 and 7. The ion exchange with Na$^+$, 1.0 g of the as-calcined AlMCM-41 sample was slurried with 2.0 L of the NaNO$_3$ solution for 30 min at room temperature, using a magnetic stirrer. The molar ratio between the metal ion present in the solution and aluminum in the AlMCM-41 was 1.5. The AlMCM-41 sample, after the slurring was finished, was filtered and washed with doubly distilled water. This procedure for ion exchange was referred to a "slurry—filtration—wash" cycle. The cycle was repeated three times to increase the ion exchange yield. The ion exchanged sample was dried in a drying oven at 370 K. The ion exchange with K$^+$, Ca$^2+$, and yttrium was carried out following the same procedure used for the Na$^+$ ion exchange, except that the Na$^+$ ion exchanged sample instead of the as-calcined sample was slurried with the other metal nitrate solutions. Elemental analysis of the ion exchanged samples using ICP gave the metal to Al ratios of 0.41 Na/Al, 0.36 K/Al, 0.37 Ca/Al, and 0.39 Y/Al.

Hydrothermal Treatments and Characterization. About 0.1 g of the calcined pure-silica MCM-41 and AlMCM-41 sample powder was uniformly spread over a fritted disk with 30 mm diameter inside a fused-silica flow reactor. Flows of dry O$_2$ and O$_2$ with 2.3 kPa of water vapor were passed downward through the sample bed at a rate of 2 L min$^{-1}$ per gram of sample, while the reactor was heated. The O$_2$ with water vapor was obtained by bubbling O$_2$ gas through a water bath at room temperature. The heating temperature was increased at a rate of 100 K h$^{-1}$ to a maximum temperature and maintained there for 2 h. The sample was characterized with XRD, BET surface area, and MAS $^{27}$Al NMR after cooling to room temperature. The BET area measurement was carried out with N$_2$ adsorption using a volumetric gas adsorption apparatus. The MAS $^{27}$Al NMR spectra were taken for both hydrated and dehydrated samples. The sample hydration was performed in an air chamber saturated with water using an aqueous solution saturated with NaCl at room temperature.

The XRD pattern was obtained with a Cu Ka X-ray source using a Rigaku D/MAX-III (3 kW) instrument. The MAS $^{27}$Al NMR spectra were obtained at 296 K with a Bruker AM 300 instrument operating at 78.2 MHz. Relaxation delay for the $^{27}$Al NMR was given as 2 s. The sample spinning rate was 3.5 kHz. For the $^{129}$Xe NMR experiment, xenon gas (Matheson, 99.995%) was equilibrated over 30 min with the sample at 296 K under given pressure. $^{129}$Xe NMR spectra were collected at 296 K with a Bruker AM 300 instrument operating at 83.0 MHz. The relaxation delay of 0.5 s was used to get the spectrum.

Results and Discussion

Quality of MCM-41 Depending on the Synthesis Procedures. XRD patterns of the MCM-41 samples synthesized in the present work are presented in Figure 1. The XRD patterns in Figure 1a,c consist of one very intense line, three weak lines, and one very weak line, which can be indexed to (100), (110), (200), (210), and (300) diffraction lines characteristic of a hexagonal structure of MCM-41, respectively. The unit cell dimension can be calculated by $a = 2d_{100}/\sqrt{3}$. The XRD patterns for the MCM-41 samples synthesized without pH adjustment in Figure 1b,d (i.e., obtained after heating the initial surfactant—silicate or aluminosilicate gel mixtures for 4 days in an oven at 370 K) are severely broadened due to a loss in the textural uniformity upon calcination of the materials. The loss of the textural uniformity has been confirmed by $^{129}$Xe NMR line broadening. Lattice contractions as much as 15–25% also follow the calcination. Such large lattice contractions and severe
The ion exchange property and hydrothermal stability. Thus, the thermal stability and textural uniformity of MCM-41 have been markedly improved by repeating the pH adjustment three times, and the SUA ratio was 39. The sample was synthesized by repeating pH adjustment to 10.2 three times in all with acetic acid; (b) pure-silica MCM-41 synthesized without pH adjustment; (c) AIMCM-41 with a Si/Al ratio of 39 synthesized from a gel composition of 6 SiO2:1.4 Al2O3:1 hexadecyltrimethylammonium chloride:0.25 dodecyltrimethylammonium bromide:0.25 tetrapropylammonium bromide:0.15 (NH4)2O:1.5 Na2O:300 H2O with pH adjustment; and (d) AIMCM-41 synthesized without pH adjustment. The as-synthesized samples were washed with doubly distilled water and dried in oven at 370 K. The calcination of the pure-silica MCM-41 was performed in air over 4 h at 773 K, while the calcination of the AIMCM-41 was performed over 10 h at 813 K.

XRD line broadening upon calcination of MCM-41 samples are similar to those reported previously from other laboratories. On the contrary, the lattice contraction for other samples synthesized by repeating pH adjustment to 10.2 three times in all is less than 5%, and the XRD line broadening is negligible. The presence of a (300) diffraction line for these MCM-41 samples indicates excellent textural uniformity after calcination. Thus, the thermal stability and textural uniformity of MCM-41 have been markedly improved by repeating the pH adjustment during hydrothermal synthesis of MCM-41. This effect can be attributed to increasing degrees of silanol group condensation in MCM-41 due to equilibrium shifts for the silicate polymerization, as proposed by Ryoo and Kim.

**Ion Exchange of AIMCM-41.** Figure 2 shows MAS 27Al NMR spectra of an AIMCM-41 sample used for the characterization of ion exchange property and hydrothermal stability. The sample was synthesized by repeating pH adjustment to 10.2 three times, and the Si/Al ratio was 39. The sample as-synthesized shows a 27Al MAS NMR spectrum (spectrum a) with only a tetrahedral aluminum NMR peak shifted to 50 ppm with respect to Al(H2O)63+. The line width for the tetrahedral aluminum NMR peak after calcination at 813 K increased in spectrum b. The NMR line width decreased markedly when the calcined sample was partially hydrated, by drying at 370 K after wetting (spectrum c). However, when the sample was fully hydrated, there appeared a narrow octahedral aluminum NMR line centered approximately at 0 ppm (spectrum d). The peak area integrated under the tetrahedral aluminum peak was approximately 4 times larger than that of the octahedral peak. Thus, the presence of octahedral aluminum NMR signal for the calcined sample depended on the degree of sample hydration. The narrow octahedral peak in Figure 2d seems to come from Al(H2O)63+ remaining as ion exchanged after dealumination from framework. Excessive line broadening due to rapid quadrupolar relaxation seems to make it difficult to detect the MAS 27Al NMR signal when octahedral symmetry is distorted by loss of ligands H2O upon dehydration. The absence of octahedral aluminum peaks in a MAS 27Al NMR spectrum of AIMCM-41 does not mean that all aluminum atoms are tetrahedral. The amount of tetrahedrally coordinated framework aluminum may be better estimated from ion exchange capacity of the AIMCM-41 than the intensity of tetrahedral aluminum NMR signal.

The ion exchange of AIMCM-41 can be confirmed by reversible uptakes of sodium and potassium when the AIMCM-41 sample is subjected to "slurry—filtration—wash" cycles (vide ante) using NaNO3 and KNO3 solutions in turn. For this purpose, the following experiment has been carried out. First, the calcined AIMCM-41 sample was treated with three "slurry—filtration—wash" cycles using NaNO3 solution. The Na content increased to 0.41 Na/Al during the treatment. Then, the sample was subjected to three more "slurry—filtration—wash" cycles using KNO3 solution. The Na content decreased to 0.01 Na/Al during the treatment, but the K content increased to 0.36 K/Al. When the sample was further subjected to three "slurry—filtration—wash" cycles using NaNO3 solution, the Na content and the K content changed to 0.40 Na/Al and 0.02 K/Al, respectively. These results clarify that ion exchanges of the...
TABLE 1: Ion Exchange and Hydrothermal Stability of Pure-Silica MCM-41 and AIMCM-41

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion^+</th>
<th>ion/Al</th>
<th>$\delta_{\text{BET}}$</th>
<th>$T_{\text{d}}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure-silica MCM-41</td>
<td>Na</td>
<td>0.41</td>
<td>1016</td>
<td>1070</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.36</td>
<td>984</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>0.37</td>
<td>982</td>
<td>1170</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.39</td>
<td>995</td>
<td>1170</td>
</tr>
<tr>
<td>AIMCM-41 (Si/Al = 39)</td>
<td>Na</td>
<td>0.41</td>
<td>1016</td>
<td>1070</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.36</td>
<td>984</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>0.37</td>
<td>982</td>
<td>1170</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.39</td>
<td>995</td>
<td>1170</td>
</tr>
</tbody>
</table>

*Ion exchange of the MCM-41 was carried out with metal nitrate solution. *Elemental analysis for the metal to aluminum ratio was performed with inductively coupled plasma emission spectroscopy. Ion exchange capacity of the pure-silica MCM-41 was less than 1% compared with same mass of AIMCM-41. BET area measurement was carried out with N$_2$ adsorption using a conventional volumetric gas adsorption apparatus. $T_{\text{d}}$ is defined as a maximum temperature to which MCM-41 and AIMCM-41 samples can be heated for 2 h in the O$_2$ flow with 2.3 kPa of water vapor, without decreasing the BET areas more than 10%.

AIMCM-41 sample with Na$^+$ and K$^+$ occurred reversibly, similar to the ion exchange of aluminosilicate zeolites.

The ion exchange levels in Table 1 are the metal to aluminum ratios obtained by elemental analysis after three "slurry-filtration-wash" cycles. The Na$^+$ exchange level has been obtained with the AIMCM-41 sample as calcined, while the K$^+$, Ca$^{2+}$, and Y$^{3+}$ ion exchange levels have been obtained with the AIMCM-41 sample after Na$^+$ ion exchange. Assuming that the ion exchange occurs with 1 monovalent metal ion per tetrahedral aluminum site, the results with 0.41 Na/Al and 0.36 K/Al in Table 1 suggest that approximately 40% of the total aluminum atoms in the calcined AIMCM-41 are tetrahedrally coordinated within framework. However, it is not evident how the ion exchange levels for calcium and yttrium are as high as 0.37 Ca/Al and 0.39 Y/Al. It may be speculated that these ions are exchanged as hydroxymetal ions that have an overall charge of +1, or silanol groups located near the tetrahedral aluminum sites may participate in the ion exchange. At any rate, our AIMCM-41 sample has a much higher capacity for ion exchange than pure-silica MCM-41 on the same mass basis as Table 1 shows. Considering a silanol group content of pure-silica MCM-41 as high as 0.3 OH/Si after calcination, the silanol group in the pure-silica MCM-41 does not have a significant capacity for cation exchange under the present experimental conditions with pH $= 6-7$, which is similar to amorphous silica.

Figure 3 shows $^{129}$Xe NMR spectra obtained from xenon adsorbed on ion exchanged AIMCM-41. The chemical shift of the xenon is plotted against the xenon pressure in Figure 4. The chemical shifts at the same pressure show a marked difference between samples with different cations. The difference has occurred without significant changes in the textural uniformity or the specific surface area upon the ion exchange. The XRD pattern and the BET area of the ion exchanged AIMCM-41 are shown in Figure 7.

In Figure 4, the $^{129}$Xe NMR chemical shift for the Na$^+$-exchanged AIMCM-41 is almost independent of xenon pressure changes. However, the chemical shift for the Ca$^{2+}$-exchanged AIMCM-41 is much larger than the chemical shift for the Na$^+$-exchanged AIMCM-41. Their chemical shift difference at the same pressure increases as xenon pressure decreases. The chemical shift increase for the Ca$^{2+}$-exchanged AIMCM-41 against the pressure decrease is very similar to that for Ca$^{2+}$-exchanged Y zeolite (CaY zeolite), which has been attributed to strong adsorption of xenon on Ca$^{2+}$ ions located inside the supercage. It seems that the xenon adsorption on Ca$^{2+}$ ions in the AIMCM-41 is also strong while the adsorption on other parts of the mesopore wall is weak. Similar to CaY zeolite, the strong adsorption of xenon on Ca$^{2+}$ seems to become saturated as xenon pressure increases above 30 kPa whereas the weak xenon adsorption increases approximately linearly with pressure according to the Henry's law. If the strong adsorption causes a much larger chemical shift than the weak adsorption as for CaY zeolite and the chemical shift is averaged due to rapid exchange of xenon between different adsorption sites, the average value will decrease as the relative population of xenon on the weak adsorption sites increases with the pressure increase.

The heat of adsorption of xenon on the AIMCM-41 with
various ion exchange has been measured at 296 K by using the Clausius-Clapeyron equation, \( \Delta H_{ad}/R = -\left[ \ln p/(1/T) \right]_{m} \), for the xenon adsorption isotherms obtained precisely at 293, 296, and 299 K. This \( \Delta H_{ad} \) is plotted in Figure 5 as a function of the total amount of adsorbed xenon \((m)\). The \( \Delta H_{ad} \) for the \( \text{Ca}^{2+} \)-exchanged AlMCM-41 shown in Figure 5 is much larger than that for the \( \text{Na}^{+} \)-exchanged AlMCM-41. At 6.7 kPa, the \( \Delta H_{ad} \) for the \( \text{Ca}^{2+} \)-exchanged AlMCM-41 is as large as \(-50 \text{ kJ mol}^{-1}\). However, the magnitude of \( \Delta H_{ad} \) decreases with the increase of \( m \), approaching to an almost constant value of \(-15 \text{ kJ mol}^{-1}\), which equals to \( \Delta H_{ad} \) for the \( \text{Na}^{+} \)-exchanged sample. This result confirms strong adsorption of xenon on \( \text{Ca}^{2+} \) inside the AlMCM-41 channel.

**Thermal Stability and Hydrothermal Stability of MCM-41.** Figures 6 and 7 display changes in XRD pattern and BET area when calcined pure-silica MCM-41 and AlMCM-41 (Si/Al = 39) samples were heated at various temperatures. The sample heating was carried out for 2 h at each temperature in flows (at 2 L min\(^{-1}\) g\(^{-1}\)) of dry \( \text{O}_2 \) and \( \text{O}_2 \) with 2.3 kPa of water vapor. The XRD patterns were obtained under same experimental conditions after cooling all the samples to room temperature. The XRD intensities in Figures 6 and 7 are directly comparable to each other since the values are plotted using the same scale. Both the XRD intensity and the BET area show similar decreasing tendencies with increase of the heating temperature. Therefore, both XRD intensity and BET area may equally be used to probe thermal stability of MCM-41 samples.

The XRD patterns for the pure-silica MCM-41 in Figure 6 show that the XRD lines broadened gradually as the heating temperature increased to 1143 K in dry \( \text{O}_2 \). Although the XRD patterns show somewhat decreasing in the \( d_{100} \) spacing, the magnitude of the lattice size contraction is still much less than those reported by Chen et al.\(^{10}\) The height of the (100) XRD line after the heating at 1073 K does not show a considerable decrease, compared with the as-synthesized sample. Decreases in the BET area of the sample is still less than 10% even after heating at 1143 K. Thus, it may be stated that the thermal stability of the pure-silica MCM-41 material extends to 1143 K in dry \( \text{O}_2 \). Similarly, the hydrothermal stability of the sample in the \( \text{O}_2 \) with 2.3 kPa of water vapor can be stated to extend to 980 K.

In Table 1, \( T_m \) is defined as a maximum temperature to which AlMCM-41 samples can be heated for 2 h in the \( \text{O}_2 \) flow with 2.3 kPa of water vapor, without decreasing the BET areas more than 10%. Figure 7 and Table 1 show that \( T_m \) is affected by...
the ion exchange as follows: $\text{Y}^{3+}$ (1170 K) $\sim \text{Ca}^{2+} > \text{Na}^+$ (1070 K) $\sim$ as-calced AlMCM-41 $> \text{pure-silica MCM-41}$ (980 K). Thus, the AlMCM-41 samples show excellent hydrothermal stability particularly after the ion exchange with Ca$^{2+}$ and yttrium. As shown in Figure 2e, MAS $^{27}$Al NMR spectra obtained after heating in the O$_2$ flow with 2.3 kPa of water vapor at $T_m$ still shows a tetrahedral aluminum NMR peak centered at 50 ppm with a signal intensity 4 times greater than the octahedral aluminum NMR peak.

Conclusion

In the present investigation, AlMCM-41 with a Si/Al ratio of 39 exhibited ion exchange capacities up to 0.41 Na/Al, 0.36 K/Al, 0.37 Ca/Al, and 0.39 Y/Al. On the contrary, pure-silica MCM-41 showed no significant levels of the ion exchange. The ion exchange in AlMCM-41 occurred onto framework aluminum sites. The ion-exchanged AlMCM-41 showed a remarkable thermal stability when heated in O$_2$ flow saturated with water vapor at room temperature, for 2 h at various temperatures. The maximum temperatures, at which the BET areas decreased less than 10%, depended on the cation exchange as follows: $\text{Y}^{3+}$ (1170 K) $\sim \text{Ca}^{2+} > \text{Na}^+$ (1070 K) $\sim$ as-calced AlMCM-41 $> \text{pure-silica MCM-41}$ (980 K). High ion exchange capacity and good thermal stability of MCM-41 suggest that the material can be used for such applications as requiring metal ion exchange and high-temperature stability.

References and Notes

(16) XRD patterns show that the structure of AlMCM-41 can be readily destroyed during Na$^+$ ion exchange when the exchange level is high. The details are being investigated.