

Understanding of the Effect of Al Substitution on the Hydrothermal Stability of MCM-41

S.-C. Shen and S. Kawi*

Department of Chemical and Environmental Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260, Singapore

Received: June 7, 1999

The effect of Al substitution on the hydrothermal stability of Si–Al–MCM-41 (Si/Al = 50) under different treatment conditions has been investigated in detail, and a fundamental understanding is discussed based on its effect on both geometrical and chemical properties of MCM-41. Compared with Si–MCM-41, the small amount of Al substituted in the framework of Si–Al–MCM-41 is shown to give remarkable improvement of the hydrothermal stability of Si–Al–MCM-41 in boiling water for days. It is found that the existence of Al and Na species in Si–Al–MCM-41 yields less uniformly arranged pore structures than Si–MCM-41, providing a better hydrothermal stability for Si–Al–MCM-41. Both the Al in the framework and the nonstructural Al species on the surface help to protect the mesoporous structure from degradation in boiling water. In addition, the presence of TEOH during the synthesis of Si–Al–MCM-41 may result in a better condensation of the Si–O–Si bonds, enhancing the stability of Si–Al–MCM-41 under the hydrothermal treatment conditions.

Introduction

The discovery of a series of new mesoporous materials of the MCM-41 family having regular pore size distribution, which can be systematically varied between 20 and 100 Å, has opened up new possibilities in the field of heterogeneous catalysis and adsorption.¹ A lot of research effort has been focused on the application of MCM-41 as a catalyst or a catalyst support since the mesoporous structure of MCM-41 facilitates mass transfer of reactants to the catalytic sites. MCM-41 containing metals or metallic ions (prepared by impregnation, ion-exchange, or substitution) have been reported to have outstanding catalytic activities.^{2–9} Due to the potential applications of MCM-41 materials as catalysts and adsorbents, it is very crucial to investigate and understand in depth the hydrothermal stability of MCM-41 materials subjected to various conditions because the hydrothermal stability of MCM-41 is of great interest with respect to the regeneration of MCM-41 catalysts and adsorbents in superheated steam.

It has been found that the purely siliceous MCM-41 (named herein as Si–MCM-41) has a high thermal stability in air and in oxygen containing a low concentration (2.3 kPa) of water vapor at 700 °C for 2 h.¹⁰ However, after MCM-41 samples were steamed in 100% water vapor at 750 °C for 5 h, their surface areas were found to be lower than that of amorphous silica–alumina, and no mesoporous structure could be identified by XRD measurement.¹¹ In addition, the mesoporous structure of MCM-41 collapsed in hot water and aqueous solution due to silicate hydrolysis,^{12,13} limiting its applications associated with aqueous solutions. Research efforts have thus been made to improve the hydrothermal stability of MCM-41 by either changing the synthesis procedure or postsynthesis modification. For examples, the addition of various sodium salts into the gel mixtures was reported to make Si–MCM-41 stable in boiling water for 12 h.¹⁴ MCM-41 has also been stabilized by postsynthesis modification with trimethylsilylation.¹⁵

In this paper we report the fundamental understanding of the effect of Al substitution in the framework of MCM-41 on the hydrothermal stability of aluminosilicate MCM-41 (named herein as Si–Al–MCM-41) under various hydrothermal treatment conditions. This study is believed to be of great interest because, from a practical point of view, the potential application of MCM-41 is very likely to involve the presence of aluminum in the materials, high-temperature treatment in high concentration of water vapor, and even treatment in hot aqueous solution. The fundamental understanding of the effect of Al substitution is believed to be helpful to further improve the hydrothermal stability of this mesoporous material. In addition, the incorporation of Al in the framework of MCM-41 generally improves the acidity and ion-exchange capacity of MCM-41,^{16–18} which are crucial properties for catalysts.

Experimental Section

All MCM-41 samples were prepared by hydrothermal synthesis with a low surfactant:Si mole ratio (surfactant:Si = 0.2:1.0), using cetyltrimethylammonium hydroxide (CTMAOH) as a template. CTMAOH was prepared by the ion exchange of a C₁₆TMABr (Aldrich) solution with IRA-400 resin (Aldrich). Ludox (Dupont) and NaAlO₂ (Hanawa) were used as Si and Al sources, respectively.

For the preparation of Si–Al–MCM-41, NaAlO₂ was first dissolved in deionized water and mixed with tetraethylammonium hydroxide (TEAOH 20%) solution. SiO₂ (40%) (Ludox) was then added to the solution under stirring and stirred for 30 min, followed by dropwise addition of CTMAOH to the reaction mixture. The mole ratio of components for the mixed Si–Al gel was Si:Al:CTMAOH:TEAOH:H₂O = 1.0:0.02:0.2:0.19:28.6. After being stirred for an additional 6 h at room temperature, the mixture gel was then transferred into a polypropylene bottle and statically heated at 100 °C for 72 h. The resulting solid product was recovered by filtration, washed with deionized water, and dried at 50 °C for 24 h. To remove the organic surfactant in the pores of MCM-41, the as-synthesized samples

* To whom correspondence should be addressed. Phone: (65) 8746312. Fax: (65) 7791936. E-mail: chekawis@nus.edu.sg.

were calcined in air at 600 °C for 10 h, with a heating rate of 1 °C/min. Si-MCM-41 was prepared using a similar procedure, except that no NaAlO₂ and TEAOH were used in the gel mixture.^{19,20} These samples are assigned as "fresh" Si-Al-MCM-41 and Si-MCM-41 samples.

The thermogravimetric (TGA) and differential thermal (DTA) analyses of MCM-41 materials were performed simultaneously on a SHIMADZU DTG-50 thermogravimetric analyzer. A 15 mg portion of sample was used in each experiment. The sample was heated in air with a heating rate of 10 °C/min.

The surface areas and pore properties of MCM-41 materials before and after hydrothermal treatments were analyzed by nitrogen physisorption at 77 K using a Quantachrome Auto-Sorb1 Analyzer. Before nitrogen adsorption-desorption measurements, each MCM-41 sample was heated at 300 °C under vacuum for 2 h. The specific surface areas of the samples were determined from the linear portion of the BET plots. The pore size distribution was calculated from the desorption branch of N₂ adsorption-desorption isotherms using the conventional Barrett-Joyner-Halenda (BJH) method, as suggested by Tanev and Vlaev.²¹

The powder X-ray diffraction patterns of MCM-41 samples were recorded using a Shimadzu XRD-6000 powder diffractometer, where Cu target K α -ray (operating at 40 kV and 30 mA) was used as the X-ray source. The scanning range began from 2 θ of 1.5°. The d_{hkl} indices of materials were calculated by the Bragg diffraction equation.

The IR spectra were measured using a Shimadzu FTIR-8700 spectrometer with a resolution of 2 cm⁻¹. A 15 mg portion of sample was pressed (under a pressure of 2 ton/cm² for 30 min) into a self-supported wafer 16 mm in diameter. The wafer was heated at 150 °C under vacuum (<10⁻⁵ mbar) for 2 h before the IR spectra of the sample were measured.

The hydrothermal stability study of MCM-41 materials was conducted using a stainless steel reactor (o.d. = 1/2 in.) by exposing the samples to an air stream containing 3–20 vol % water vapor at 600 °C. The flow rate of the air stream was kept at 50 mL/min during hydrothermal treatment. The concentration of water vapor was controlled by the temperature of the water bubbler. In addition, MCM-41 samples were also treated in boiling water in polypropylene bottles and retained at 100 °C for different periods to evaluate the durability of the mesoporous structure of MCM-41 materials under more severe hydrothermal conditions.

Results and Discussion

To investigate the effect of Al substitution on the effect of the hydrothermal stability of MCM-41, the samples were synthesized using CTMAOH as the surfactant and without pH adjustment by any acid so that the synthesis was carried out in the absence of the influence of salt.¹⁴ Figure 1 displays the XRD patterns of fresh Si-MCM-41 and Si-Al-MCM-41 samples. An intensive peak observed at 2 θ = 2.2–2.4° for both samples corresponds to the (100) diffraction peak.²² Although the separation of (110) and (200) diffraction peaks is not clear, the XRD pattern is in very good agreement with that reported by Kresge et al.²³

There are some differences between the (100) diffraction peaks of Si-MCM-41 and Si-Al-MCM-41. The intensity of the (100) diffraction peak of the Si-Al-MCM-41 sample is lower and broader than that of Si-MCM-41, indicating that the mesoporous structures of MCM-41 become less uniform upon the introduction of Al into the framework. In addition, the 2 θ angle corresponding to the (100) diffraction peak of Si-

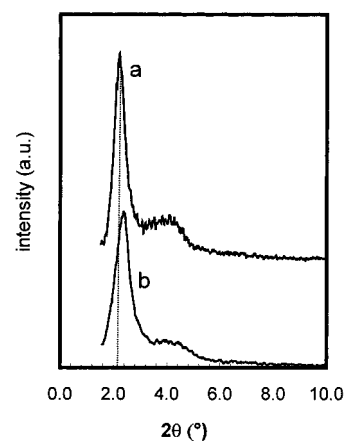


Figure 1. Powder XRD patterns of (a) Si-MCM-41 and (b) Si-Al-MCM-41.

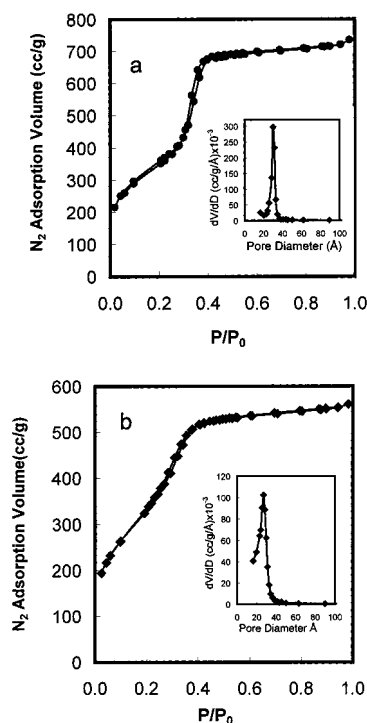


Figure 2. Nitrogen adsorption-desorption isotherms and pore size distributions of (a) Si-MCM-41 and (b) Si-Al-MCM-41.

Al-MCM-41 shifts higher by 0.2°, showing that the distance between the pore center shrinks upon Al incorporation. Indeed, on the basis of the calculation according to the formula for the hexagonal unit cell (i.e., $a_0 = 2d_{100}/\sqrt{3}$), the distance between the pore centers for Si-MCM-41 and Si-Al-MCM-41 is 46.7 and 44.3 Å, respectively.

Figure 2 shows the nitrogen adsorption-desorption isotherms of Si-MCM-41 and Si-Al-MCM-41. Type IV isotherms are obtained for these two mesoporous MCM-41 materials. Figure 2a shows that the pore filling (by capillary condensation) for Si-MCM-41 is restricted to a narrow range of P/P_0 = 0.3–0.4, which is a typical feature for mesoporous MCM-41 materials. The inflection point for Si-Al-MCM-41 (Figure 2b) is, however, less unambiguous as compared with that of Si-MCM-41. Consequently, the pore size distribution of Si-Al-MCM-41 is much broader than that of Si-MCM-41. The results imply that the mesoporous structure of Si-Al-MCM-41 is less perfectly arranged than that of Si-MCM-41. In addition, the thickness of the pore wall can be estimated on the basis of the difference between the pore center distance and the pore

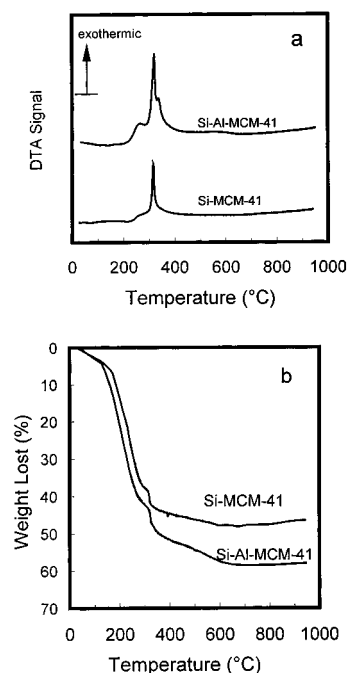


Figure 3. DTA (a) and TGA (b) curves of as-synthesized MCM-41 samples.

diameter. Si-Al-MCM-41 has a thinner pore wall (18.6 Å) than Si-MCM-41 (19.6 Å).

Parts a and b of Figure 3 show the DTA and TGA results, respectively, for as-synthesized Si-MCM-41 and Si-Al-MCM-41. A sharp DTA peak is observed for both samples at around 320 °C (Figure 3a). This sharp peak is attributed to the strong exothermic process due to the combustion and removal of the surfactant from the mesopores of MCM-41. Besides, a small shoulder at around 340 °C is also observed on the DTA curve of Si-Al-MCM-41. As this shoulder does not appear on the DTA curve of Si-MCM-41, the result shows that a slightly higher temperature is required to remove some of the surfactant from Si-Al-MCM-41 completely. This result implies that there is some interaction between the occluded surfactant and Al in the framework.²⁴ From the corresponding TGA results (Figure 3b), it can be observed that the slope of the weight loss curve for Si-Al-MCM-41 is greater than that for Si-MCM-41 in the range of temperatures between 100 and 600 °C. The physisorbed water is believed to be removed below 125 °C, and most of the surfactant is removed between 125 and 450 °C.²⁴ The combustion of surfactant causes a sudden decrease of the TGA signal at 300–320 °C, followed by a broad region of weight loss up to 600 °C; this weight loss has been attributed to the dehydroxylation process on the surface. From 600 to 920 °C, the absence of the DTA peak together with the rather flat TGA curves indicates that both Si-MCM-41 and Si-Al-MCM-41 are relatively stable up to 900 °C in air for a short period.

Table 1 lists the surface areas and pore parameters of Si-MCM-41 and Si-Al-MCM-41 after treatment in air streams containing different concentrations of water vapor at 600 °C. Both samples suffer a slight decrease of their specific surface areas after the hydrothermal treatment. In addition, the pore diameter and pore volume of Si-Al-MCM-41 decrease more than those of Si-MCM-41, even though both samples have been subjected to the same treatment conditions. Table 1 also shows that an increase in the water vapor concentration causes a larger loss of the surface area and pore volume of the material, indicating that water vapor concentration is an important factor

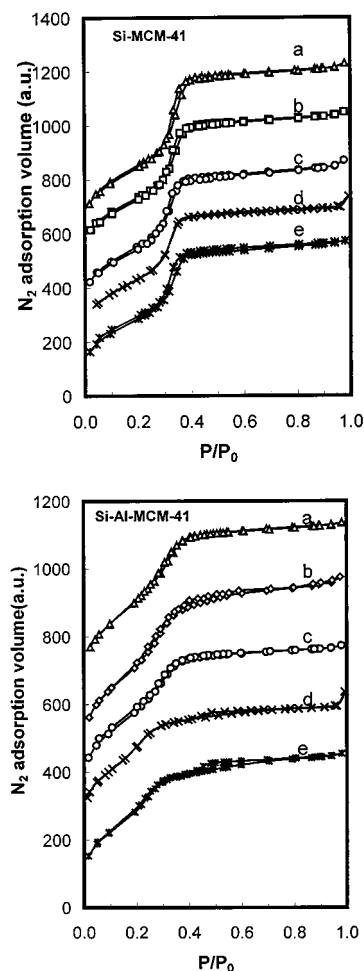


Figure 4. Nitrogen adsorption-desorption isotherms of Si-MCM-41 and Si-Al-MCM-41 after treatment in air streams containing various water vapor concentrations at 600 °C: (a) fresh sample, (b) 3 vol % H₂O for 40 h, (c) 10 vol % H₂O for 40 h, (d) 10 vol % H₂O for 1 week, and (e) 20 vol % H₂O for 40 h.

TABLE 1: Effect of Various Hydrothermal Treatments at 600 °C on the Surface Area, Pore Diameter, and Pore Volume of Si-MCM-41 and Si-Al-MCM-41

sample	treatment condition	surface area (m ² /g)	pore diameter (Å)	total pore volume (cm ³ /g)
Si-MCM-41	fresh	1301	28.4	1.13
	3% H ₂ O/40 h	1147	28.4	0.94
	10% H ₂ O/40 h	1136	27.0	0.94
	10% H ₂ O/1 week	1099	27.0	0.86
	20% H ₂ O/40 h	1066	27.1	0.87
Si-Al-MCM-41	fresh	1289	27.1	0.86
	3% H ₂ O/40 h	1192	26.8	0.89
	10% H ₂ O/40 h	1151	25.7	0.76
	10% H ₂ O/1 week	1169	22.0	0.67
	20% H ₂ O/40 h	1096	23.1	0.69

affecting the stability of MCM-41. For example, exposing the samples under 20 vol % water vapor at 600 °C for only 40 h results in more loss of their pore volumes and surface areas than the treatment under 10 vol % water vapor at 600 °C for one week.

The N₂ adsorption-desorption isotherms of the samples treated in air streams containing different vapor concentrations (Figure 4) show that both Si-MCM-41 and Si-Al-MCM-41 still maintain their mesoporous structure. For Si-MCM-41, the N₂ adsorption-desorption isotherms are almost the same as those of the fresh sample after various treatment conditions.

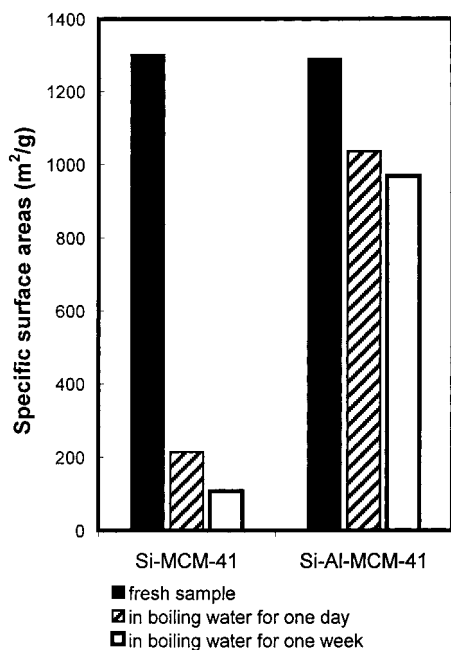


Figure 5. Effect of different hydrothermal treatments on the surface areas of Si-MCM-41 and Si-Al-MCM-41.

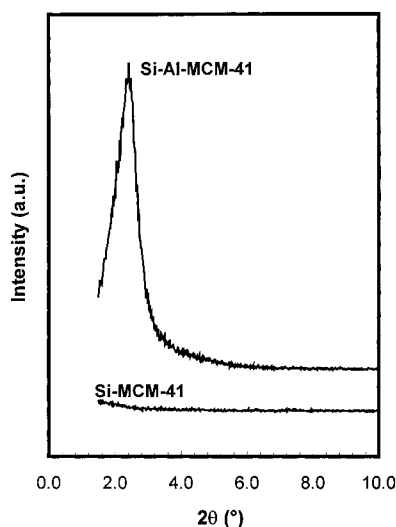


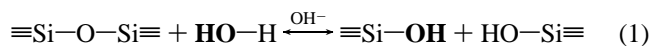
Figure 6. Powder XRD patterns of Si-MCM-41 and Si-Al-MCM-41 after treatments in boiling water for 1 week.

However, a slight change in the isotherms of Si-Al-MCM-41 can be clearly observed. After hydrothermal treatment, the inflection step in the isotherm of Si-Al-MCM-41 (due to the filling of nitrogen in the pores) is shifted to lower P/P_0 , especially at higher water vapor concentration. The results suggest that the pore structure of Si-Al-MCM-41 has constricted during hydrothermal treatment.

However, when Si-MCM-41 and Si-Al-MCM-41 samples are treated in boiling water, Figure 5 shows that there is a remarkable difference in the surface areas of the two samples. Si-MCM-41 loses most of its surface area (from 1301 to 214 m²/g) after it has been soaked in boiling water for 24 h; its specific surface area further decreases to 107 m²/g after being treated in boiling water for 1 week. In contrast, Si-Al-MCM-41 still maintains its surface area around 1000 m²/g even after treatment in boiling water for 1 week. Figure 6 shows that the (100) diffraction peak of Si-MCM-41 disappears after it has been treated in boiling water for 1 week; the XRD result shows that the drastic decrease of the surface area of Si-MCM-41 in

boiling water is attributed to the degradation of its mesoporous structures. On the contrary, the (100) diffraction peak is clearly observed for Si-Al-MCM-41 that has been treated in boiling water for one week. The XRD result shows that the incorporation of Al in the framework of MCM-41 helps to maintain its mesoporous structure and greatly improves the hydrothermal stability of MCM-41 in boiling water. Although it has been reported that the stability of MCM-41 can be improved by controlling the synthesis parameters which can lead to a thicker pore wall,²⁵ the results of this study show that the remarkable difference in the hydrothermal stability between Si-MCM-41 and Si-Al-MCM-41 is actually not caused by the thickness of the pore wall. This is shown by the XRD and N₂ adsorption measurements, which show that Si-Al-MCM-41 (18.6 Å) has thinner pore walls than Si-MCM-41 (19.6 Å).

The instability of the mesoporous structures of Si-MCM-41 in boiling water can be attributed to the chemical reaction between water molecules and the surface framework of MCM-41. On the basis of ²⁹Si MAS NMR study, it has been reported that the degradation of the mesoporous structure of Si-MCM-41 in water can be attributed to the hydrolysis of Si-O-Si linkages.²⁶ Under the hydrothermal treatment condition, the energy-rich Si-O-Si bonds are easily attacked by H₂O according to the following "alkaline" reaction, which can be catalyzed by the hydroxide ions in water:



The resulting terminal OH groups on the surface make Si-MCM-41 more easily attacked by hydroxide ions of water, leading consequently to the destruction of the mesoporous structure.

It is worthwhile to mention here that, although Si-MCM-41 is not stable in boiling water, the above result shows that it is relatively stable in an air stream containing 3~20% water vapor at 600 °C. The relative stability of Si-MCM-41 in an air stream containing a low concentration of water vapor at high temperature can be explained by the fact that (1) the contact time between molecular H₂O in the gas phase with $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds on the surface of Si-MCM-41 is shorter and (2) at high temperature, the dehydroxylation of Si-OH may cause the restoration of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ linkage on the surface.²⁷ At high temperature, reaction 1 and the reverse of reaction 1 may reach equilibrium, preventing the surface framework from continuous hydrolysis. On the other hand, the instability of Si-MCM-41 in boiling water can be explained by the fact that Si-MCM-41 could be easily hydrolyzed in boiling water as it has direct contact with the liquid water and no dehydroxylation processes are expected to occur on the surface at the temperature of boiling water.

This result is not quite surprising as similar results have been observed by Chen et al.,¹² who reported that Si-Al-MCM-41 was quite stable in boiling water for 4 h but Si-MCM-41 lost most of its surface area under the same treatment. Unfortunately, they have not reported the stability of Si-Al-MCM-41 in boiling water under much longer treatment time. From a practical point of view, an investigation for much longer treatment of MCM-41 in boiling water is critical to evaluate the potential application of MCM-41 materials in aqueous solution.

The possible mechanism for the improvement of the hydrothermal stability of MCM-41 by substitution of Al into its framework can be explained on the basis of the effects of the presence of Al on both geometric and chemical properties of materials. On the geometrical properties of MCM-41 materials,

Luan *et al.*²⁸ observed that even a small amount of Al in the Si–Al–MCM-41 framework would cause the pore structure to be less uniform than that of Si–MCM-41. This observation has been verified in this study (shown in Figures 1 and 2). In addition, each Al atom incorporated in the framework is accompanied by a relevant Na^+ or H^+ ion to balance the charge. These interfacial ions possibly make the mesoporous channels of Si–Al–MCM-41 somewhat distorted, indirectly contributing to the enhancement of the hydrothermal stability for Si–Al–MCM-41.

Experimental evidence by Chen *et al.*²⁹ further supports the role of interfacial ions in improving the hydrothermal stability of MCM-41. In their study, one type of mesoporous siliceous material prepared from Na–Kanemite shows a pore structure similar to that of MCM-41, except that some of its channels are distorted or cross-arranged rather than perfectly uniformly arranged like the channels of Si–MCM-41. They found that this “distorted” mesoporous siliceous material had better hydrothermal stability than Si–MCM-41. Similarly, Ryoo *et al.*¹³ improved the hydrothermal stability of MCM-41 by adding EDTA– Na_4 into the mixture gel during synthesis, yielding a mesoporous material having completely disordered pore channels as evidenced from TEM. They found that the resulting material had a three-dimensional network consisting of short wormlike structures, which were different from the regular hexagonal packing of straight uni-dimensional channels of Si–MCM-41. On the basis of thermodynamics consideration, this disordered structure should be more favorable due to its higher entropy or higher thermodynamic stability. Therefore, the existence of both Al in the framework and Na ions in the interface would generally cause Si–Al–MCM-41 to have less uniform pore structures than Si–MCM-41, leading to the improved hydrothermal stability of Si–Al–MCM-41. Similar improvement of hydrothermal stability has also been observed when other metals or oxides, such as Fe, La, and La_2O_3 , have been substituted in the framework of MCM-41,³⁰ which we suggest to be possibly due to the formation of more random pore structures upon the substitution of metal in the framework.

Similarly, it is found in this study that a more random mesoporous structure can be observed with Si–Al–MCM-41 after it has been hydrothermally treated. Figure 7 shows that the exposure of Si–Al–MCM-41 in an air stream containing 20 vol % water vapor at 600 °C for 40 h results in the decrease of its main pore size distribution from ~ 27 to ~ 23 Å, and the formation of a larger pore structure with a pore diameter of around 37 Å. The formation of this larger pore structure is not observed with Si–MCM-41 although it has undergone similar hydrothermal treatment, showing that its formation is related to the presence of Al in the material. This pore size redistribution on Si–Al–MCM-41 causes the mesoporous structure of Si–Al–MCM-41 to be even less uniform than that of Si–MCM-41, rendering Si–Al–MCM-41 to be more refractory under further hydrothermal treatment.

The concomitant reduction and enlargement of the mesopores observed during the hydrothermal treatment of Si–Al–MCM-41 are likely to be attributed to the partial dealumination of Si–Al–MCM-41. It has been reported that the incorporated Al in the MCM-41 framework was unstable and could be converted to nonstructural aluminum species under a mild thermal–chemical treatment.³¹ The partial dealumination during hydrothermal treatment is suggested to be responsible for the formation of these larger mesopores in Si–Al–MCM-41. During the dealumination process, the substituted Al may have migrated out of the structural framework to the surface to form

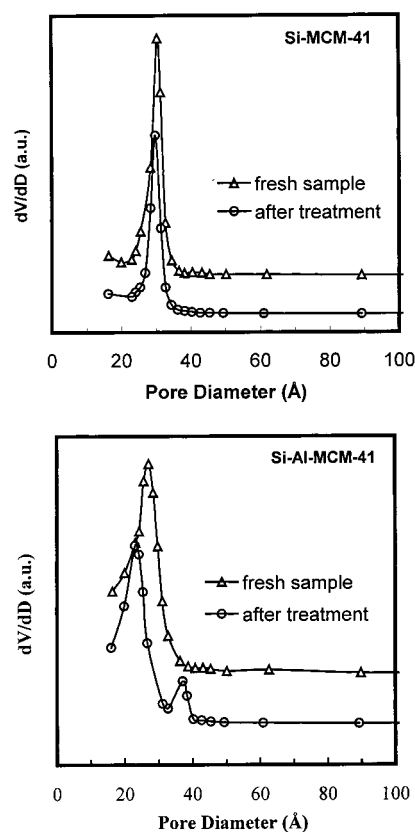


Figure 7. Changes of the pore size distribution of Si–MCM-41 and Si–Al–MCM-41 before and after treatment in an air stream containing 20 vol % H_2O at 600 °C for 40 h.

nonstructural Al species, causing the original pore channel to be partially clogged by these nonstructural Al species and the pore size distribution to be shifted to smaller size. This partial pore blocking by aluminum species can be generally observed on the N_2 adsorption–desorption isotherm of Si–Al–MCM-41 (Figure 4), which shows the formation of a hysteresis loop (at $P/P_0 = 0.4$ – 0.6). The structural defect sites created by the migrating Al species can then be suggested to contribute to the formation of the larger mesopores on the hydrothermally treated Si–Al–MCM-41. This role of the migrating Al species in concomitantly reducing and enlarging the mesopores of Si–Al–MCM-41 during hydrothermal treatment is also testified by the observation that, during hydrothermal treatment, the pore size reduction of Si–MCM-41 is not as serious as that of Si–Al–MCM-41 as dealumination does not happen in Si–MCM-41.

In addition to the effect of the presence of Al on the geometrical structure of MCM-41, the chemical property of MCM-41 may be affected by the presence of TEOH in the synthesis procedure and the Al substitution. The presence of TEOH in the synthesis of Si–Al–MCM-41 may improve the stability of the Si–O–Si linkages during the formation of the framework of MCM-41, contributing to the better hydrothermal stability of Si–Al–MCM-41. It was recently reported that the hydrothermal stability of MCM-41 could be improved by adding tetraalkylammonium ions, including TEA^+ or TMA^+ , in the gel mixture during the synthesis.³² From ^{29}Si MAS NMR results, the presence of tetraalkylammonium ions was suggested to facilitate the condensation of silanol groups during the formation of the mesoporous structure. The better condensed silica wall may contribute to the improved stability under hydrothermal treatment conditions. The presence of TEA^+ ions in our study

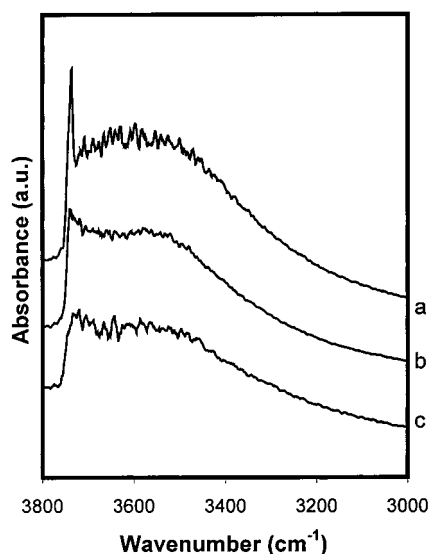


Figure 8. IR spectra characterizing the hydroxyl groups of Si-Al-MCM-41 which has been treated in boiling water for (a) 0 h, (b) 3 h, and (c) 24 h.

may be one of the reasons for the significant improvement of the hydrothermal stability of Si-Al-MCM-41.

The dealumination process during the initial step of hydrothermal treatment is suggested to produce nonstructural aluminum species not only as random structures (which enhance the stability of the resulting pores) but also as aluminum-rich surface species (which prevents the surface framework from hydrolysis). This can be explained as follows. On the basis of a study on Y zeolite having a high Si/Al ratio, Lutz *et al.*³³ reported that the hydrothermal stability of Y zeolite could be enhanced by an external introduction of nonstructural aluminum species on the surface of the inner pores of Y zeolite. The surface layer of Al-rich aluminosilicate was suggested to block the terminal OH groups and energy-rich $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds on the surface of Y zeolite, hence minimizing the attack of water molecules on the zeolite framework. In addition, the negative charge of the aluminosilicate layer caused by the 4-fold coordination of the aluminum atoms repels hydroxide ions of water which catalyze the dissolution of zeolite. Due to these chemical properties, the surface layer of nonstructural aluminum species can then function as a protective layer for the framework under hydrothermal treatment conditions.

The same mechanism can be employed to explain the remarkable improvement of the hydrothermal stability of Si-Al-MCM-41 as observed in this study. Due to the instability of Al in the framework of MCM-41, some of the incorporated Al species may leach out from the framework of MCM-41 as a separate aluminosilicate phase during calcination. The existence of the additional aluminosilicate phase may not only cause a less uniform mesoporous structure of Si-Al-MCM-41, but also form a more stable Al-rich surface species. In addition to the effect from calcination, the initial step of hydrothermal treatment also formed an Al-rich surface species by the migration of Al from the framework of Si-Al-MCM-41 to the pore surface. This Al-rich surface is then suggested to partially block the surface OH groups and protect the surface framework of MCM-41 from further disintegration. Figure 8 shows the IR spectra of the hydroxyl groups of Si-Al-MCM-41 that has been treated in boiling water at different treatment times. The sharp band at 3745 cm^{-1} for the fresh sample is assigned to isolated Si-OH groups.³⁴ Having a considerable width at half-height, the broad band at 3530 cm^{-1} is assigned

to hydrogen-bonded hydroxyl groups³⁵ which can be formed on defect sites derived from structural imperfection or dealumination.^{36,37} After Si-Al-MCM-41 has been treated in boiling water, it can be observed that the intensity of the absorbance of these hydroxyl groups on the sample decreases clearly in the first 3 h of treatment and becomes much weaker after 24 h of treatment. The decrease of the absorbance is caused by the coverage of the alumina-rich surface species, which are formed from dealumination, on the surface hydroxyl groups. This Al-rich surface is suggested to play a role in protecting the surface framework from collapsing in boiling water by preventing the hydroxyl groups from hydrolysis with water molecules. This phenomenon is not surprising as it has been reported that the isolated silanols could act as the centers for the adsorption of water;³⁸ the adsorbed water molecules can then attack the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ linkage, leading to the rehydroxylation of the surface and consequently to the hydrolysis of the surface framework.

Although the concentration of nonstructural and structural Al species in MCM-41 is not enough to form aluminum-rich surface species to cover all the surface of MCM-41, it has been suggested that the surface aluminum species protect not only the adjacent silicon atoms but also those far away from the aluminum species.³⁹ Hence, a small amount of Al-rich surface species can help MCM-41 to maintain its mesoporous structure in boiling water. In addition, it was reported that not only the nonstructural Al species but also the tetrahedrally coordinated aluminum in the framework of molecular sieves may play the same role in preventing the structure of the siliceous framework from the attack of water and thus in improving the hydrothermal stability of the material.⁴⁰

To give further evidence of the existence of these nonstructural or structural Al species as a "protective Al-rich surface" of the MCM-41 framework, a small amount of Al_2O_3 is externally introduced onto the surface of Si-MCM-41. (The Si-MCM-41 sample was impregnated in a certain amount of 1 M $\text{Al}(\text{NO}_3)_3$ solution under stirring, followed by drying at $100\text{ }^\circ\text{C}$ and calcination at $500\text{ }^\circ\text{C}$ for 5 h; the resulting sample contains about 1.0 wt % Al_2O_3 on the surface of Si-MCM-41.) Most of the Al species may have existed on the surface as nonstructural Al species, although it is possible that, during calcination, some of the Al species could be anchored into the framework as tetrahedrally coordinated Al species.⁴¹ It is clearly observed that, after treatment in boiling water for 1 day, the Al_2O_3 -containing Si-MCM-41 maintains a much higher surface area ($824\text{ m}^2/\text{g}$) than Si-MCM-41 ($214\text{ m}^2/\text{g}$). It is interesting to note that, even after treatment in boiling water for 1 week, the surface area of the Al_2O_3 -containing Si-MCM-41 is still maintained at $814\text{ m}^2/\text{g}$, while that of Si-MCM-41 has decreased to $107\text{ m}^2/\text{g}$. The nitrogen adsorption-desorption isotherms, shown in Figure 9, indicate that the mesoporous structures of Si-MCM-41 easily collapse in boiling water for just 1 day. However, the adsorption-desorption isotherms of the Al_2O_3 -containing Si-MCM-41 shows that most of the mesoporous structures of this sample could be maintained in boiling water for 1 day and even for 1 week. As the isotherms of the Al_2O_3 -containing Si-MCM-41 treated in boiling water for 1 day and 1 week are almost identical, the result shows that most of these mesoporous structures can be stabilized by a small amount of surface alumina species during the initial period of hydrothermal treatment and almost not affected by the duration of the treatment in boiling water. The results lead us to propose that the Al-rich surface species formed from the partial dealumination of Si-Al-MCM-41, together with the tetrahe-

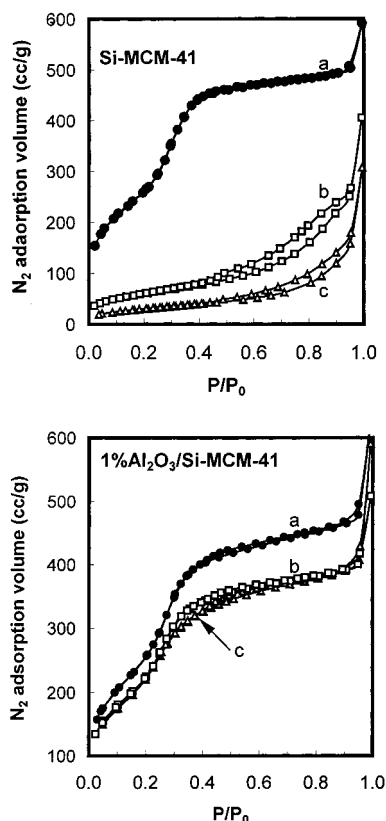


Figure 9. Nitrogen adsorption-desorption isotherms of Si-MCM-41 and 1% Al_2O_3 -containing Si-MCM-41 after being treated in boiling water for different periods: (a) fresh, (b) 1 day, and (c) 1 week.

drally coordinated Al species in the network, plays a role similar to that of the externally introduced Al species on the pore surface of MCM-41 in preventing the structural framework of MCM-41 from degradation and in contributing to the remarkable improvement of the hydrothermal stability of Si-Al-MCM-41 in boiling water.

Conclusion

The introduction of Al in the framework of MCM-41 shows little effect on its hydrothermal stability in an air stream containing 3–20 vol % water vapor at 600 °C. Both Si-MCM-41 and Si-Al-MCM-41 maintain their mesoporous structures after 1 week of exposure in 10 vol % water vapor at 600 °C. However, Si-Al-MCM-41 shows remarkable stability in boiling water for days as compared with Si-MCM-41. While Si-MCM-41 loses its uniform mesoporous structure after being soaked in boiling water for 24 h, the mesoporous structure of Si-Al-MCM-41 could still be identified even after 1 week of treatment in boiling water. The significant difference in hydrothermal stability is due to the effect of Al substitution and the presence of TEOH in the synthesis mixture on both the bulk geometrical and surface chemical properties of MCM-41.

Acknowledgment. This research work has been generously supported by the Environmental Technology Enterprise and the National University of Singapore. The assistance provided by Professor Paul W. S. Heng in the XRD experiments is gratefully acknowledged.

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