

On the Hydrothermal Stability of Mesoporous Aluminosilicate MCM-48 Materials

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Aluminosilicate MCM-48 materials with Si/Al ratio between 4 and 50 were prepared via direct mixed-gel synthesis, and their hydrothermal stability in boiling water and steam was investigated using a variety of techniques including powder XRD, N₂ sorption studies, and elemental analysis. The stability of Al-containing MCM-48 in boiling water was found in all cases to be higher than that of the pure silica material. The improvement in boiling water stability was dependent on the Al content and went through maxima as Al content increased. The optimum Al content for enhancing boiling water stability was found to be in the Si/Al range 8–15. The relationship between Al content and steam stability was somewhat the reverse of that observed for boiling water stability. Small amounts of Al (Si/Al = ca. 50) afforded better protection of the mesoporous structure against steaming than larger amounts (Si/Al = 4). The influence of Al content on the hydrothermal stability is explained with respect to the role played by the framework Al within the MCM-48 pore walls and its effect on the processes that occur when the Al–MCM-48 framework is in contact with water at low (refluxing) or high (steaming) temperature. The balance between the key processes, i.e., dehydroxylation, hydrolysis (dissolution of silica) and dealumination, determines the stability. Under refluxing conditions, hydrolysis predominates and therefore the presence of medium to large amounts of Al (and the formation of water resistance Si–O–Al bonds) helps protect the framework. Under steaming conditions, both hydrolysis and dehydroxylation (which have opposing effects) occur but dealumination predominates and therefore the presence of significant amounts of Al buried within the framework (which are removed during steaming) acts to diminish stability. It is proposed that, in general, Al positioned on the surface/near surface region of the pore walls provides the greatest protection against water attack under either refluxing or steaming conditions.

Introduction

Since mesoporous materials of the M41S family were first reported a decade ago,^{1,2} increasing interest has been focused on their properties and uses.^{3,4} In particular, due to their regular structure, large pore size, and high surface area, mesoporous materials have the potential to function as catalysts and catalytic supports. Mesoporous silica materials with isomorphously substituted catalytically active heteroatoms have been shown to exhibit considerable reactivity due to easily accessible active sites within the (meso) porous network.^{5,6} In addition, the size of their uniform pores can be tuned in the range 15–100 Å which provides the possibility for shape selective conversion of bulky molecules and pharmaceutical products.

To date, most published work on mesoporous materials has focused on the hexagonal phase MCM-41 materials. Although the basic synthesis principles for MCM-41 can be applied to the preparation of MCM-48, the synthesis of the cubic phase MCM-48 is much more difficult. Indeed the synthesis of MCM-48 materials is still a challenge because the MCM-48 phase is obtained only under certain synthesis conditions. For example, the MCM-48 phase is often an intermediate during the transformation from a hexagonal phase or disordered surfactant/silica mesophase to a lamellar phase.^{7–12} However, compared to the one-dimensional structure of MCM-41, the cubic phase MCM-48, which has a highly branched and interwoven bicontinuous pore structure, is a more interesting candidate for catalysis, adsorption, or ion-exchanger. Due to its potential applications,

it is crucial to investigate the hydrothermal stability of MCM-48 especially with respect to its use in applications involving the presence of water. It is known that pure silica MCM-48 and MCM-41 materials exhibit poor hydrothermal stability in boiling water^{13–15} due to the fast hydrolysis of the silica in their relatively thin amorphous silica pore walls. Due to their inherently poor hydrothermal stability considerable research effort has been directed at attempts to improve the hydrothermal stability of mesoporous materials either by using carefully selected synthesis procedures or by postsynthesis treatment. These strategies include addition of inorganic or organic salts to the synthesis gel during the crystallization process,^{15–18} postsynthesis hydrothermal restructuring which increase either the pore wall thickness¹⁹ or the degree of polymerization in the silica wall,^{19,20} hydrophobization of the silica surface by silylation reaction.^{21,22} A two-step synthesis method or long crystallization time has been developed by us^{19,23} to increase the hydrothermal stability of MCM-41. Other reports^{24–26} have illustrated that the incorporation of heteroatoms into the walls of mesoporous materials by direct synthesis or grafting modifies both the structural ordering and hydrothermal stability.

There are, however, very few reports focused on the detailed study or improvement of the hydrothermal stability of MCM-48 materials. Ryoo and co-workers^{15,27} reported that the hydrothermal stability of MCM-48 can be improved either by addition of salts during the synthesis procedure or by postsynthesis treatment of the as-synthesized materials in salts solution. Vansant et al.²² reported on the steam stability of Si–MCM-48 and V-grafted methylsilylated MCM-48. However, there has so far been no systematic study of the influence of Al content

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on the hydrothermal stability of MCM-48 materials in boiling water or under steaming conditions, although there are many such reports on Al-MCM-41.^{26,28,29} It is known that the incorporation of Al into mesostructured silica frameworks changes the structural ordering of the materials and in some cases alters the hydrothermal stability. It is of interest to understand how the Al content affects the structure and hydrothermal stability of the mesoporous framework of MCM-48. It is also of interest to find out how the stability of MCM-48 and Al-MCM-48 compare to that of MCM-41 materials, given that MCM-48 is thought to be more hydrophobic due to its cubic pore geometry.²² In this report, MCM-48 materials with varying amounts of Al have been prepared and their hydrothermal stability in boiling water or under steaming conditions has been studied using powder XRD, N₂ sorption analysis, and elemental analysis.

Materials and Methods

Materials. The Al-MCM-48 materials were prepared as follows. The surfactant, cetyltrimethylammonium bromide (CTAB) and sodium hydroxide (NaOH) were dissolved in distilled water under stirring at 35 °C. The required amount of silica (tetraethyl orthosilicate) and aluminum (aluminum isopropoxide) were then added to the template solution under stirring. The molar ratio of the resulting synthesis gels were SiO₂:xAl:0.5NaOH:0.12CTAB:118H₂O (where $x = 0.017, 0.033, 0.067, 0.125, \text{ or } 0.25$). After stirring for 1 h, the synthesis gel was transferred to a Teflon-lined autoclave and heated at 150 °C for 8 h. The autoclave was then cooled to room temperature and the solid product obtained by filtration and repeatedly washed with a large amount of distilled water. After air-drying at room temperature, the as-synthesized materials were calcined in air at 550 °C for 6 h. The five samples prepared were designated Al-MCM-48-*X* where *X* is the Si/Al ratio in the synthesis gel, i.e., 60, 30, 15, 8, or 4. Pure silica MCM-48 (designated Si-MCM-48) was also prepared using the same procedure as outlined above except that the Al source was excluded from the synthesis gel.

To assess hydrothermal stability, the MCM-48 materials were refluxed in distilled water at a water-to-sample ratio of 1 L/g for various periods of time. The refluxed samples were dried at 150 °C prior to further characterization. The high-temperature hydrothermal (steam) stability of the materials was evaluated by subjecting them to heat treatment at 800 °C for 4 h in a flow of nitrogen saturated with water vapor at room temperature.

Characterization. Elemental compositions were determined by a Philips MiniPal PW4025 X-ray fluorescence (XRF) instrument. Powder X-ray diffraction (XRD) patterns were recorded using a Philips 1830 powder diffractometer with Cu K α radiation (40 kV, 40 mA), 0.02° step size and 1 s step time. Nitrogen sorption isotherms and textural properties of the materials were determined at 77 K using nitrogen in a conventional volumetric technique by a Coulter SA3100 sorptometer. Before analysis, the samples were oven dried at 150 °C and evacuated for 12 h at 200 °C under vacuum. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P_0) range 0.05 to 0.2 and total pore volume was determined from the amount of the nitrogen adsorbed at $P/P_0 = \text{ca. } 0.99$.

Results and Discussion

Parent Materials. The quality and structural ordering of Si-MCM-48 and Al-MCM-48 materials were assessed by powder

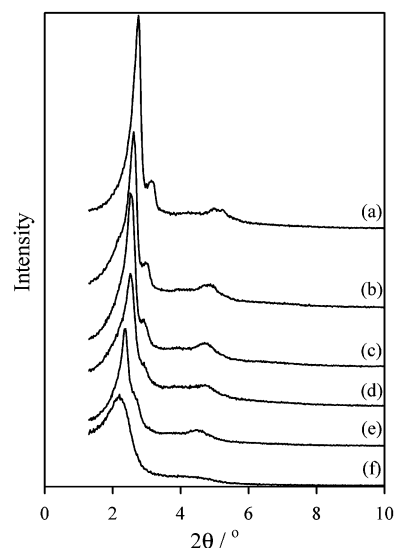


Figure 1. Powder XRD patterns of Si-MCM-48 (a) and Al-MCM-48 (b–f) containing different amounts of Al. The synthesis gel Si/Al ratios used were (b) 60, (c) 30, (d) 15, (e) 8, and (f) 4.

XRD and N₂ sorption studies. Figure 1 shows the XRD patterns of calcined samples with different Si/Al ratios. For Si-MCM-48, four diffraction peaks, i.e., (211), (220), (420) and (332), which can be indexed to *la3d* cubic structure, are clearly observed.^{1,2} On the introduction of a small amount of Al into the structure, the resulting Al-MCM-48 materials exhibit XRD patterns largely similar to that of Si-MCM-48 but with reduced intensity peaks. A gradual increase in the amount of Al (lowering of Si/Al ratio) results in decrease in the intensity of (211) and (220) diffraction peaks. Indeed for sample Al-MCM-48-8 (Si/Al = 8), the (220) diffraction peak is poorly defined and the (420) and (332) peaks merge into a diffuse broad peak. For sample Al-MCM-48-4 (Si/Al = 4), only the basal (211) diffraction peak is clearly observed. These results indicate that the incorporation of Al via direct mixed-gel synthesis diminishes the structural ordering of Al-MCM-48 (compared with Si-MCM-48). Similar trends have previously been observed for Al-MCM-41 materials prepared via direct synthesis.^{26,28,29} Figure 1 also indicates that, with increasing Al content, the basal diffraction peak (211) shifts to lower 2θ values, i.e., the basal spacing increases. The increase in basal spacing suggests an expansion of the lattice. The distance between two nearest pore centers (a_0), calculated on the basis of the cubic unit cell, where $a_0 = \sqrt{6}d_{211}$, increases as shown in Table 1. The most likely explanation for the lattice expansion is the formation of Al–O bonds (which are longer than Si–O bonds) occasioned by the substitution of increasing amounts of Al for Si in the framework.

Figure 2 presents the N₂ sorption isotherms of the Si-MCM-48 and Al-MCM-48 materials. In general, for mesoporous molecular sieves, the sharpness and height of the capillary condensation step in the isotherms indicate the pore size uniformity. Departure from a sharp and clearly defined capillary condensation step usually implies an increase in pore size heterogeneity, i.e., broadening of the pore size distribution. Both Si-MCM-48 and Al-MCM-48 materials exhibit type IV isotherms with a typical capillary condensation step into uniform mesopores in the relative pressure (P/P_0) range 0.2 to 0.4. This indicates that all of the samples possess good mesopore structural ordering and a relatively narrow pore size distribution and that any structural changes resulting from Al incorporation are not necessarily at the expense of pore uniformity. The mesopore filling step for Al-MCM-48 samples is generally at

TABLE 1: Elemental Composition and Textural Properties of Studied Materials before and after Refluxing in Water for Various Periods of Time

sample	Si/Al	d_{211} spacing (Å) ^a	lattice parameter a_0 (Å) ^{a,b}	surface area (m ² /g)	pore volume (cm ³ /g) ^c	pore size (Å) ^d	wall thickness (Å) ^e
Si-MCM-48		31.0 (37.0)	75.9 (90.6)	1088	0.80 (0.78)	28.7	10.2
refluxed 6 h				368	0.75		
Al-MCM-48-60	46.6	34.0 (36.4)	83.3 (89.2)	1065	0.92 (0.90)	33.8	10.1
refluxed 12 h	23.8			596	0.75		
refluxed 24 h	20.0			585	0.65		
Al-MCM-48-30	24.2	34.4 (37.0)	84.3 (90.6)	963	0.83 (0.81)	33.6	10.5
refluxed 12 h	10.7			698	0.78		
refluxed 24 h	10.4			594	0.66		
Al-MCM-48-15	14.9	35.6 (37.2)	87.2 (91.1)	875	0.86 (0.77)	35.2	10.6
refluxed 12 h	7.4			704	0.81		
refluxed 24 h	7.3			577	0.69		
Al-MCM-48-8	8.3	37.3 (37.7)	91.4 (92.3)	696	0.68 (0.61)	35.1	12.0
refluxed 12 h	4.5			511	0.56		
refluxed 24 h	4.4			518	0.55		
Al-MCM-48-4	4.5	37.3 (38.1)	91.4 (93.3)	537	0.60 (0.46)	34.3	12.4
refluxed 12 h	3.0			427	0.56		
refluxed 24 h	2.8			380	0.60		

^a Values in parentheses are data for as-synthesized samples. ^b The lattice parameter a_0 is obtained using the formula $a_0 = d_{211}\sqrt{6}$. ^c Values in parentheses are mesopore volume. ^d Pore size obtained from the formula, pore size = $4V_{\text{meso}}/S$, where V_{meso} is the mesopore volume and S is the surface area. ^e Wall thickness is calculated from the equation, wall thickness = $a_0/3.0919 - \text{pore size}/2$.

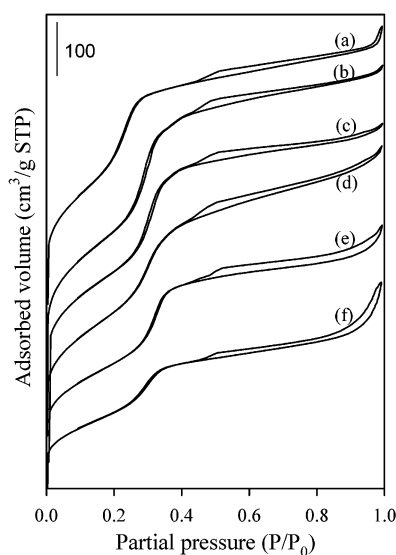


Figure 2. Nitrogen sorption isotherms of Si-MCM-48 (a) and Al-MCM-48 (b–f) containing different amounts of Al. The synthesis gel Si/Al ratios used were (b) 60, (c) 30, (d) 15, (e) 8, and (f) 4. For clarity, isotherms a–e are offset on the y-axis.

higher partial pressures compared to the pure silica sample and shifts to higher relative pressure with increasing Al content. This is consistent with the lattice expansion noted from the XRD patterns. The surface area, pore volume, pore size, and wall thickness of the study materials are given in Table 1. All of the samples have high surface area, which however generally decreases with an increase in Al content. The pore volume of Al-MCM-48 samples also decreases with increasing Al content. The pore wall thickness of the studied samples, calculated from the pore diameter and the lattice parameter (a_0) according to the formula described by Ravikovitch et al.,^{30,31} wall thickness = $a_0/3.0919 - \text{pore size}/2$, where 3.0919 is a constant representing the minimal surface area for MCM-48 *Ia3d* space group, is also shown in Table 1. The pore wall thickness increases with the Al content, which is consistent with the formation of Al–O linkages within the framework.

Hydrothermal Stability in Boiling Water. The powder XRD pattern and N₂ sorption isotherm of the pure silica MCM-48

before and after refluxing in boiling water for 6 h are displayed in Figure 3. It is clear that the Si-MCM-48 sample lost its mesoporous structure completely after 6 h refluxing in boiling water, which is in agreement with previous reports.^{13–15} As shown in Table 1, the surface area of the refluxed Si-MCM-48 sample reduced by ca. 65%. The isotherm of the refluxed sample (Figure 3B) suggests that the pore volume associated with ordered mesopores was completely lost. The refluxed sample, at best, had a very wide pore size distribution which was quite unlike the parent sample. It is likely that as a result of the gradual collapse and dissolution of the silica pore walls, new larger pores of varying sizes are generated, thus broadening the pore size distribution. It is known that the structural collapse of mesoporous silicas in water is caused by the hydrolysis of Si–O–Si bonds.³² If the pore walls of the materials are thin and/or less polymerization (as in the present case), the structure collapses at a relatively fast rate. The XRD patterns and nitrogen sorption isotherms, before and after refluxing in water for 12 and 24 h, of the Al-containing samples (Al-MCM-48-60, Al-MCM-48-30, Al-MCM-48-15, Al-MCM-48-8, and Al-MCM-48-4) are presented in Figures 4–6 and in the supporting information (Figures S1 and S2). The low Al content (Al-MCM-48-60) sample with Si/Al ratio of 46.6 exhibits slightly improved hydrothermal stability compared to the pure silica analogue (see Figures 3 and 4). An ill-defined peak is observed in the XRD pattern of the sample refluxed in water for 12 h. However, after refluxing for 24 h, the structure of Al-MCM-48-60 is completely destroyed. It is noteworthy that after refluxing for up to 24 h, the Al-MCM-48-60 sample still retains a ca. 60% of surface area compared to the pure silica Si-MCM-48 which retains only 35% of its surface area after a much shorter period (6 h) in boiling water.

At higher Al content, the Al-MCM-48 materials show improved hydrothermal stability in boiling water. The XRD patterns of refluxed samples presented in Figure 5, Figure 6 and the supplementary Figures S1 and S2, indicate that the refluxed samples (with the exception of Al-MCM-48-4) mainly display a reduced (211) basal diffraction peak and virtually no higher order peaks. This suggests a significant reduction in long-range structural ordering but without the total loss of mesopore ordering. Nitrogen sorption isotherms also provide evidence to

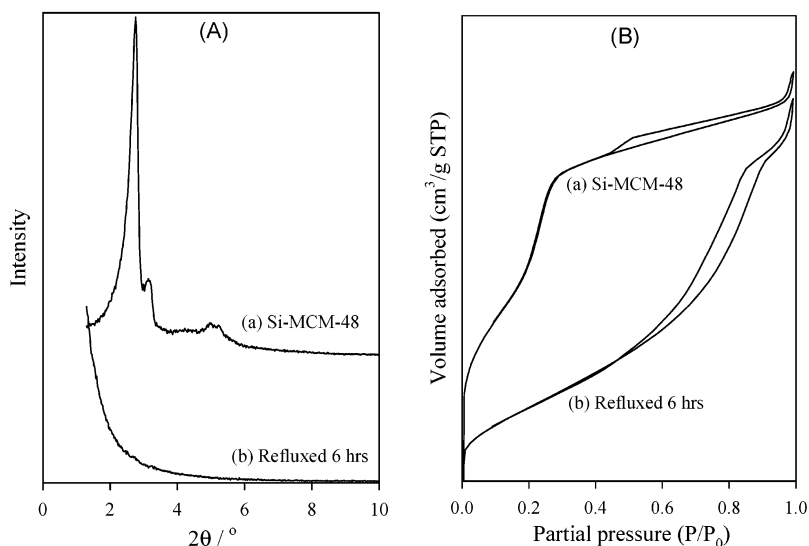


Figure 3. Powder XRD patterns (A) and nitrogen sorption isotherms (B) of Si-MCM-48 before and after refluxing in water for 6 h.

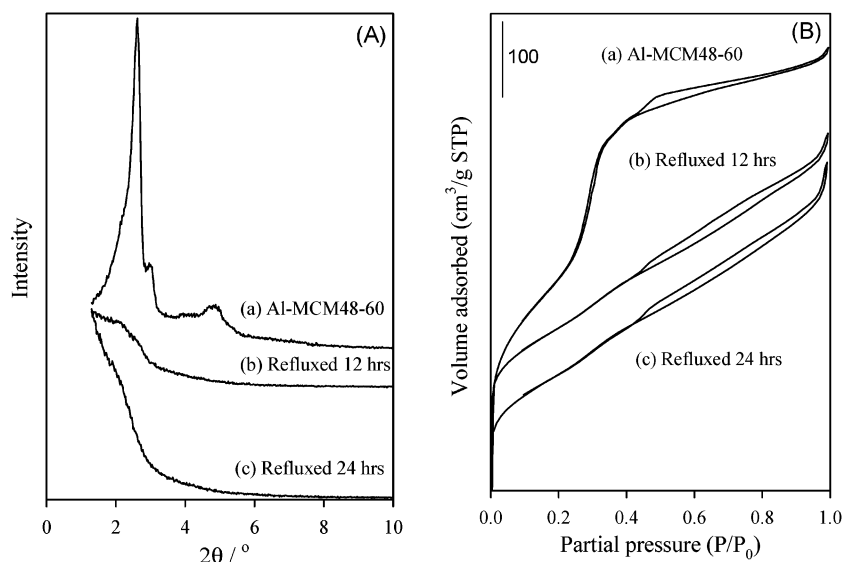


Figure 4. Powder XRD patterns (A) and nitrogen sorption isotherms (B) of Al-MCM-48-60 before and after refluxing in water for 12 or 24 h.

indicate that the mesoporous structural ordering is retained to some extent in the refluxed samples prepared at gel Si/Al ratio = 30, 15, and 8. The nitrogen sorption isotherms of these Al-MCM-48 samples subjected to refluxing in water for 12 and 24 h still exhibit a much reduced mesopore filling step. The samples refluxed for 12 h retain between 70 and 80% of surface area while those refluxed for 24 h retain 60 to 75% of surface area. From these observations it is clear that the introduction of certain amounts of Al into the mesoporous materials enhances the stability of MCM-48 in boiling water. Similar observations have previously been reported for Al-MCM-41.^{26,28,29} The XRD patterns and nitrogen sorption isotherms clearly indicate that the more Al-rich MCM-48 samples (Al-MCM-48-30, Al-MCM-48-15, and Al-MCM-48-8) are more stable in boiling water than the low Al content (Al-MCM-48-60) sample. Similar results have been reported by Sano et al.³³ in a study on the hydrothermal stability of ZSM-5. They found that the dissolution rate of ZSM-5 in water decreased with an increase of the Al content in the ZSM-5 framework and they suggested that Al incorporated into the framework protected the zeolite framework from hydrolysis. Similarly, in this study, we found that a higher content of Al incorporated into MCM-48 is advantageous for the protection of the MCM-48 framework from

hydrolysis. However, when too much Al is used in the synthesis gel (as in the case of Al-MCM-48-4 with a Si/Al of ca. 4), stability in boiling water is compromised probably due to the lower structural ordering of the parent material. It appears therefore that for the MCM-48 materials studied here, the stability in boiling water decreases in the following order Al-MCM-48-8 > Al-MCM-48-15 and Al-MCM-48-30 > Al-MCM-48-4 > Al-MCM-48-60 \gg Si-MCM-48. This order implies that there is an optimum amount of Al with respect to stability in boiling water. It is also clear that, in general, the incorporation of appropriate amounts of Al into the MCM-48 framework can enhance stability in boiling water since all the Al-containing samples studied here exhibit higher stability compared to the pure silica (Si-MCM-48) material.

The structural collapse of pure silica mesoporous materials in boiling water is due to the hydrolysis of Si-O-Si bonds. As the hydrolysis proceeds, the proportion of terminal silanol groups increases, further exposing the silica framework and accelerating its destruction. When Al is incorporated into the mesoporous materials, Si-O-Al bonds, which are more resistant to attack from water, are formed. On the other hand, the incorporation of Al via direct synthesis introduces Al buried within the pore wall, which results in the degradation of the

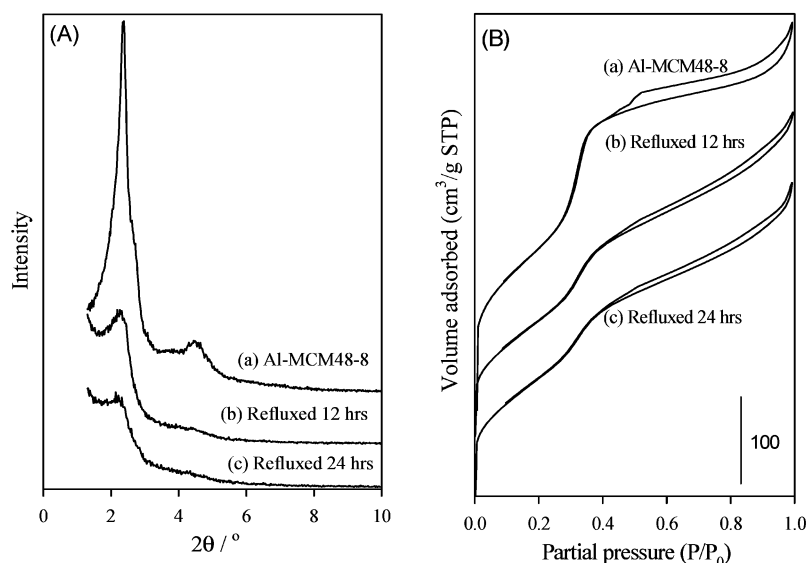


Figure 5. Powder XRD patterns (A) and nitrogen sorption isotherms (B) of Al-MCM-48-8 before and after refluxing in water for 12 or 24 h. For clarity, isotherms a and b are offset on the y-axis.

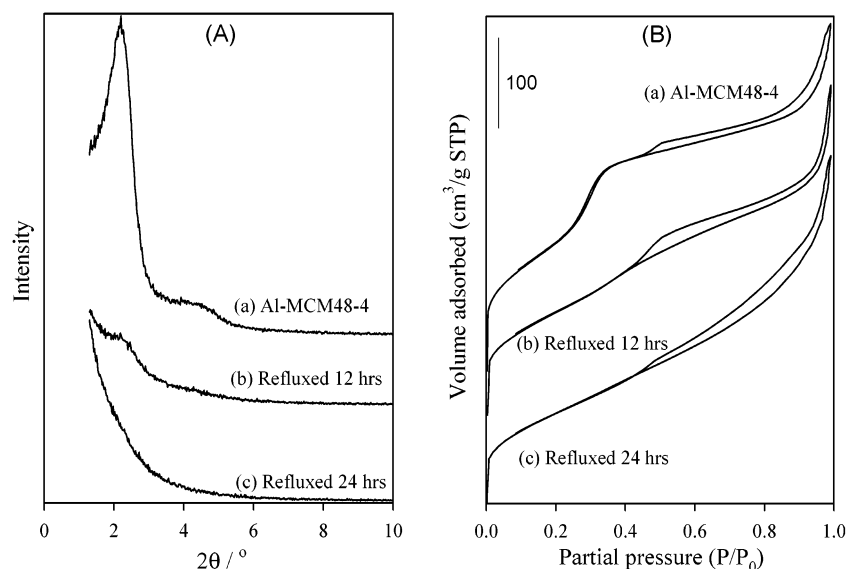


Figure 6. Powder XRD patterns (A) and nitrogen sorption isotherms (B) of Al-MCM-48-4 before and after refluxing in water for 12 or 24 h. For clarity, isotherms a and b are offset on the y-axis.

structural ordering. At high Al content, the presence of Al within the pore walls can therefore have a negative effect on (hydrothermal) stabilization of the framework.³⁴ It appears, therefore, that to improve the hydrothermal stability of Al-MCM-48 materials while at the same time maintaining good structural ordering, it is necessary to carefully control the Al content. In this work, it was found that Al content in the Si/Al ratio range between 8 and 15 improves the hydrothermal stability without too much compromise on the structural ordering. We have previously reported that Al-MCM-41 materials prepared by postsynthesis alumination^{22,23,35–38} or direct synthesis (at low Al content),²⁸ show significant enhancement of stability in boiling water due to the presence of (framework) Al on or near the surface of the pore walls. This assumption, on the position occupied by Al, was recently confirmed by Du et al. using NMR techniques.³⁹ Therefore, it is reasonable to assume that when optimal amounts of Al (for example Si/Al = 8–15) are incorporated into MCM-48 by direct synthesis, some of the Al is predominantly located on or near the surface and that at higher Al content (Si/Al \leq 4) the Al occupies positions within the

pore walls⁴⁰ and thus compromises both the structural ordering and stability.

Table 1 shows the changes in the elemental composition (Si/Al) of the Al-MCM-48 materials as a result of refluxing. In all cases, refluxing results in a decrease of the Si/Al ratio of the Al-MCM-48 samples, namely refluxed samples have a higher Al content per given weight of sample than their corresponding parent materials. This implies that silica is much easier to dissolve in boiling water than alumina or silica/alumina. The trend in elemental composition after refluxing is therefore consistent with the fact that Al stabilizes the framework. The compositional changes after 12 and 24 h refluxing also suggest that the silica dissolution occurs mainly in the early stages of contact with water. It is also reasonable to interpret the compositional changes as suggesting that after initial water attack, a protective layer of aluminosilicate is formed, which then protects the mesostructure from further hydrolysis.

Steam Stability. Figure 7 shows the XRD patterns and nitrogen sorption isotherms for the pure silica Si-MCM-48 and Al-MCM-48 materials after steaming at 800 °C for 4 h. Table

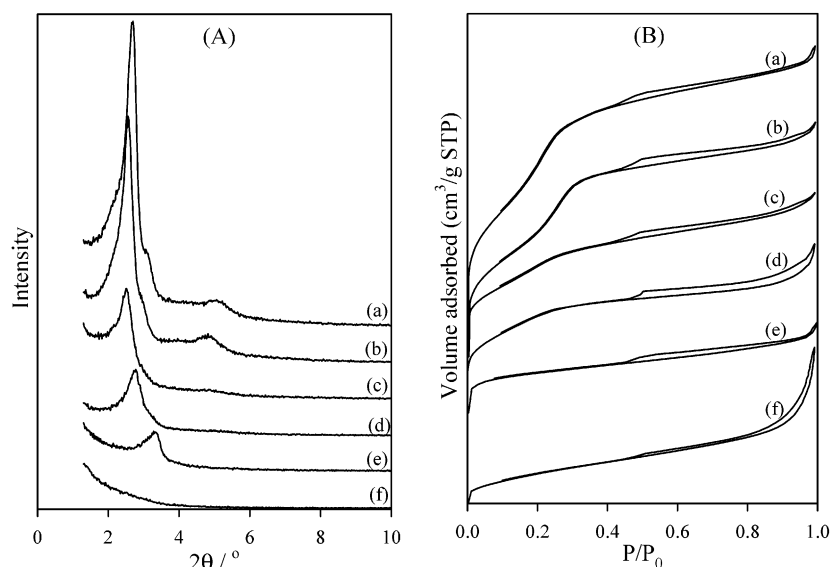


Figure 7. Powder XRD patterns (A) and nitrogen sorption isotherms (B) of Si–MCM-48 (e) and Al–MCM-48 materials after steaming at 800 °C for 4 h. The synthesis gel Si/Al ratios for the Al–MCM-48 materials are (a) 60, (b) 30, (c) 15, (d) 8, and (f) 4. For clarity, isotherms a–e are offset on the y-axis.

TABLE 2: Elemental Composition and Textural Properties of Si-MCM-48 and Al-MCM-48 Materials before and after Steaming at 800 °C for 4 Hours

sample	Si/Al	d_{211} spacing (Å)	lattice parameter a_0 (Å) ^a	surface area (m ² /g)	pore volume (cm ³ /g)
Si–MCM-48		31.0	75.9	1088	0.80
steamed at 800 °C for 4 h		26.2	64.2	204	0.18
Al–MCM-48-60	46.6	34.0	83.3	1065	0.92
steamed at 800 °C for 4 h	47.3	32.3	79.1	910	0.61
Al–MCM-48-30	24.2	34.4	84.3	963	0.83
steamed at 800 °C for 4 h	25.1	34.0	83.3	667	0.51
Al–MCM-48-15	14.9	35.6	87.2	875	0.86
steamed at 800 °C for 4 h	15.2	35.0	85.7	429	0.33
Al–MCM-48-8	8.3	37.3	91.4	696	0.68
steamed at 800 °C for 4 h	9.0	31.5	77.2	412	0.32
Al–MCM-48-4	4.5	37.3	91.4	537	0.60
steamed at 800 °C for 4 h	4.2			168	0.28

^a The lattice parameter a_0 is obtained using the formula $a_0 = d_{211}\sqrt{6}$.

2 gives the textural properties and elemental composition of the steamed materials. As expected, the elemental composition is not affected to any significant extent by the steaming. The XRD patterns and isotherms of the steamed samples given in Figure 7 should be compared with those for the parent materials shown in Figures 1 and 2. The XRD patterns of the steamed samples clearly show that the steam stability is dependent on the Al content. The pure silica sample is severely degraded after steaming at 800 °C; the XRD pattern of steamed Si–MCM-48 exhibits only a very low intensity basal (211) peak and no higher order peaks. The N₂ sorption isotherm of steamed Si–MCM-48 (see Figure 7) exhibits virtually no mesoporous character and its surface area and pore volume are reduced by ca. 80% as shown in Table 2.

The Al–MCM-48 materials are (with the exception of Al–MCM-48-4) more steam stable than the pure silica analogue. Furthermore their steam stability decreases with increasing Al content. The sample with the lowest amount of Al, Al–MCM-48-60, exhibits the highest steam stability. The XRD pattern of steamed Al–MCM-48-60 is comparable to that of the parent sample. The sorption isotherm of steamed Al–MCM-48-60 exhibits a clear mesopore filling step which is only slightly broader than that of the parent material; the surface area and pore volume of Al–MCM-48-60 are reduced by only 15 and

34%, respectively, after steaming. Sample Al–MCM-48-30 is only slightly less steam stable compared to Al–MCM-48-60. However, samples with higher Al content (Si/Al between 8 and 15) are much more degraded after the steam treatment. The XRD patterns of steamed Al–MCM-48-15 and Al–MCM-48-8 both exhibit a basal peak with very low intensity and virtually no higher order peaks. There is also very little evidence of mesoporosity in their sorption isotherms and their surface area and pore volume are reduced by 40–60%. Sample Al–MCM-48-8 also undergoes a drastic lattice contraction after refluxing. The most aluminous sample, Al–MCM-48-4, is completely destroyed by the steaming; the XRD pattern and sorption isotherm of steamed Al–MCM-48 show no evidence of mesoporosity.

The trend observed for the steam stability of Al–MCM-48 materials is similar to that previously reported for Al–MCM-41, i.e., that stability is reduced with increasing Al content.²⁸ We note that this relationship is somewhat the reverse of that observed above between Al content and stability of Al–MCM-48 in boiling water. As previously pointed out,^{26,28} the main differences between steaming and refluxing are (i) the temperature (which is much higher for steaming), and (ii) the contact time between the sample and molecular water (which is shorter for steaming).²⁶ High temperature, i.e., steaming, favors two processes: dehydroxylation (of silanol groups) and dealumination. These two processes, however, hardly occur under refluxing conditions. Furthermore, under refluxing conditions, long contact time between molecular water and the mesoporous framework accelerates hydrolysis of siloxane bonds. The slightly better steaming stability (compared to stability in boiling water) observed here for pure silica MCM-48 is probably due to two factors: (i) the short contact time with molecular water (which reduces the extent of hydrolysis), and (ii) dehydroxylation, which reverses the effects of hydrolysis. During steaming, an equilibrium between hydrolysis and dehydroxylation can be attained, thus protecting the framework from further degradation. Under refluxing conditions, such an equilibrium is not possible and hydrolysis of the pure silica framework occurs continuously. The scenario is different for Al-containing MCM-48 materials. The high temperature causes dealumination to occur which is accompanied by structural collapse especially when (at high Al

contents) the Al resides within the framework.^{28,39,40} In other words, at high Al content the framework is more permeated by Al, and therefore dealumination (removal of the aluminum) causes greater structural disruption.

It is worth noting that the MCM-48 materials in this report were synthesized using NaOH to control the pH of the synthesis gel. The use of NaOH inevitably results in the presence of Na⁺ ions in the MCM-48 material. Pinnavaia and co-workers⁴¹ recently pointed out that the presence of Na⁺ ions in the framework of MCM-41 materials plays a crucial role in limiting hydrothermal stability. They found that sodium ions entrapped within the MCM-41 framework catalyze the collapse of the mesostructure upon exposure to steam. It is therefore possible that Al-MCM-48 materials with even higher stability may be obtained via preparation routes that avoid the use of alkali metal ions. Indeed we have previously observed²⁸ that the amount of Al required to confer hydrothermal stability on Na-free Al-MCM-41 materials is much less than that required here for the Na-containing Al-MCM-48 samples. The optimum Al content for stabilizing Na-free Al-MCM-41 was as low as 0.4 mmol/g²⁸ compared to ca. 1–1.7 mmol/g observed here for Na-containing Al-MCM-48. It is also possible that MCM-48 frameworks are inherently less stable in boiling water compared to MCM-41. This would be an interesting supposition given that Si-MCM-48 has been reported as being more steam stable than Si-MCM-41 due to its more hydrophobic character.²² Our results on the steam stability of MCM-48 materials tend to agree with this previous report.²² Indeed, we may speculate that the very poor steam and boiling-water stability of the very high Al content Al-MCM-48-4 sample is in part due to a highly hydrophilic character. Al is known to increase the hydrophilicity of mesoporous silicas.

Conclusions

In summary, a series of Al-MCM-48 materials were synthesized via direct synthesis and the relationship between the Al content and hydrothermal stability (in boiling water and under steaming conditions) was demonstrated. The incorporation of Al into the framework of MCM-48 materials results in the reduction of long-range structural ordering which is, in general, accompanied by improvement in hydrothermal stability. The improvement in boiling water stability depends, to some extent, on the Al content and is optimum for materials with Si/Al ratio in the range 8–15. On the other hand, steam stability is optimized at much lower Al contents (Si/Al = ca. 50). Any increase in Al content generally reduces the steam stability to the extent that materials with high Al content (Si/Al = 4) are even less stable than pure silica MCM-48. The role of Al in determining hydrothermal stability is related to the position it occupies within the Al-MCM-48 framework and its fate (e.g., dealumination) during hydrothermal treatment. The findings of this study show that, by careful choice of the Al content, it is possible to prepare Al-MCM-48 materials with good structural ordering and hydrothermal stability.

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Supporting Information Available: Figures showing powder XRD patterns and nitrogen sorption isotherms of samples

Al-MCM-48-15 and Al-MCM-48-30, before and after refluxing in water for 12 or 24 hours. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (3) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 56.
- (4) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.
- (5) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*, 321.
- (6) Baltes, M.; Cassiers, K.; Van Der Voort, P.; Weckhuysen, B. M.; Schoonheydt, R. A.; Vansant, E. F. *J. Catal.* **2001**, *197*, 160.
- (7) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.
- (8) Gallis, K. W.; Landry, C. C. *Chem. Mater.* **1997**, *9*, 2035.
- (9) Corma, A.; Kan, Q. B.; Rey, F. *Chem. Commun.* **1998**, 579.
- (10) Xu, J.; Luan, Z.; He, H.; Zhou, W.; Kevan, L. *Chem. Mater.* **1998**, *10*, 3690.
- (11) Ryoo, R.; Joo, S. H.; Kim, J. M. *J. Phys. Chem. B* **1999**, *103*, 7435.
- (12) Sayari, A. *J. Am. Chem. Soc.* **2000**, *122*, 6504; Xia, Y. D.; Mokaya, R. *J. Mater. Chem.* **2003**, *13*, 657.
- (13) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.
- (14) Kawi, S.; Shen, S. C. *Mater. Lett.* **2000**, *42*, 108.
- (15) Jun, S.; Kim, J. M.; Ryoo, R.; Ahn, Y. S.; Han, M. H. *Microporous Mesoporous Mater.* **2000**, *41*, 119.
- (16) Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317.
- (17) Kim, J. M.; Jun, S.; Ryoo, R. *J. Phys. Chem. B* **1999**, *103*, 6200.
- (18) Das, D.; Tsai, C. M.; Ceng, S. *Chem. Commun.* **1999**, 473.
- (19) Mokaya, R. *J. Phys. Chem. B* **1999**, *103*, 10204.
- (20) Chen, L. Y.; Horiuchi, T.; Mori, T.; Maeda, K. *J. Phys. Chem. B* **1999**, *103*, 1216.
- (21) Koyano, K. A.; Tatsumi, T.; Tanaka, Y.; Nakata, S. *J. Phys. Chem. B* **1997**, *101*, 9436.
- (22) Van Der Voort, P.; Baltes, M.; Vansant, E. F. *J. Phys. Chem. B* **1999**, *103*, 10102; Cassiers, K.; Linssen, T.; Mathieu, M.; Benjelloun, M.; Schrijnemakers, K.; Van Der Voort, P.; Cool, P.; Vansant, E. F. *Chem. Mater.* **2002**, *14*, 2317.
- (23) Mokaya, R.; Zhou, W. Z.; Jones, W. *Chem. Commun.* **1999**, 51; Mokaya, R.; Zhou, W. Z.; Jones, W. *J. Mater. Chem.* **2000**, *10*, 1139; Mokaya, R. *Chem. Commun.* **2001**, 933; Mokaya, R. *J. Mater. Chem.* **2002**, *12*, 3027.
- (24) Mokaya, R.; Jones, W. *Chem. Commun.* **1998**, 1839; Mokaya, R. *Chem. Commun.* **2001**, 633.
- (25) Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950.
- (26) Shen, S. C.; Kawi, S. *J. Phys. Chem. B* **1999**, *103*, 8870.
- (27) Kim, J. M.; Kim, S. K.; Ryoo, R. *Chem. Commun.* **1998**, 259.
- (28) Mokaya, R. *J. Phys. Chem. B* **2000**, *104*, 8279.
- (29) Shen, S. C.; Kawi, S. *Langmuir* **2002**, *18*, 4720.
- (30) Ravikovitch, P. I.; Neimark, A. V. *Langmuir* **2000**, *16*, 2419.
- (31) Schumacher, K.; Ravikovitch, P. I.; Du Chesne, A.; Neimark, A. V.; Unger, K. K. *Langmuir* **2000**, *16*, 4648.
- (32) Tatsumi, T.; Koyano, K. A.; Tanaka, Y.; Nakata, S. *Chem. Lett.* **1997**, 469.
- (33) Sano, T.; Nakajima, Y.; Wang, Z. B.; Kawakami, Y.; Soga, K.; Iwasaki, A. *Microporous Mater.* **1997**, *12*, 71.
- (34) Luan, Z.; He, H. Y.; Zhou, W.; Cheng, C. F.; Klinowski, J. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2955.
- (35) Mokaya, R. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2930.
- (36) Mokaya, R. *Adv. Mater.* **2000**, *12*, 1681.
- (37) Mokaya, R. *ChemPhysChem* **2002**, *3*, 360.
- (38) O'Neil, A. S.; Mokaya, R.; Poliakoff, M. *J. Am. Chem. Soc.* **2002**, *124*, 10636.
- (39) Du, H.; Tersikh, V. V.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 4216.
- (40) Dedecek, J.; Zilkova, N.; Cejka, J. *Microporous Mesoporous Mater.* **2001**, *44–45*, 259.
- (41) Pauly, T. R.; Petkov, V.; Liu, Y.; Billinge, S. J. L.; Pinnavaia, T. *J. Am. Chem. Soc.* **2002**, *124*, 97.