# Steam Stable Mesoporous Silica MCM-41 Stabilized by Trace Amounts of Al

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ABSTRACT: Evaluation of low and ultralow Al content (Si/Al between 50 and 412) aluminosilicate Al-MCM-41 materials synthesized via three contrasting alumination routes, namely, direct mixed-gel synthesis, post-synthesis wet grafting, and post-synthesis dry grafting, indicates that trace amounts of Al introduced via dry grafting can stabilize mesoporous silica MCM-41 to steaming at 900 °C for 4 h. It was found that trace amounts of Al (Si/Al > 400) introduced via so-called dry grafting of Al stabilize the virtually purely siliceous MCM-41 to steaming, whereas Al incorporated via other methods that involve aqueous media such as direct mixed gel synthesis or wet grafting of Al offer only limited protection at low Al content. It is particularly remarkable that a post-synthesis dry grafted Al-MCM-41 material possessing trace amounts of Al (i.e., Si/Al ratio of 412) and surface area and pore volume of 1112 m^2/g and 1.20 cm^3/g, respectively, retains 90% (998 m^2/g) of the surface area and 85% (1.03 cm^3/g) of the pore volume after exposure to steaming at 900 °C for 4 h. Under similar steam treatment conditions, the mesostructure of pure silica Si-MCM-41 is virtually destroyed and undergoes a 93% reduction in surface area (958 m^2/g to 69 m^2/g) and 88% decrease in pore volume (0.97 cm^3/g to 0.12 cm^3/g). The steam stable ultralow (i.e., trace) Al containing MCM-41 materials is found to be virtually similar to mesoporous pure silica Si-MCM-41 with hardly any detectable acidity. The improvement in steam stability arises from not only the presence of trace amounts of Al, but also from an apparent increase in the level of silica condensation that is specific to dry grafted aluminosilicate MCM-41 materials. The more highly condensed framework has fewer silanol groups and therefore is more resistant to hydrolysis under steaming conditions.

KEYWORDS: mesoporous silica MCM-41, alumination, steam stability, Al-grafted MCM-41, dry grafting, Al content, Si/Al ratio
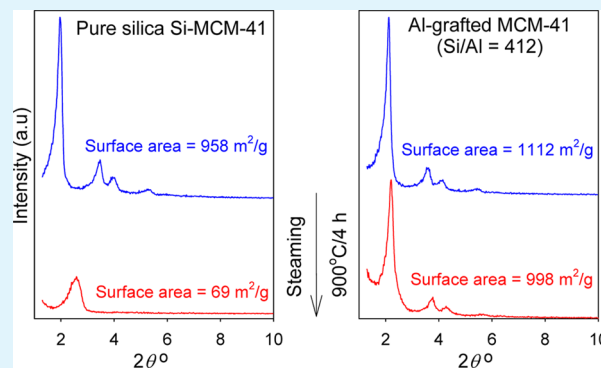
1. INTRODUCTION

Mesostructured materials such as pure silica MCM-41 possess well-ordered mesopores, which make them attractive for use in a range of applications including as sorbents, molecular separators or hosts, membranes and catalysts.[1−7] However, in general, mesostructured silicas possess thin pore walls that are amorphous, which means that they have poor hydrothermal stability compared to crystalline silicates such as zeolites.[8] The mesostructural ordering of pure silica MCM-41 is usually destroyed by thermal treatment under steaming conditions at relatively low temperature or when contacted with boiling water or hot aqueous environments for short periods of time.[8−11] The poor hydrothermal stability means that pure silica MCM-41 cannot be used in applications that require hot aqueous conditions. The hydrothermal stability of pure silica mesostructures may be improved by adopting modified preparation methods that include (i) addition of various salts to the synthesis gel prior to hydrothermal synthesis,[9−11] or (ii) increasing the hydrothermal synthesis or crystallization time and/or temperature.[12−15] The later improves hydrothermal stability by increasing the thickness of pore walls and the level of silica condensation within the mesoporous framework.[12−20] However, such stabilization methods may not be suitable for

the formation of certain forms of mesoporous silica such as films or monoliths that may require low synthesis temperatures.

It is known that aluminosilicate materials prepared via alumination routes, so-called Al-grafted, wherein Al is grafted onto pure silica MCM-41, have good stability in hot aqueous environments (e.g., boiling water) and that the choice of alumination method has little influence on such hydrothermal stability.[21−24] On the other hand, the method used to graft Al during postsynthesis alumination is an important factor in determining the steam stability of Al-grafted MCM-41.[25] Indeed, we have previously shown that Al-MCM-41 with excellent steam stability may be prepared via grafting pathways that deposit (i.e., coat) the Al onto the outermost parts (i.e., surface) of the pure silica MCM-41 sample.[25] Deposition of Al in such a manner, onto the surface, reduces the concentration of silanol groups, because they function as anchoring points for the deposited Al. The reduction of silanol groups improves hydrothermal stability as they are considered to be "weak" points with respect to hydrolysis. Furthermore, the deposited

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Al forms Si−O−Al bonds on the surface or near surface regions, which protect siloxane (Si−O−Si) bonds from steam induced hydrolysis. Moreover, any steam-induced dealumination will not significantly alter the mesostructural integrity of the MCM-41 framework because the Al is displaced from the surface rather than deep within the framework. The removal of such "surface" Al causes limited disruption to the overall integrity of the MCM-41 mesostructure.

What is not known is the lower limit of the amount of Al necessary to provide steam stability to pure silica based MCM-41 materials. Although high Al contents are interesting in generating acidity and related catalytically active sites, there is also a need for stability in MCM-41 materials that are virtually purely siliceous. To date, there is no known method of generating steam stable MCM-41 materials except via high temperature hydrothermal synthesis,[14,15] which is not amenable to the synthesis of films or monolith. In this study, we attempted to identify a lower limit of Al content in MCM-41 (i.e., tending toward purely siliceous Si-MCM-41) that may still offer steam stability, which is an interesting challenge given that pure silica MCM-41 has poor stability in steam.[26] More generally, an analysis of literature regarding stability of MCM-41 reveals that no investigation has been done on the possible lower limit of Al content at which the Al may still offer steam stability.[26−33] Our previous work suggested that for aluminosilicate mesostructures with Si/Al ratio in the range 5 − 50, a lower Al content (i.e., Si/Al ratio closer to 50) favors greater steam stability.[29,32] However, in contrast, pure Si-MCM-41 is unstable under steaming conditions. Therefore, there is a likelihood of the existence of an optimum Al content with regards to steam stability and it is reasonable to assume that it would be at low Al content (i.e., Si/Al ratio higher than 50). The aim of this investigation, therefore, was to examine the effects of very high Si/Al ratios (trace Al content) on the steam stability of mesoporous silica MCM-41. Three alumination methods were used, namely, direct mixed-gel synthesis, wet grafting, and dry grafting. The high-temperature hydrothermal stability of the generated Al-MCM-41 materials was evaluated under steaming conditions.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. Pure silica Si-MCM-41 and direct mixed-gel synthesized Al-MCM-41 were prepared according to established procedures wherein tetramethylammonium hydroxide (TMAOH) and the surfactant cetyltrimethylammonium bromide (CTAB) were simultaneously added to water and stirred at 35 °C to form the template solution. After 1 h of stirring, the silica source, fumed silica (Sigma), and where appropriate the Al source (aluminum isopropoxide) were added to the template solution to give a gel of composition; Si:xAl:0.25CTAB:0.2TMAOH:40H$_2$O. The x values used for samples in this investigation were 0 and 0.005 for the pure silica Si-MCM-41 and the Al-MCM-41, respectively. The gels were allowed to stand for 20 h under ambient temperature and then placed in Teflon lined autoclaves and heated at 150 °C for 48 h. After cooling, the solid products were recovered by filtration and thoroughly washed with copious amounts of distilled water, air-dried at room temperature and finally calcined for 8 h under static air conditions at 550 °C. The samples were designated as Si-MCM-41 (pure silica) and Al-MCM-41 (Si/Al ratio = 182).

In the post-synthesis wet grafting process, a known amount of aluminum chlorohydrate (ACH) and Si-MCM-41, which was prepared as describe above, were added to distilled water slowly under continuous stirring over a period of 2 h at room temperature. The concentration of Al in the ACH grafting solution was varied to generate aluminosilicate materials with Si/Al ratios = 50 or 150. The

grafted samples were recovered by filtration, washed with distilled water, dried at room temperature and finally calcined at 550 °C in air for 4 h to generate the wet grafted Al-MCM-41 samples designated as WGAlM1 (Si/Al = 154) and WGAlM2 (Si/Al = 50).

In the post-synthesis dry grafting pathway, known quantities of Si-MCM-41 and aluminum isopropoxide were added to dry hexane over a period of 1 h at Si/Al ratio of 100, 200, or 400. The grafting mixture was then stirred for 24 h at room temperature, following which the powder was recovered and washed with dry hexane, dried at room temperature and calcined at 550 °C for 4 h to generate three samples designated as DGAlM1 (Si/Al = 412), DGAlM2 (Si/Al = 189), and DGAlM3 (Si/Al = 92).

Stability under steaming conditions was evaluated by heating the samples in a tube furnace at 900 °C for 4 h under a flow of nitrogen saturated with water vapor at room temperature. The designation of the steamed samples is identified with an s suffix, e.g., DGAlM1s is DGAlM1 after steaming at 900 °C for 4 h.

2.2. Material Characterization. A Philips MiniPal PW4025 X-ray fluorescence (XRF) instrument and a Perkin-Elmer Optima 2000 DV ICP-OES were used to determine the Al content of the materials. For powder XRD analysis, a Philips 1830 powder diffractometer utilizing Cu Kα radiation (40 kV, 40 mA) was used. Porosity analysis to determine nitrogen sorption isotherms and textural properties was performed via conventional volumetric techniques at −196 °C using a Coulter SA3100 sorptometer or a Micromeritics ASAP 2020 sorptometer. Prior to porosity analysis, the already calcined samples were dried in an oven at 150 °C and then evacuated at 200 °C on degass port of the sorptometer. The Brunauer−Emmett−Teller (BET) method was used to calculate surface area utilizing adsorption data in the relative pressure (P/Po) range between 0.05 and 0.2. The total pore volume was calculated from the amount of the nitrogen adsorbed at relative pressure close to 1 (i.e., P/P_o = 0.99). ^{29}Si MASNMR spectra were acquired at silicon-29 frequency of 59.56 MHz. The other variables for ^{29}Si MASNMR measurements were an acquisition time of 30−50 ms, total spectral width of 30 kHz, recycle delay of 30 s, and MAS rate of 5.1 kHz. The acid content of the samples was determined using established procedures employing thermal desorption of cyclohexylamine as previously described.[22,25,34,35]

3. RESULTS AND DISCUSSION

3.1. Material Properties and Steam Stability. *Direct Mixed-Gel Synthesized Samples.* The powder XRD patterns of the pure silica (Si-MCM-41) and aluminosilicate (Al-MCM-41) samples are shown in Figure 1A. The XRD patterns show that the long-range mesostructural ordering of pure silica Si-MCM-
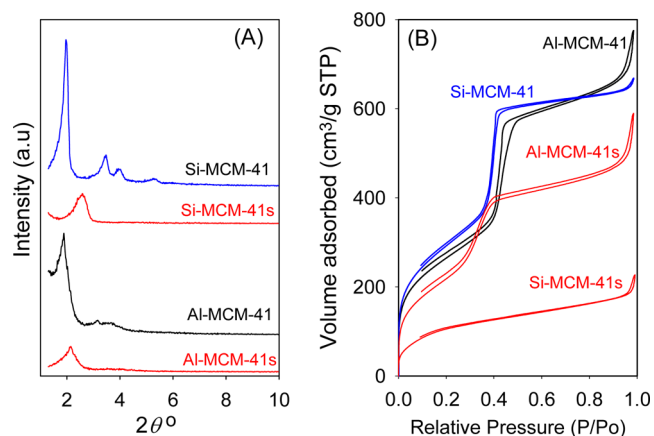
Figure 1. (A) Powder X-ray diffraction patterns and (B) nitrogen sorption isotherms of pure silica Si-MCM-41 and direct mixed-gel synthesized Al-MCM-41 before (black and blue) and after (red) steaming at 900 °C for 4 h. See Experimental Section for sample designation.

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41 is better than that of the direct mixed-gel synthesized Al-MCM-41 sample. The XRD pattern of the pure silica (Si-MCM-41) sample displays a very strong basal (d_{100}) diffraction peak and in addition also shows some well-defined higher order peaks. In contrast, the XRD pattern of the aluminosilicate Al-MCM-41 sample displays a basal diffraction peak of lower intensity and poorly discernible higher order peaks, which suggests a less well ordered mesoporous structure or a lower level of long-range mesostructural ordering. The mixed-gel synthesis occlusion of Al, therefore, disrupts the mesostructural ordering of the Al-MCM-41.[4,27−30,33−35] As summarized in Table 1, sample Si-MCM-41 has a lower basal spacing of 42.1 Å

Table 1. Elemental Composition, Textural Properties, and Acidity of Various Pure Silica and Aluminosilicate Mesoporous MCM-41 Materials before and after Steaming at 900°C for 4 h[a]

sample	Si/Al ratio	basal spacing (Å)	surface area (m²/g)	pore volume (cm³/g)	acidity (mmol H⁺/g)
Si-MCM-41		42.1	958	0.97	
Si-MCM-41s		36.4	69	0.12	
Al-MCM-41	182	46.7	964	1.20	0.08
Al-MCM-41s		41.1	808	1.01	0.04
WGAlM1	154	41.5	855	0.82	0.13
WGAlM1s		33.8	59		0.09	0.03
WGAlM2	50	41.1	876	0.87	0.28
WGAlM2s		35.8	406	0.31	0.11
DGAlM1	412	42.5	1112	1.20	nil
DGAlM1s		40.3	998	1.03	nil
DGAlM2	189	42.5	894	0.92	0.09
DGAlM2s		39.2	826	0.77	0.07
DGAlM3	92	41.5	991	0.98	0.17
DGAlM3s		40.2	840	0.73	0.14

[a]Steamed samples are suffixed with an s. A nil entry for acidity means no acidity was detected.

compared to 46.7 Å for the Al-MCM-41 sample. The difference may be attributed to creation of longer Si−O−Al bonds (compared to Si−O−Si) in the aluminosilicate sample.[27−30,33−35] As shown in Figure 1B, the nitrogen sorption isotherms of Si-MCM-41 and Al-MCM-41 are comparable in shape and display a clear mesopore filling step in the relative pressure (P/P_o) range of 0.3 − 0.5. The mesopore filling step of Si-MCM-41 is, however, steeper than that of Al-MCM-41, indicating sharper pore size distribution. Unlike the pure silica Si-MCM-41 sample, the isotherm of sample Al-MCM-41 shows considerable adsorption at higher relative pressures ($P/P_o >$ 0.9), which we attribute to textural mesoporosity. As shown in Table 1, the direct mixed-gel synthesized samples have similar surface area of ca. 960 m²/g. However, Al-MCM-41 has a slightly higher pore volume (1.20 cm³/g) compared to Si-MCM-41 (0.97 cm³/g) due to the presence of textural mesoporosity in the former.

We first note that the pure silica sample (Si-MCM-41) is virtually destroyed after exposure to steam at 900 °C for 4 h. The powder XRD patterns in Figure 1A show that the mesostructural ordering of Si-MCM-41 was severely degraded after steaming; the basal peak reduced greatly in intensity, was shifted to higher 2θ values (basal spacing thus shrinks from 42.1 to 36.4 Å) and no higher order peaks are present for the

steamed (Si-MCM-41s) sample. The fact that the mesoporous structure of Si-MCM-41 was severely degraded during the steaming process is also indicated by the change in the shape of the nitrogen sorption isotherm (Figure 1B); a sharp and steep mesopore filling step observed for the isotherm of sample Si-MCM-41 is completely lost after steaming (i.e., sample Si-MCM-41s). This means that the steamed Si-MCM-41s sample no longer contains ordered mesopores, they having collapsed under steam hydrolysis. Indeed, the surface area of Si-MCM-41s was reduced to only 7% (i.e., 69 m²/g) of its original value of 958 m²/g for Si-MCM-41. The steaming induced decrease in surface area by 93% was accompanied by an 88% reduction in the total pore volume from 0.97 to 0.12 cm³/g. The drastic decrease in both surface area and pore volume indicate a near complete disintegration of the ordered structure of the pure silica Si-MCM-41 sample during the steaming process.

Figure 1 indicates that although the direct mixed-gel synthesized Al-MCM-41 sample (Si/Al ratio = 182) is more steam stable that Si-MCM-41, it is still significantly degraded. The XRD pattern of the steamed (Al-MCM-41s) sample has a basal peak with much reduced intensity and there are no higher order peaks, indicating severe diminution of mesostructural ordering. The basal spacing shrinks from 46.7 to 41.1 Å after steaming. Furthermore, the mesopore filling step of the steamed (Al-MCM-41s) sample is much reduced, and the nitrogen sorption isotherm shows a lower total adsorption at $P/P_o \sim 1$. Textural data in Table 1 show that both the surface area and pore volume of Al-MCM-41 reduce by ca. 16% after steaming. Thus although the Al-MCM-41 sample, with Si/Al ratio of 182, is more steam stable that the pure silica Si-MCM-41, it clearly is not overall steam stable, and exhibits steam stability lower than that of previously reported more aluminous samples with Si/Al ratio of between 30 and 50.[29,30] Therefore, the Al-MCM-41 with Si/Al ratio of 182, appears to have too low an Al content with respect to steam stability and is thus already beyond the optimally low Al content for providing steam stable samples. Indeed, an aluminosilicate MCM-41 sample prepared via direct mixed-gel synthesis at a nominal gel Si/Al ratio of 400 had steam stability similar to that of pure silica Si-MCM-41. Given that our aim was an attempt to reach much lower (i.e., trace) Al content while retaining steam stability, the observations for sample Al-MCM-41s meant that we did not extensively investigate or report on samples with lower Al content than Si/Al = 182. This, therefore, also indicates that it is unlikely to obtain steam stable ultralow Al content MCM-41 samples via the direct-mixed gel synthesis route.

Postsynthesis Wet Grafted Samples. Powder XRD patterns of the wet grafted aluminosilicate samples (Figure 2A) suggest that the structural integrity of the Si-MCM-41 sample was hardly affected by the wet grafting process. The two wet grafted samples (with Si/Al = 50 and 154) have very similar XRD patterns (Figure 2A) that are comparable to that of the pure silica Si-MCM-41 (cf Figure 1A), except for a small decrease in the intensity of higher order peaks, denoting a slight decrease in long-range mesostructural ordering. The basal (d_{100}) diffraction peaks of the wet grafted samples are slightly shifted to higher 2θ values due to a small decrease in the basal spacing from 42.1 Å for Si-MCM-41 to 41.5 Å and 41.1 Å for WGAlM1 (Si/Al = 154) and WGAlM2 (Si/Al = 50), respectively. The nitrogen sorption isotherms of the wet grafted samples (Figure 2B) confirm their high mesostructural ordering; both samples exhibit a steep mesopore filling step that is consistent with a

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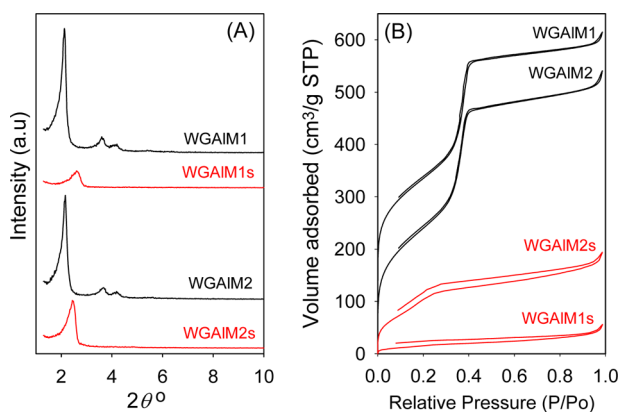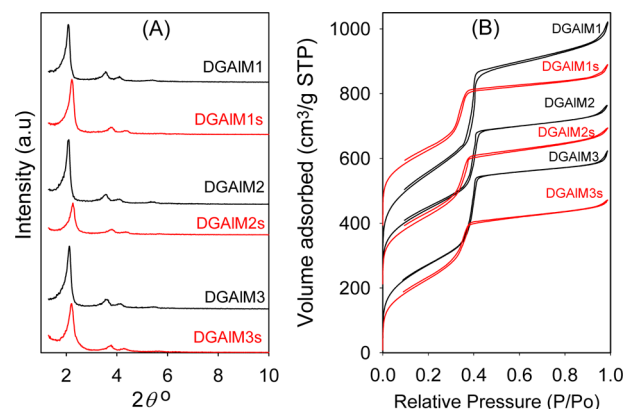
Figure 2. (A) Powder X-ray diffraction patterns and (B) nitrogen sorption isotherms of wet grafted Al-MCM-41 samples of varying Al content before (black) and after (red) steaming at 900 °C for 4 h. See experimental section for sample designation. For clarity, the isotherm of sample WGAlM1 is offset (y-axis) by 100.

narrow pore size distribution. The wet grafted samples have surface area of ca. 860 m^2/g and pore volume of ca. 0.85 cm^3/g, i.e., ca. 90% of the corresponding values for the pure silica Si-MCM-41 sample. The slight decrease in textural parameters is due to uptake of Al, and thus the Al content, already low (i.e., Si/Al ratio of 50 and 154), exerts no significant effect on the textural properties.

Previous work has shown that wet grafted Al-MCM-41 samples with Si/Al ratio of ca. 40 exhibit high steam stability,[25] and can retain a high proportion of surface area and ca. 70% of pore volume after steam treatment at 900 °C for 4 h. This study, therefore, investigated wet grafted Al-MCM-41 with lower Al content; Si/Al ratio of 50 (WGAlM2) and 154 (WGAlM1). The XRD patterns in Figure 2A indicate that the lower Al content sample (WGAlM1) undergoes greater structural degradation after steam treatment. The XRD patterns of both steamed wet grafted samples exhibit only a low intensity basal peak but the reduction in the intensity of the basal peak is much greater for WGAlM1 and the basal spacing shrinks by 19% compared to 13% for WGAlM2 (Table 1). The nitrogen sorption isotherms in Figure 2B indicate that steaming of WGAlM1 causes a total loss of mesoporosity, whereas for WGAlM2, some limited porosity is retained. As shown in Table 1, the surface area and pore volume of WGAlM1 reduce by 93 and 90%, respectively, whereas for WGAlM2 the reductions are 54 and 65%, respectively. The steam induced loss of structural ordering and textural parameters in WGAlM1 are similar to that of the pure silica Si-MCM-41 sample (Figure 1). Wet grafting allows Al species to penetrate into the silica walls and to be located in the interior of the Si-MCM-41 framework. In such a scenario, steaming induced dealumination removes Al from within the pore walls, disrupts the pore wall network and compromises the structural integrity of the MCM-41. Furthermore, such disruption allows increased structural degradation to occur as water molecules attack the interior of the pore walls. Our textural and XRD data suggest that the steam stability of wet grafted Al-MCM-41 greatly reduces at lower Al content, and that at a Si/Al = 154, steam stability is comparable to that of the pure silica Si-MCM-41 sample. These findings indicate that, despite the high steam stability of higher Al content wet grafted Al-MCM-41 materials,[25] it is not possible to obtain steam-stable ultralow Al content MCM-41 samples via the wet grafting alumination route.

Postsynthesis Dry Grafted Samples. Three samples were synthesized via dry grafting at Si/Al ratio of 412 (DGAlM1), 189 (DGAlM2), and 92 (DGAlM3). As shown by the powder XRD patterns in Figure 3A, the dry grafting process did not

Figure 3. (A) Powder X-ray diffraction patterns and (B) nitrogen sorption isotherms of dry grafted Al-MCM-41 samples of varying Al content before (black) and after (red) steaming at 900 °C for 4 h. See Experimental Section for sample designation. For clarity, isotherms are offset (y-axis) by 200 for DGAlM2 and DGAlM2s, and by 250 for DGAlM1 and DGAlM1s.

cause any structural degradation to the parent Si-MCM-41 sample; the XRD patterns of the dry grafted DGAlMx samples are very similar to that of the pure silica Si-MCM-41 (cf Figure 1A and Figure 3A). Furthermore, dry grafting does not cause any change in the basal (d$_{100}$) spacing as shown in Table 1. The nitrogen sorption isotherms of the dry grafted samples (Figure 3B) are of similar shape to that of Si-MCM-41 (Figure 1B), again attesting to the retention of mesostructural ordering after dry grafting. As shown in Table 1, the surface area and pore volume of the dry grafted samples with Si/Al ratio of 92 (DGAlM3) and 189 (DGAlM2) is similar to that of the starting Si-MCM-41. However, the dry grafted sample with Si/Al ratio of 412 (DGAlM1), has higher surface area and pore volume of 1112 m^2/g and 1.20 cm^3/g, respectively.

It is known that dry grafted mesoporous aluminosilicates exhibit good steam stability.[25,26,31−33] We have previously shown that steamed (at 900 °C for 4 h) dry grafted Al-MCM-41 with Si/Al ratio of 10 retains 68 and 78% of surface area and pore volume, respectively, and that at Si/Al ratio of 40, the retention is 90 and 93%, respectively.[25] This previous findings gave an early indication that low Al content dry grafted samples are more steam stable. In this work, we investigated samples with much lower Al content, i.e., up to Si/Al ratio >400. The XRD patterns in Figure 3A indicate that all three dry grafted samples retain their structural ordering after steaming. The patterns of all the dry grafted samples are unchanged after steaming and are indeed similar to that of the starting Si-MCM-41 sample (Figure 1A) and exhibit a high intensity basal peak and several higher-order peaks. The only apparent change indicated by the XRD patterns after steaming is a slight shift of basal peak to higher 2θ values because of minor basal spacing shrinkage of 5, 8, and 3% for DGAlM1 (Si/Al = 412), DGAlM2 (Si/Al = 189), and DGAlM3 (Si/Al = 92), respectively. The shrinkage is lower than the 10% previously reported for a sample with Si/Al ratio of 40,[25] which is an indication that the present dry grafted samples are highly steam stable despite their very low Al content. The high steam stability of the dry grafted

samples is confirmed by the nitrogen sorption isotherms in Figure 3B, which are similar to those before steaming except for a slight shift of the mesopore filling step to lower relative pressure (P/P_o). Such a contraction may simply be ascribed to normal contraction due to exposure to thermal treatment at 900 °C. Indeed, samples calcined at 900 °C in air have nitrogen sorption isotherms similar to those of the steamed samples in Figure 3B. The steamed dry grafted samples retain ca. 90% of surface area and between 75 and 85% of pore volume (Table 1). It is particularly remarkable that the dry grafted sample (DGAlM1) with a Si/Al ratio of 412, which is an ultralow or trace amount of Al, retains 90% of surface area and 85% of pore volume.

The excellent steam stability displayed by sample DGAlM1, which contains trace amounts of Al is surprising. We note that sample DGAlM1 exhibited virtually no acidity, as shown in Table 1, and exhibited ^{27}Al MAS NMR spectra comparable to that of pure silica Si-MCM-41. The Al content was therefore too low to investigate using ^{27}Al MAS NMR. Indeed, the Si/Al ratio of 412 for sample DGAlM1 is higher than that of commercially available Silicalite, which despite possessing Si/Al ratio of ≥200 is considered to be purely siliceous.[36] We confirmed that a Si-MCM-41 sample treated with hexane in the absence of Al and then calcined showed no improvement in steam stability. The improvement in the stability of the dry grafted Al-MCM-41 sample is therefore due to the incorporation of trace amounts of Al and not simply treatment in hexane. The presence of Al is known to engender stability under steam and hot aqueous conditions in aluminosilicate MCM-41 materials and related mesoporous silicates.[37−52] However, given that sample DGAlM1 has only trace amounts of Al, there may be other factors contributing to the excellent steam stability.

Another factor that is known to contribute to steam stability is the extent of silica condensation, and/or the absence of silanol groups. Silanol groups are considered to be weak points with respect to hydrolysis during steaming. The grafting of Al is expected to reduce the silanol concentration as existing OH groups are the anchoring points, especially under nonaqueous (i.e., dry) grafting conditions where no more OH groups are generated. Thus, to further explore the nature of the silicate framework in the aluminated samples, we performed Si MASNMR of the parent pure silica Si-MCM-41, hexane-treated MCM-41, wet grafted (WGAlM1) and dry grafted (DGAlM1) samples. The ^{29}MAS NMR spectra, shown in Figure 4, in all cases exhibit three resonances at ca. −90 ppm (Q^2), −100 ppm (Q^3), and −110 ppm (Q^4). The resonances are due to silicon in $Si(OSi)_2(OH)_2$ (Q^2), $Si(OSi)_3OH$ (Q^3), or $Si(OSi)_4$ (Q^4) environments.[53] It is also worth noting that the presence of Al can generate a chemical environment [Si(3Si, 1Al)], which may contribute to the resonance at 100 ppm.[54] A comparison of the relative intensity of the resonances suggests that a vast majority of the Si is in Q^3 and Q^4 sites as might be expected for calcined samples. A high proportion of Q^4 sites along with low content of Q^2 and Q^3 sites is expected to favor high steam stability. Following deconvolution of the spectra, we calculated the $Q^4/(Q^3+Q^2)$ ratio and therefore estimated the extent of silica condensation in the samples; a higher $Q^4/(Q^3+Q^2)$ ratio indicates a more highly condensed silica framework. The calculated $Q^4/(Q^3+Q^2)$ ratios are 1.30 for the pure silica Si-MCM-41, 1.32 for the pure silica Si-MCM-41 treated in hexane and then calcined, 1.45 for the wet grafted WGAlM1 sample and 2.20 for the dry grafted DGAlM1 sample.
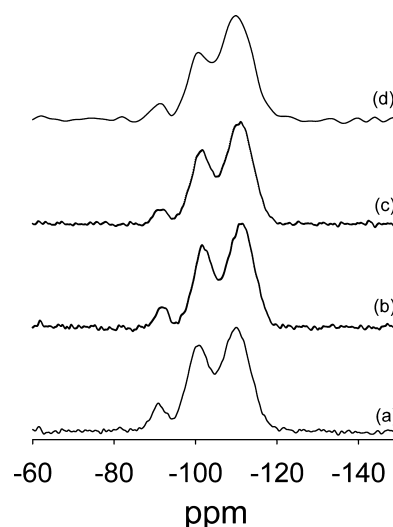
Figure 4. ^{29}Si MAS NMR spectra of various calcined MCM-41 samples: (a) pure silica MCM-41, (b) hexane treated pure silica MCM-41, (c) wet grafted WGAlM1, and (d) dry-grafted DGAlM1.

Thus, according to the amount of Q^2 and Q^3 sites, hexane treatment on its own has no effect on the concentration of OH groups and level of silica condensation. Wet grafting slightly reduces the concentration of OH groups, while dry grafting significantly reduces the proportion of OH groups. Thus the dry grafted DGAlM1 sample appears to have a higher proportion of fully connected Q^4 Si sites, which, along with the presence of Al, act to enhance steam stability. We note that this apparent change in level of silica condensation is only observed in the presence of Al; hexane alone has no effect as shown in Figure 4 where the $Q^4/(Q^3+Q^2)$ ratio of Si-MCM-41 remains unchanged before and after treatment in hexane. We propose, therefore, that the presence of trace amounts of Al anchored onto the surface of the MCM-41 silica walls, act as fortification points, via the formation of stable ≡Si−O−Al≡ bonds, and together with the higher level of silica condensation generate the high steam stability. This outcome is only possible if the alumination is performed under nonaqueous (dry) conditions where no further OH groups can be generated during the Al grafting process.

Our findings offer the opportunity of using trace amounts of Al to generate stabilized MCM-41 materials that are virtually similar to pure silica Si-MCM-41. Our data show that the trace amounts of Al act to protect the mesoporous MCM-41 structure from degradation during the steaming process. There are two main processes that occur during steaming, namely, (i) hydrolysis of siloxane bonds and dehydroxylation of silanol groups, and (ii) dealumination. Dehydroxylation and hydrolysis are opposing processes; the former acts to maintain the structural integrity of MCM-41, the later leads to structural degradation. It is likely that trace amounts of Al reduce the extent of hydrolysis and provide 'fortified' points in the MCM-41 framework, which in combination with the benefits of dehydroxylation and the fact that any dealumination will not affect the structural ordering may be the basis of the excellent steam stability at trace amounts of Al such as for sample DGAlM1.

3.2. Discussion. First, we note that a number of clear trends emerge from the structural analysis of the various aluminosilicate MCM-41 samples. The direct mixed-gel synthesis method causes significant decrease in mesostructural

ordering and generates textural porosity leading to an increase in the total pore volume. The wet grafted samples retain a high proportion of their structural ordering after the grafting process, but the Al incorporated on the pore walls causes the pore space to shrink leading to a decrease in total pore volume and surface area. The quantity of Al introduced during wet grafting does not appear to affect the structure of the resulting Al-grafted MCM-41 materials. On the other hand, the structural ordering of dry grafted samples is virtually unchanged after the grafting process.

Second, the steam stability test experiments show that the mode of Al incorporation greatly affects the steam stability of the aluminosilicate MCM-41 samples. The pure silica Si-MCM-41 sample is highly susceptible to structural degradation during the steaming process and is virtually destroyed under our steam test regime. The incorporation of Al via the direct mixed-gel and wet grafting methods offers only limited steam stability. It is known that the aqueous nature of these two alumination processes allows Al to penetrate into the interior of the pore walls and that when dealumination occurs during steaming, the removal of the "internal" Al causes structural disruption and degradation. Thus the protection against hydrolysis, offered by the formation of strong Si−O−Al bonds is overshadowed by the destructive dealumination process. The considerable stability of the directly synthesized Al-MCM-41 sample with Si/Al ratio of 182 was rather unexpected. As the Al was added when the MCM-41 structure is formed, it is expected that some Al would be located deep within the pore walls of the MCM-41 structure, while some will be sited nearer the pore surface. It is likely that at low Al content (Si/Al = 182) the surface/near surface Al contributes to some steam stability which is counterbalanced by dealumination of any Al sited deeper in the pore walls resulting in moderate overall steam stability. The dry grafted samples, on the other hand, display highly impressive steam stability. This is ascribed to the fact that the trace Al atoms are positioned on, rather than in, the pore walls of the sample, due to their inability to efficiently penetrate the pore walls during the dry (in the absence of water) grafting process. Furthermore, according to the ^{29}Si MAS NMR data, the dry grafting process generates an MCM-41 framework with a higher level of silica condensation, which also contributes to the steam stability.

4. CONCLUSION

Mesoporous pure silica Si-MCM-41 may be rendered steam stable by the incorporation of low to ultralow (i.e., trace) amounts of Al. At such low Al content the MCM-41 has hardly any detectable acidity and is virtually similar to pure silica Si-MCM-41. Evaluation of low and ultralow Al content (Si/Al between 50 and 412) Al-MCM-41 materials prepared via three alumination routes (direct mixed gel synthesis, post synthesis wet grafting and post synthesis dry grafting) indicates that trace amounts of Al introduced via dry grafting stabilize the mesoporous silica MCM-41 to steaming at 900 °C for 4 h. It is particularly remarkable that a dry grafted sample with a Si/Al ratio of 412 and surface area and pore volume of 1112 m^2/g and 1.20 cm^3/g, respectively, retains 90% (998 m^2/g) of surface area and 85% (1.03 cm^3/g) of pore volume after steaming at 900 °C for 4 h. Trace amounts of Al (Si/Al > 400) introduced via postsynthesis dry grafting of Al stabilize the virtually purely siliceous MCM-41 to steaming, whereas Al incorporated via direct mixed gel synthesis offers only limited protection and wet grafting of Al offers little protection at low Al content.

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Notes
The authors declare no competing financial interest.

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