# Supercritical Fluid-Mediated Alumination of Mesoporous Silica and Its Beneficial Effect on Hydrothermal Stability

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Mesoporous materials developed over the past decade have expanded the range of structurally well-ordered porous catalysts beyond microporous zeolites and into the mesopore range.[1−3] Mesoporous aluminosilicates are in particular attracting considerable research interest as solid acid catalysts.[1−3] A key requirement for the successful use of mesoporous aluminosilicates as solid acids or ion exchangers is good hydrothermal stability.[2,3] Significant progress has been achieved recently in synthesizing materials with improved hydrothermal stability either by the use of preformed zeolite seeds as framework units[4−6] or via postsynthesis alumination of pure silica materials.[7,8]

Mesoporous aluminosilicates prepared via postsynthesis alumination offer advantages over *similar* but directly synthesized materials with respect to accessibility to active (Al) sites and structural ordering.[1,9−11] However, despite the obvious advantages of postsynthesis alumination (grafting), there still remains the challenge of obtaining Al-grafted materials with a well-dispersed (uniform) distribution of Al within the host silica. This arises due to the fact that during grafting the Al is first in contact with the outer surface of the host silica material before being transported (or penetrating) into the internal pore channel system (or bulk). Distribution of the Al into the internal pore channels may also be hindered by the rather long (compared to those in zeolites), and in some cases (MCM-41, SBA-15) one-dimensional, pore channels in mesoporous silicas. Here we investigate the use of supercritical fluids (SCFs) as carriers/solvents for postsynthesis alumination of mesoporous silica. The low viscosity and high diffusivity inherent to SCFs[12,13] are ideally suited for rapid transport of Al into mesoporous silica and should achieve better Al dispersion. Another motivation for carrying out alumination under supercritical fluid conditions is that a better dispersion (and surface coverage) of Al should result in improved hydrothermal stability.[7−11,14] We present results demonstrating that the use of SCFs (as compared to aqueous or organic solvents) leads to Al-grafted MCM-41 materials that exhibit exceptional hydrothermal (steam) stability even for relatively highly aluminated materials.

The Al-grafted materials were prepared via the reaction of pure silica MCM-41 with aluminum isopropoxide in SCF. The required amounts of calcined mesoporous silica and aluminum isopropoxide (to give Si/Al = 10) were placed in a 60-mL magnetically stirred, high-pressure autoclave, and while vigorous stirring continued, the temperature was raised to the required value (40 °C for $CO_2$ or 110 °C for propane) before pressurization with the appropriate fluid (150 bar). Vigorous stirring was continued for 19 h, after which the autoclave was depressurized slowly over 15 min. The autoclave was allowed to cool to room temperature and the (dry) sample recovered. The samples were then calcined at 600 °C for 4 h to
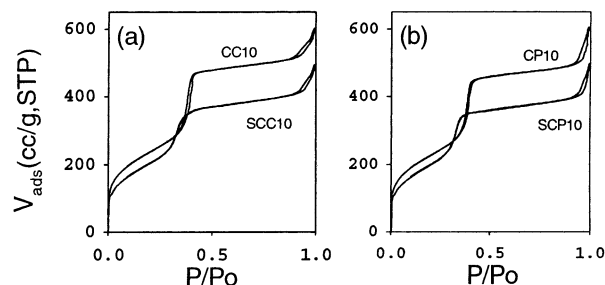
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**Figure 1.** Nitrogen sorption isotherms for Al-grafted MCM-41 materials grafted (at a Si/Al ratio of 10) in (a) supercritical $CO_2$ and (b) supercritical propane before (top) and after (bottom) steaming at 900 °C for 4 h.

***Table 1.*** Textural Properties of Al-Grafted Materials before and after Steaming

| sample | $d_{100}$ (Å) | $S_{BET}$ (m²/g) | pore vol (cc/g) |
|--------|--------------|------------------|-----------------|
| CC10   | 39.8         | 864              | 0.91            |
| SCC10  | 38.7         | 744              | 0.74            |
| CP10   | 39.6         | 833              | 0.92            |
| SCP10  | 39.4         | 729              | 0.73            |
| P10    | 42.0         | 846              | 0.88            |
| SP10   | 36.6         | 643              | 0.51            |

obtain the Al-grafted materials. The sample grafted in supercritical $CO_2$ was designated CC10, while that grafted in supercritical propane was designated CP10. $^{27}$Al MAS NMR indicated that ca. 40% of the Al in the dry samples was tetrahedrally coordinated, increasing to at least 60% after calcination.[10] The acid content of the samples (ca. 0.75 mmol $H^+$/g) was consistent with the proportion of tetrahedrally coordinated Al.[8,10] The steam stability of the Al-grafted samples was tested by calcination at 900 °C for 4 h in a flow of nitrogen saturated with water vapor at room temperature. The steamed samples were designated SCC10 and SCP10.

Figure 1 shows the nitrogen sorption isotherms of samples CC10 and CP10 before and after steaming at 900 °C. The materials exhibit very high steam stability; the isotherms of both the parent and steamed samples exhibit a sharp mesopore-filling step characteristic of well-ordered MCM-41 materials. Both samples retain 80−85% of their surface area and pore volume after steaming (Table 1). Figure 2 shows the powder X-ray diffraction (XRD) patterns of CC10 and CP10 before and after steaming. The XRD patterns of the steamed samples, SCC10 and SCP10, are broadly similar to those of the parent materials, indicating excellent retention of structural ordering. Furthermore, the basal spacing of CC10 and CP10 hardly changes after steaming (see Table 1). The steamed samples suffered some dealumination but still retained at least 80% of their acid content. Such high steam stability has not been previously observed for Al-grafted or other Al-MCM-41 materials with a Si/Al ratio as low as 10.[8]
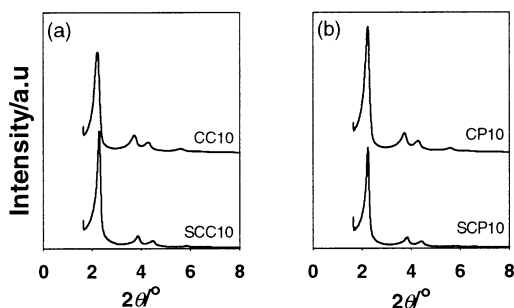
**Figure 2.** X-ray diffraction patterns of Al-grafted MCM-41 materials grafted (at a Si/Al ratio of 10) in (a) supercritical $CO_2$ and (b) supercritical propane before (top) and after (bottom) steaming at 900 °C for 4 h.
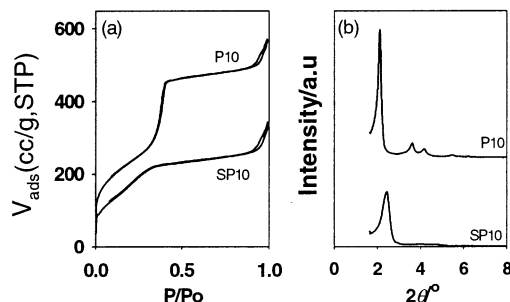


**Figure 3.** Nitrogen sorption isotherms (a) and X-ray diffraction patterns (b) of Al-grafted MCM-41 grafted in liquid propane (at a Si/Al ratio of 10) before (top) and after (bottom) steaming at 900 °C for 4 h.

Al-grafted MCM-41 materials prepared via so-called "dry" grafting (i.e., pure silica MCM-41 grafted using aluminum isopropoxide in hexane) are known to exhibit considerable steam stability especially at low Al content (Si/Al·40).[8] The hydrothermal stability of such materials, however, is reduced at higher Al content.[8] In the present study we also prepared an Al-grafted material (designated P10) using the same experimental setup but with liquefied propane instead of supercritical propane as the solvent. This enabled us to establish whether the resulting material would exhibit behavior closer to that of dry (hexane) or supercritically grafted materials. Figure 3 shows the nitrogen sorption isotherms and XRD patterns of sample P10 before and after steaming at 900 °C which indicate that P10 is considerably degraded after the hydrothermal treatment. The nitrogen sorption isotherm of the steamed sample, SP10, has a much-reduced mesopore-filling step, and the XRD pattern exhibits a basal (100) peak with much lower intensity. This behavior is similar to that previously observed[8] for Al-grafted MCM-41 materials, dry-grafted in hexane at a Si/Al ratio of ca. 10. Sample P10 retains 76% of its original surface area and 58% of the pore volume after steaming (Table 1). Interestingly the corresponding values for the hexane-grafted sample[8] are almost the same: 78 and 53% for retained surface area and pore volume, respectively.

Treatment of pure silica MCM-41 in SCFs as described above but in the absence of Al has no effect on hydrothermal stability, that is, SCF-treatment on its own does not improve hydrothermal stability. We therefore ascribe the high steam stability observed for supercritically grafted samples to either or both of two reasons; (1) better dispersion of Al and (2) the way in which the Al interacts

with the host silica. The better dispersion of Al achieved under SCF conditions can be expected to coat efficiently the surface of the host Si-MCM-41 with an *aluminosilicate layer*. This reduces the number of free silanol groups (anchoring sites for the Al) and protects siloxane (Si−O−Si) bonds from hydrolysis.[14] Furthermore, under SCF conditions, it is likely that the Al is sorbed on the surface of the pore walls with little penetration into the pore wall region. We have previously shown that the extent to which Al is sorbed *onto* rather than *into* the pore wall region is an important factor in determining hydrothermal stability.[8] Hydrothermally stable Al-grafted materials are best prepared via alumination pathways that *efficiently* graft Al onto the pore wall surfaces without introducing Al deep into the pore wall region. It is likely that in the present case, the low solvating power of SCFs ensures the deposition of Al *onto* rather than *into* the silica framework. This is because the host silica framework cannot undergo any significant hydrolysis during the SCF mediated alumination. This differs from alumination in liquid (especially aqueous) media where the Al may penetrate the pore walls (due to hydrolysis of the silica framework) and occupy both surface and near-surface sites. Indeed Al-grafted materials prepared in aqueous media tend to exhibit low steam stability.[4,8] In contrast, as shown here, dealumination which occurs during steaming is less detrimental to the structural integrity of supercritically grafted samples since it does not involve the removal of Al from deep within the pore walls. On a more general note, this work shows that SCFs may be used for efficient transport of any reagents into mesoporous materials.

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