Improvement of Both the Acidity and Stability of MCM-41 by Post-synthesis Alumination

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Post-synthesis alumination of MCM-41 is found to substantially enhance the material's: (1) surface acidity, by increasing its number of Lewis and Brønsted acid sites; (2) physical stability, by improving its hydrothermal stability in boiling water and in high-temperature steam; (3) mechanical stability, by minimizing the collapse of its mesopores under high pressure compression; and (4) chemical stability, by improving its resistance in high pH aqueous solution.

A novel MCM-41 material, which has a well defined array of uniform hexagonal mesopores systematically adjustable in the range of 20-100 Å, has potential applications for processing large organic molecules,[1] especially as catalysts and adsorbents.[2,3] However, purely siliceous MCM-41 shows limited application as it has poor hydrothermal stability and lacks of acidity.[4] Although it is possible to improve the acidity and hydrothermal stability of MCM-41 by incorporation of Al into its framework,[5] the substituted aluminum has been shown to be not stable, leading to a less uniform pore structure.[6] The dealumination under thermal or hydrothermal conditions may cause structural defect in the framework and blockage in the pore channels. Thus, post-synthesis modification was considered to improve the stability of MCM-41 by organic or metallorganic compounds.[7,8]

In this study, alumina is introduced onto purely siliceous MCM-41 (designated here as PSM) using post-synthesis alumination process. Post-synthesis alumination is used here as it does not cause serious structural deformation of the resulting material. Most importantly, post-synthesis alumination is found to increase both Lewis and Brønsted acidities as well as the physical, mechanical and chemical stabilities of the alumina-modified MCM-41 materials.

PSM was prepared as follows: Silicate gel was prepared by adding 6 g of silica aerosol to 92 g of 0.55N NaOH solution under stirring and heating until all aerosol was dissolved. A solution of CTMABr (prepared by dissolving 9.1 g of CTMABr in 50 g of water) was added dropwise to the silicate gel under stirring at 25 °C. The pH value of the gel mixture was adjusted to 11.5 using 2 N of HCl solution. After stirring continuously for additional 6 h at 25 °C, the gel mixture was transferred into a polypropylene bottle and statically heated at 100 °C for 72 h. The resulting solid product was recovered by filtration, washing, and drying at 50 °C for 24 h. The solids were calcined in air at 600 °C for 10 h, using a heating rate of 1 °C/min.

For post-synthesis alumination, 1.0 g of PSM was impregnated with 5 ml of $Al(NO_3)_3$ solution. The slurry was heated at 50 °C under stirring and dried at 100 °C. Finally, the sample was calcined in an airflow at 550 °C for 5 h using a heating rate of 1 °C/min. Three alumina-modified MCM-41 materials (designated as AlM1, AlM5 and AlM10) were prepared to have the alumina loading of 1, 5 and 10 wt%, respectively.

Table 1. The surface areas and pore properties of PSM and AlM samples

Sample	Surface areas m^2/g	Pore diameter (Å)	2θ [100] (degree)	Pore wall thickness (Å)
PSM	1311	29.77	2.2	16.54
AlM1	1165	27.45	2.2	18.86
AlM5	1076	27.09	2.2	19.22
AlM10	997	26.72	2.2	20.59

The X-ray diffraction patterns for all AlM samples generally consist of one large peak along with three small peaks, which are characteristic of MCM-41 materials.[1] Although the [110] diffraction peak slightly decreases with the increase of Al content, the 2θ angle of this diffraction peak for all AlM samples is quite constant (≈ 2.2°), as shown in Table 1. Nitrogen adsorption results show that pore size distributions of all AlM samples are as sharp as that of PSM, although the surface area decreases upon alumination (Table 1). The results indicate that the uniform mesopores are still preserved after modification.

Figure 1 shows the FTIR spectra characterizing the adsorption of pyridine on PSM and AlM samples; pyridine was adsorbed on the materials at 25 °C and then desorbed at 200 °C and 10^{-1} Torr of vacuum. The IR peaks characterizing pyridine adsorption on PSM and AlM1 materials were very weak. In comparison with PSM and AlM1, AlM5 and AlM10 materials have much stronger IR peaks characterizing the adsorption of pyridine on Lewis and Brønsted acid sites. The adsorption band at 1490 cm^{-1} attributed to pyridine adsorbed on both Lewis and Brønsted acid sites[9] is clearly observed. Besides this band, Brønsted acid sites have two additional bands at 1545 and 1640 cm^{-1} and Lewis acid sites have two additional bands at 1450 and 1623 cm^{-1}. These results show that post-synthesis alumination substantially improves both Brønsted and Lewis acidities of MCM-41. Using aluminium isopropoxide precursor in a non-aqueous solution, Mokaya et al.[8] found that post-grafting of Al onto MCM-41 increased its Brønsted acidity. However, using aluminum nitrate precursor in an aqueous solution, the results of

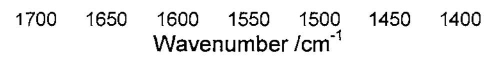

Figure 1. FTIR spectra characterizing the adsorption of pyridine on PSM and AlM samples (degassed at 200 °C).

this study show that post-synthesis alumination of PSM increases both its Brønsted and Lewis acidities.

Dehydration of isopropanol was performed on all these samples to confirm the formation of acid sites on AlM samples. Due to the lack of strong acid sites, dehydration of isopropanol on PSM was very low; conversion was < 1% at 200 °C and only 10% at 250 °C. Due to the improved acidity of AlM materials, dehydration of isopropanol on AlM samples was significantly higher than that on PSM; conversion of isopropanol on AlM1 was 91.6% at 200 °C and reached 100% at 250 °C.

Post-synthesis alumination enhances the hydrothermal stability of MCM-41 substantially. After treatment in boiling water for 10 days, N_2 adsorption-desorption isotherms of PSM become similar to that of amorphous silica, showing that PSM loses most of its mesoporous structure in boiling water. In contrast, the N_2 adsorption-desorption isotherms of AlM samples show that AlM samples still maintain their mesoporous structure even after treatment in boiling water for days. The results indicate that the externally introduced Al species maintain the mesoporous structure of MCM-41 during long duration in boiling water.

FTIR spectra show that PSM have absorption bands at 3745 and 3530 cm^{-1}, which characterize the presence of isolated SiOH and hydrogen-bonded hydroxyl groups in the material, respectively.[10,11] However, after post-synthesis alumination, the intensity of IR absorbance for these hydroxyl groups is substantially suppressed, indicating that the externally introduced Al species may have blocked the terminal OH groups on the surface of MCM-41 and prevent the attack of water molecules. These results suggest that the interaction of the Al species with the surface hydroxyl groups is responsible for the enhancement of the hydrothermal stability of MCM-41.[12]

The hydrothermal stability of PSM and AlM samples is also investigated in 100% of water vapor at 600 °C. After treatment, the (100) X-ray diffraction peak of PSM is very low, showing severe degradation of the mesopores of PSM in steam. In contrast, all AlM samples treated similarly have a much stronger (100) diffraction peak, showing that the externally introduced Al species on the surface of MCM-41 also prevent the degradation of the mesopores in high temperature steam.

Post-synthesis alumination also increases mechanical stability of MCM-41. Before compression, PSM has a higher surface area than any of the AlM materials. However, after compression at a range of pressures from 200 to 800 MPa, all AlM samples maintain higher surface areas than PSM pressed at the same pressure. Besides maintaining higher surface area, AlM samples also maintains their mesoporous structures better than PSM; for example, AlM5 has a slighter change in its N_2 adsorption-desorption isotherms than PSM after the same treatment. It is found that high-pressure compression decreases both the surface area and pore volume of the materials but not their pore diameter, indicating that high pressure compression breaks partial framework but does not constrict the mesopores of MCM-41 to smaller diameter. These results show that the externally introduced Al species improves the mechanical stability of MCM-41. The enhanced mechanical stability is suggested to be due to the effect of recrystallization from post-synthesis modification, healing defect sites in the mesoporous structure of MCM-41 and making them more resistant to structural collapse under compression.[13] In addition, the thicker pore walls of AlM sample may contribute to the better mechanical stability of AlM sample than PSM.

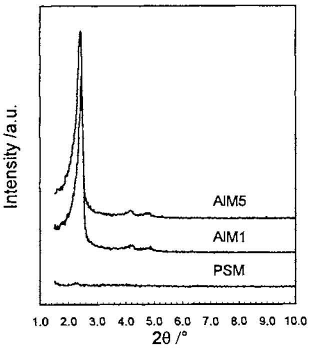

Figure 2. XRD patterns of PSM and AlM materials after treatment in basic solution for 12 h.

In addition to the improvement of hydrothermal and mechanical stabilities, post-synthesis alumination also improves the chemical stability of MCM-41 materials in high pH solution. Figure 2 shows the XRD patterns of PSM and AlM samples after treatment in NaOH solution (pH = 11) for 12 h. No XRD peak can be detected for PSM after it has been treated in basic solution, indicating that the uniform mesoporous structure of PSM is completely destroyed by base molecules. The result is not surprising as it has been well recognized that PSM is unstable in basic solution.[14] In contrast, it can be clearly observed that both AlM1 and AlM5 samples exhibit well defined XRD patterns even after they have been treated at the same condition, indicating that the textural uniformity of the alumina-modified MCM-41 sample is well maintained in the high pH solution. The results of this study show that the chemical stability of the mesoporous structure of MCM-41 material in basic solution can be substantially improved by the external introduction of Al_2O_3 onto the pore surface.

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