Remarkable Improvement in Hydrothermal Stability of MCM-41 by Surface Modification with Grignard Reagents

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(Received March 6, 2000; CL-000221)

Grignard reagents were employed for the first time as a surface modifier for a mesoporous silica, MCM-41. Through this modification method, stable Si-C bonds were formed from surface silanol groups via alkoxy species. Thus modified MCM-41 exhibited high hydrophobicity and remarkable hydrothermal stability.

Mesoporous molecular sieves such as MCM-41[1,2] and FSM-16[3] have been attracting much attention because they have extremely large surface areas and highly ordered structures. Owing to these characteristics, mesoporous materials naturally fascinated researchers to apply them to catalysts for processes dealing with bulky reactant molecules. They have been reported to have low catalytic activities compared with zeolites, partly due to their hydrophilicity.[4] We have already reported that increased hydrophobicity improves not only hydrothermal stability[5] but also catalytic activity for liquid phase oxidations.[6] In this work, Grignard reagents were employed as a surface modifier for MCM-41, revealing a new route to the improvement of their hydrophobicity.

MCM-41 was synthesized by using Aerosil 200 and dodecyltrimethylammonium bromide (DTMABr) as a silica source and a template, respectively. The mother gel composition was SiO_2 : DTMABr : 0.6NaOH : $60H_2O$. MCM-41 was first esterified by alcohols[7] to form Si-OR' from Si-OH, and successively allowed to react with Grignard reagent to convert Si-OR' to Si-R. This two-step procedure is required because Grignard reagents are easily spoiled by silanol groups. For esterification, calcined MCM-41 was treated with refluxing BuOH for 48 h to give BuO-MCM-41. BuO-MCM-41 was filtered and dried at 473 K overnight under vacuum. Then, this was treated with MeMgI in refluxing ethyl ether (ca. 0.2 mol dm^{-3}) for 72 h to produce Me-MCM-41. After the reaction, Me-MCM-41 was filtered, washed with 1 M HCl and H_2O and then dried at 473 K overnight under vacuum.

MCM-41 samples were characterized by XRD, N_2 and H_2O adsorption, and ^{29}Si- and ^{13}C-NMR. Their hydrothermal stability was evaluated by comparing the XRD peak intensities before and after treatment in boiling water.

Physical properties of calcined MCM-41, BuO-MCM-41, and Me-MCM-41 are summarized in Table 1. The X-ray diffraction patterns of these materials indicated that their ordered structures were preserved after each step of modification, although the (100) peak positions slightly shifted. N_2 adsorption isotherms also certified their ordered mesoporosity. Based on BET surface areas and H_2O monolayer adsorption capacities, the amount of adsorbed H_2O molecules per 1 nm^2 of surface was calculated. These values clearly suggest that Me-MCM-41 was much more hydrophobic than calcined MCM-41. Additionally, in H_2O adsorption isotherms (Figure 1), the hysteresis loop of Me-MCM-41 was almost closed, while that of calcined MCM-41 was still open even at low relative pressure,[8] indicating the absence of irreversible H_2O adsorption probably owing to the hydrophobicity of Me-MCM-41. It is also to be noted that BuO-MCM-41 is the most hydrophobic among these samples.

Table 1. Physical properties of MCM-41

	d_{100}	Pore diameter[a,b]	BET surface area[a]	Adsorbed water[c]	
	Å	Å	$m^2 g^{-1}$	$ml g^{-1}$	molecule nm^{-2}
calcined MCM-41	31.5	21	934	68.8	2.0
BuO-MCM-41	33.3	<19	826	6.8	0.22
Me-MCM-41	31.5	<19	848	19.7	0.62

[a]Based on N_2 adsorption at 77 K, [b]D-H method, [c]At 298 K.

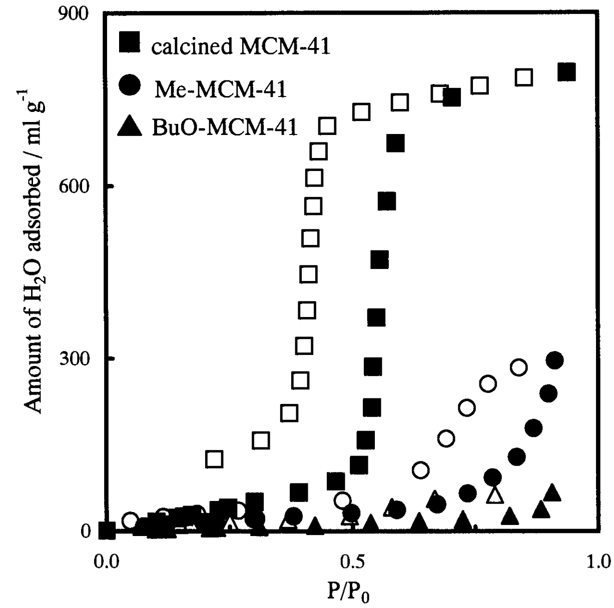

Figure 1. H_2O adsorption isotherms of MCM-41 materials. Solid: adsorption, open: desorption.

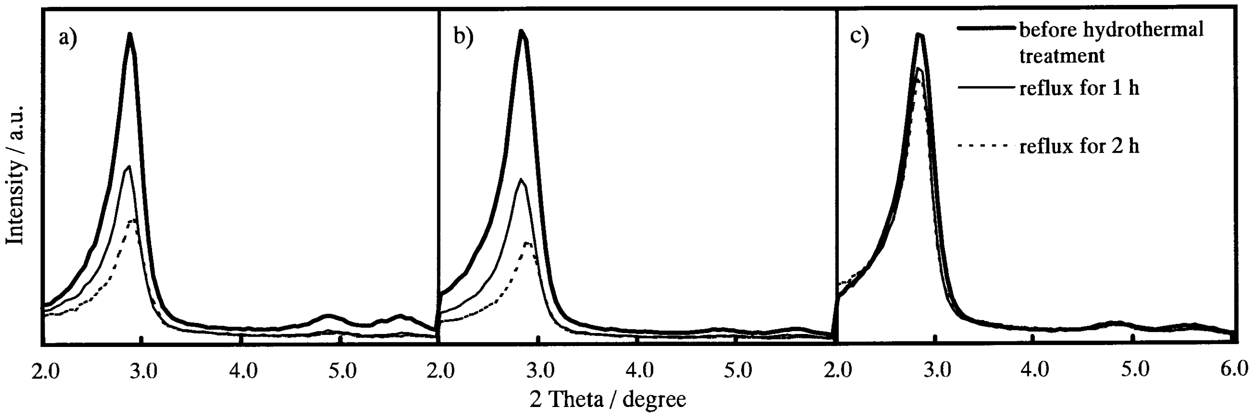

Figure 2. XRD patterns of MCM-41 materials before/after hydrothermal treatment. a) calcined MCM-41, b) BuO-MCM-41, c) Me-MCM-41.

However, the hydrothermal stability test of these samples showed quite a different result. After the hydrothermal treatment, the XRD peak intensities for BuO-MCM-41 drastically decreased to almost the same extent as those for calcined MCM-41 (Figures 2a and 2b). On the other hand, the ordered structure of Me-MCM-41 was almost preserved even after 2 h treatment (Figure 2c). Obviously, this difference should be ascribed to the nature of the surface modifiers. That is, the BuO-Si species on BuO-MCM-41 would be easily hydrolyzed under the conditions employed, and turn back to their original forms, silanol groups. In contrast, the Me-Si bond on Me-MCM-41 would be strong enough to be resistant to the hydrolysis. Therefore, Me-MCM-41 maintained its hydrophobicity even after hydrothermal treatment, and is by far the most hydrothermally stable.

The ^{29}Si-MAS NMR spectra (Figure 3a) and ^{13}C MAS NMR spectra (Figure 3b) of Me-MCM-41 exhibited new resonance peaks not observed before the Grignard modification step. The peaks in ^{29}Si-NMR at -64 and -53 ppm are assigned to T^3 and T^2, respectively, indicating the formation of Si-C bonds in Grignard modification step. Moreover, it should be noted that Me-MCM-41 showed at least two peaks in addition to T^3 and T^2. They can be assigned to Si having the connection with two or three alkyl groups, $Me_2Si(OSi)_2$ and $Me_3Si(OSi)$ species, here denoted by D^2 and S^1, respectively. Although these species must be formed from $(BuO)_2Si(OSi)_2$ and $(BuO)_3Si(OSi)$ derived from Q^2 and Q^1, respectively, the original calcined MCM-41 contained negligible Q^2 and Q^1. These facts suggest that alcohol molecules could attack and break siloxane bonds in the esterification step, or that H_2O molecules formed during the esterification could attack the neighboring siloxane bonds. When Me-MCM-41 was synthesized via MeO-MCM-41, an MCM-41 material esterified with refluxing MeOH instead of refluxing BuOH, no S^1 peak was observed. The absence of S^1 is presumably due to the low esterification temperature; the MeOH refluxing conditions were not so severe as to break three siloxane bonds to form $(RO)_3Si(OSi)$ species.

We have succeeded in planting other organic groups such as ethyl, allyl, and phenyl by using the corresponding Grignard reagents. Thus Grignard modification method can easily improve hydrothermal stability of mesoporous materials, with protecting their ordered structures from decomposition. The application of this modification method to catalytically active mesoporous silica would be highly promising and currently under way.

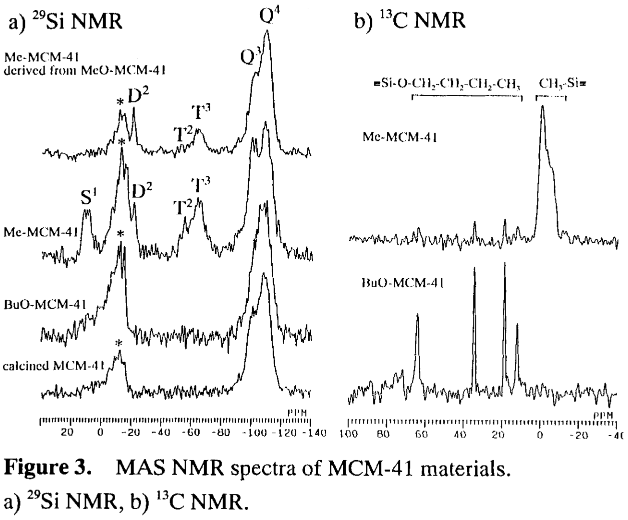

Figure 3. MAS NMR spectra of MCM-41 materials. a) ^{29}Si NMR, b) ^{13}C NMR.
* Background.

We are grateful to Mr. Y. Tanaka at Chiyoda Corp. for measuring ^{29}Si- and ^{13}C-MAS NMR spectra.

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