Mesoporous Materials

Dehydroxylation Route to Surface Modification of Mesoporous Silicas by Using Grignard Reagents[**]

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Since researchers at the Mobil company reported the syntheses of mesoporous silicas such as MCM-41 and MCM-48,[1] there have been a lot of development in their synthesis, structural characterization, and applications due to their large-pore diameters compared with those of conventional microporous zeolites.[2] The modification of silica materials with various organic functional groups[3] is desirable for applications such as catalysts, adsorbents, use in reversed-phase chromatography, and advanced materials.[2–4] Organic modification has been conventionally conducted by the reaction of organoalkoxysilane or organosilyl chloride with surface silanols (SiOH) to form SiO−SiR bond.[3] However, the attached organic group leaches out under harsh conditions through cleavage of the Si−O bonds.[4c] Moreover, some unwanted side reactions, for example, self-polymerization of organoalkoxysilane, may occur on the surface during the modification.[5]

A strained siloxane bridge is generated on the silica surface when the silica is subjected to vacuum degassing at temperatures above 900 K, and it was suggested that the silicon atom of the strained siloxane bridge is electron deficient, thereby acting as a Lewis acid center.[6] As the strained siloxane is reactive to the organoalkoxysilane, or acid-labile acetal or ketal groups, the moiety has been successfully used to modify the surface or to anchor organo-

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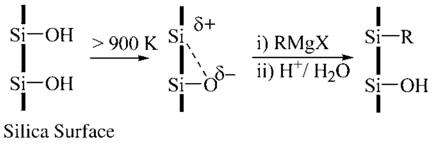
metallic catalysts.[7] However, these modification methods also result in the formation of the Si–O bond, which is susceptible to cleavage under certain harsh conditions. Herein, we propose a novel strategy for the modification of mesoporous silica surface through a dehydroxylation route by using a Grignard reagent as shown in Equation (1). The route gives not only the formation of a direct Si–C bond, which is much more resistant to hydrolytic cleavage, but also preclusion of the formation of both surface-bound oligomers and variable modes of attachment.



(1)

Treatment of the MCM-41 that had been dehydroxylated by evacuation at 1123 K for 15 h with excess *n*BuLi in hexane, subsequent quenching, and washing with water furnished modified MCM-41 that contained 12 % carbon (2.5 mmol butyl g^{-1}). However, the X-ray diffraction (XRD) pattern reveals that the mesoscopically ordered structures are somewhat destroyed by the treatment, which is probably due to the high reactivity of *n*BuLi. When relatively less reactive *n*BuMgCl in diethyl ether is used for the modification, the modified MCM-41 (*n*Bu-MCM-41) thus obtained exhibits relatively low carbon content (9.6 %, 2.0 mmol butyl g^{-1}). Thermogravimetric analysis (TGA) shows slight weight loss up to 773 K but rapid decrease of weight is observed at 773–873 K. The total weight losses obtained from the TGA curve (11 % butyl) are in agreement with the elemental analysis datum of 9.6 % carbon content. When the surface modification is conducted by the conventional method, that it, the reaction of calcined MCM-41 with trimethoxypropylsilane in ethanol at room temperature for 24 h, only 2.4 % carbon content ($\approx$ 0.7 mmol propyl g^{-1}) is observed.

The N_2 adsorption–desorption isotherm obtained at liquid-N_2 temperature (−196 °C) for the modified MCM-41 is type-IV with a well-defined step in the adsorption and desorption curves. The pore size and the pore volume are reduced by the modification while the surface area and wall thickness increase. Surface area, pore size, pore volume, and wall thickness are measured to be 1340 m^{2}g^{-1}, 2.3 nm, 0.79 cm^{3}g^{-1}, and 2.2 nm, respectively, for the *n*Bu-MCM-41, and 1200 m^{2}g^{-1}, 2.9 nm, 1.24 cm^{3}g^{-1}, and 1.7 nm, respectively, for the unmodified MCM-41. When the surface area and elemental analysis datum are taken into consideration, the carbon content (9.6 %) is calculated to be equivalent to the coverage of 0.90 butyl nm^{-2}. When SBA-15 is modified by the dehydroxylation route with *n*BuMgCl, the material has 5.4 % carbon content (1.1 mmol g^{-1}). The relatively low carbon content compared with that observed for the *n*Bu-MCM-41 may be attributed to the relatively low surface area of the SBA-15 ($\approx$ 700 m^{2}g^{-1}).

XRD patterns for MCM-41 and SBA-15 before and after modification with *n*BuMgCl are shown in Figure 1. All materials exhibit XRD patterns with a very intense diffraction peak and two or more weak peaks, which are characteristic of a 2D hexagonal (*P6mm*) structure.[1,2] There are no significant changes upon surface modification, except the expected slight decreases in lattice parameters due to the thermal treatment, which indicates that the mesoscopically ordered structures are retained after modification with *n*BuMgCl. The TEM image also confirms that the highly ordered 2D hexagonal structures are preserved during the modification.

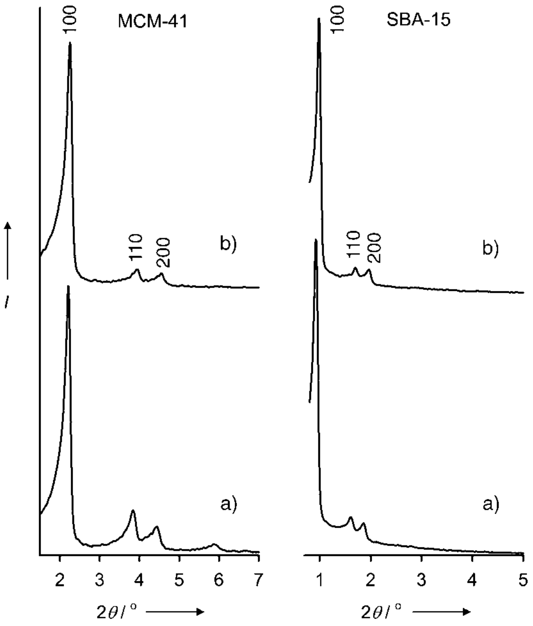


Figure 1. XRD patterns for MCM-41 and SBA-15: a) before and b) after modification with *n*BuMgCl. *I* is intensity (arbitrary units).

There are only Q^3 ($\delta = -102$ ppm) and Q^4 ($\delta = -110$ ppm) resonances in the ^{29}Si MAS NMR spectrum (MAS is magic-angle spinning) before the modification, but a new peak around $\delta = -60$ ppm (T^n,) appears after the treatment, which is attributed to the Si species directly bonded to carbon (Figure 2). The intensity of Q^3 band corresponding to the surface silanol group is also reduced after the modification. This is clear evidence of direct formation of Si–C bond as depicted in Equation (1). Two signals are observed at 12.8 ppm and 25.1 ppm in the ^{13}C CP–MAS NMR spectrum (CP is cross polarization) with almost the same intensity (Figure 2). The former signal can be assigned to the $-CH_3$ and the $-CH_2-$Si carbon atoms and the latter to the other two $-CH_2-$ carbon atoms.[8]

Figure 3 shows the TGA curves for the samples obtained by treatment with *n*BuMgCl of the MCM-41 dehydroxylated at temperatures in the range of 473–1273 K. The samples dehydroxylated at 473, 573, 673, and 773 K and modified with butyl groups show almost same curves. However, the weight loses increases rapidly by increasing the dehydroxylation temperature above 873 K. The loading amount reaches a maximum at 1123 K and decreases when the temperature is increased to 1173 K, which is attributed to the collapse of the pore structures above 1123 K.[9a,b] It was reported that an electron-deficient siloxane group is generated by evacuating

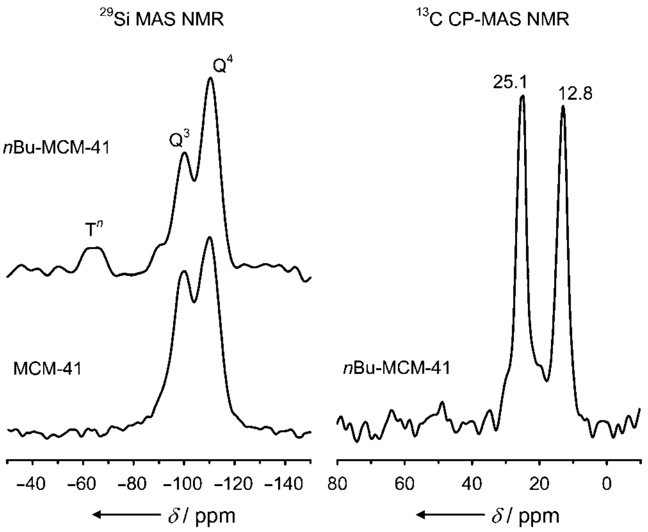


Figure 2. ^{29}Si and ^{13}C MAS NMR spectra for calcined MCM-41 and *n*Bu-MCM-41 obtained by treatment with *n*BuMgCl after dehydroxylation at 1123 K.

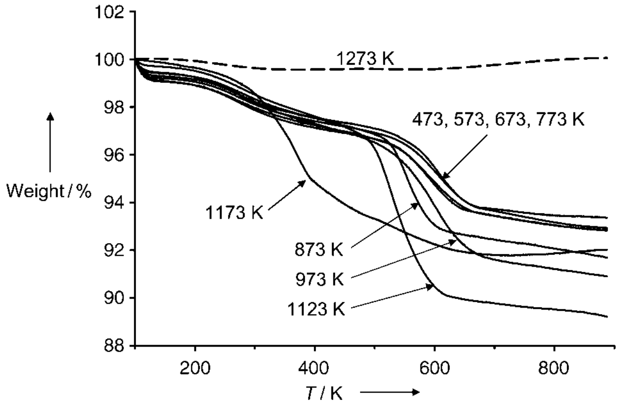
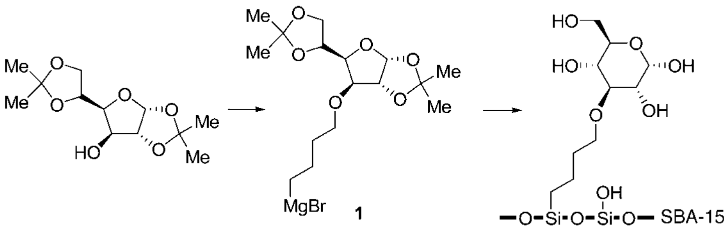


Figure 3. TGA curves for the samples obtained by treatment with *n*BuMgCl on MCM-41 dehydroxylated at temperatures in the range of 473–1273 K.

silica above 900 K, and the number of such strained siloxane group increases as the temperature increases.[6] The TGA curves in Figure 3 support the argument that the electron-deficient siloxane group, formed on the surface of mesoporous silica by evacuation above 900 K, mainly participates in the reaction with *n*BuMgCl as shown in Equation (1).

Hydrothermal stability of the mesoporous material is an important issue in many potential applications because structural disintegration is frequently observed.[9] The main feature of the XRD pattern is preserved when the *n*Bu-MCM-41 is heated to 373 K in water for five days under static conditions, whereas in the case of the unmodified MCM-41 or MCM-41 modified by the conventional method (by the reaction of trimethoxypropylsilane onto the surface silanol group) the mesostructures are completely destroyed within two days. Moreover, the TGA curve for the *n*Bu-MCM-41 is not altered by the five-day treatment in water, which supports argument that the butyl group is not cleaved. However, the MCM-41 modified by the conventional method loses most of the attached organic groups after two days.

Other functional groups can be attached on the silica surface by this novel method. Treatment with benzylmagnesium chloride or phenylmagnesium bromide on the MCM-41 dehydroxylated at 1123 K provides modified silicas that contain 9.9% (1.2 mmol g^{-1}) or 8.1% (1.1 mmol g^{-1}) carbon, respectively. The mesostructures of these modified MCM-41 materials are not affected by the treatments. Highly functionalized molecules, such as a glucose derivative, have also been attached (Scheme 1). Grignard reagent **1** that contains acetonide-protected glucose unit is easily synthesized from commercially available diacetone-D-glucose. The addition of the Grignard reagent **1** to the SBA-15 dehydroxylated at 1123 K, subsequent treatment with aqueous acidic water (2 N HCl), thus removing the acetonide protection groups to furnish diols, and finally Sohxlet extraction with methanol afforded a D-glucose modified SBA-15 that contained 4.6% carbon (0.38 mmol g^{-1}).



Scheme 1. Attachment of a glucose derivative on the surface of the dehydroxylated SBA-15.

In conclusion, a novel surface-modification strategy has been developed by treating dehydroxylated silica with Grignard reagents. High loading of organic groups can be achieved and the mesoporous structures are not destroyed by the modification. The modified materials thus obtained exhibit excellent hydrothermal stability by forming direct ≡Si–C bonds. Since highly functionalized Grignard reagents are now available,[10] we believe that the present synthesis strategy can be applied to the surface modification of various silica nanostructures in addition to mesoporous silica materials to obtain robust organic functional groups.

Experimental Section

Mesoporous silicas, MCM-41 and SBA-15, were synthesized following the procedures described elsewhere,[11] by using cetyltrimethylammonium bromide and triblock copolymer P123, respectively, as the templates. Typical procedure for surface modification: The MCM-48 and SBA-15 were dehydroxylated by evacuation at 1123 K for 15 h. A Grignard reagent (4.0 mmol) was added to a slurry of the dehydroxylated silica (1.0 g) in diethyl ether (10 mL) at room temperature and the mixture was stirred for 15 h. An aqueous HCl solution (2.5 M, 25 mL) was added and the two phase mixture was stirred for 3 h. The silica was isolated by filtration and washed successively with water, methanol, and diethyl ether. The silica was dried under vacuum. In the case of **1**, 2.0 mmol of **1** per gram of silica and THF solvent were used instead, and the Sohxlet extraction was conducted with methanol for 24 h to remove any physisorbed organics.

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