Introduction of Si–H Bond onto the Surface of Mesoporous Molecular Sieves and Functionalization by Hydrosilylation Reaction

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The Si–H bond was introduced onto the surface of MCM-41 by reduction of the butoxylated MCM-41. The hexyl and phenylalkyl-functionalized MCM-41s were obtained by reaction of the Si–H introduced MCM-41 with 1-hexene or styrene.

Organic-functionalized mesoporous molecular sieves have received much attention in terms of their application in the fields of catalysis and adsorption.[1] Recently, Tatsumi and Yamamoto reported that an organic group can be directly bonded to a silicon atom on the surface of MCM-41 by the reaction of the alkoxylated MCM-41 with several Grignard reagents.[2] Si–C bonds have good thermal and solvolytic stabilities as compared with the corresponding Si–O–Si bonds which are formed by cocondensation[3] and postsynthesis[4] method on the surface of silica.[5a]

Generally, the hydrosilylation[6] reaction, which is the addition reaction of hydrosilanes to carbon–carbon multiple bonds, is known as a more useful method for Si–C bond formation than the Grignard reaction since this reaction can incorporated a wide range of functional groups using of the corresponding olefin which can be easily obtained.[6] Hence, if the Si–H group can be introduced onto the mesoporous silica materials, the hydrosilylation reaction will be extended as a new convenient and versatile method for this functionalization.

Pesek and co-workers[5] introduced a Si–H bond onto the silica gel by the reduction of chlorinated silica produced by the reaction with thionyl chloride in refluxing toluene. However, thionyl chloride is difficult to handle because of its corrosiveness, toxicity, and high moisture sensitivity, and the formed Si–Cl bond is also moisture sensitive so that it has to be handled under an inert gas atmosphere or in dehydrated solvents. Moreover, the resulting material is generally brown in color, so its decolorization must be carried out.

We now report that the Si–H bond can be easily introduced onto the surface of MCM-41 in a high density by the reduction of a butoxylated MCM-41 under mild and atmospheric conditions, and its density can be directly measured by ^{1}H MAS NMR using the internal standard method. Furthermore, a phenylalkyl group can also be introduced onto the surface by the hydrosilylation reaction with styrene.

MCM-41 was hydrothermally synthesized by a previously described method.[7] Calcined MCM-41 was butoxylated by refluxing in 1-butanol for 3 days to give a product designated as BuO–MCM-41.[2] The reduction of BuO–MCM-41 to produce a hydrogenated MCM-41, designated as HSi–MCM-41, was carried out using an excess amount of lithium aluminium hydride (LAH) saturated in ether at room temperature for 4 days. After the reaction, the resulting materials were filtered, washed with dehydrated ether to remove the residual LAH, followed by washing with 1 M HCl, water, and ethanol, and then dried at 473 K overnight under vacuum.

The functional group loading of MCM-41 was determined by FT-IR (Shimadzu 8100). The quantitative analysis of the introduced BuO and HSi groups was carried out by ^{1}H MAS NMR. A 0.01-g (0.031 mol) portion of tetrakis(trimethylsilyl)silane as the internal standard was dissolved in a suspension of ca. 0.25 g of the MCM-41 sample in pentane. After adequately stirring them, pentane was removed under reduced pressure. The solid-state ^{1}H (500 MHz) and ^{29}Si (99.3 MHz) NMR spectra were obtained using a JEOL A500 spectrometer with the following conditions: for ^{1}H MAS NMR, 6 kHz spin rate, non-decoupling single pulse, and a repetition delay of 30 s, for ^{29}Si CPMAS NMR, 6 kHz spin rate, and a repetition delay of 30 s.

The XRD patterns, BJH pore diameter and specific surface area of HSi–MCM-41[8] indicate that the characteristic hexagonally ordered MCM-41 mesophase[7] was maintained when BuO–MCM-41 was reduced by LAH at room temperature.

The FT-IR spectra for these MCM-41 samples at room temperature are shown in Figure 1. In the spectrum of BuO–MCM-41 (curve B), the peaks attributed to the C–H stretching vibration clearly appeared at ca. 2900 cm^{-1} with the decrease in the peak at 3745 cm^{-1} attributed to the isolated silanol group for the calcined MCM-41 (curve A). This revealed that the silanol of this material was alkoxylated by 1-butanol. After the reduction of BuO–MCM-41 by LAH, a new peak at 2260 cm^{-1}, known to be responsible for the Si–H stretching vibration,[9,10] was obtained along with a decrease in the intensities of the C–H vibration peaks (curve C).

Figure 2a shows the ^{1}H MAS NMR spectra of BuO–MCM-41 and HSi–MCM-41 containing tetrakis(trimethylsilyl)silane (0.25 ppm) as the internal standard. The signals for the protons of the butoxy group were observed at 0.91 ppm (C1), 1.49 ppm (C2 and C3), and 3.87 ppm (C4) in the spectra of BuO–MCM-41. The amount of the BuO group was calculated to be 2.9 mmol/g based on the ratio of the deconvoluted peak areas for C4 and the internal standard.

After reduction by LAH, a new signal was observed at 3.41 ppm which is definitely assigned as a proton in the Si–H group on analogous to silicone chemistry.[11] The signals of the butoxy group were negligible. The broad peaks centered at ca. 1.9 and 4.2 ppm were assigned to the proton of the reproduced

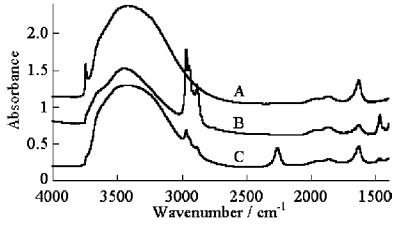

Figure 1. FT-IR spectra of MCM-41 (A), BuO–MCM-41 (B), and HSi–MCM-41 (C) at room temperature after pre-heating at 393 K for 2 h.

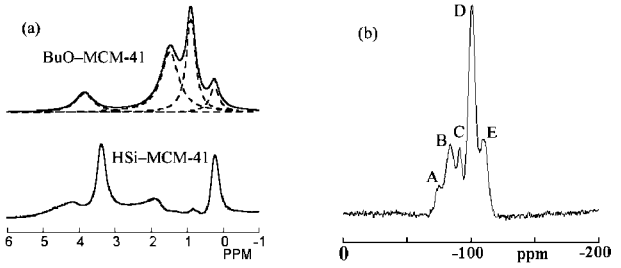

Figure 2. (a) ^{1}H MAS NMR spectra of BuO–MCM-41, and HSi–MCM-41. The broken lines are deconvoluted peaks. (b) ^{29}Si CPMAS NMR spectrum of HSi–MCM-41. A; H–Si(OH)(SiO≡)$_2$, B; H–Si(SiO≡)$_3$ and H–Si(OBu)(SiO≡)$_2$, C; Si(OH)$_2$(SiO≡)$_2$, D; Si(OH)(SiO≡)$_3$, E; Si (SiO≡)$_4$ and Si(OBu)(SiO≡)$_3$.

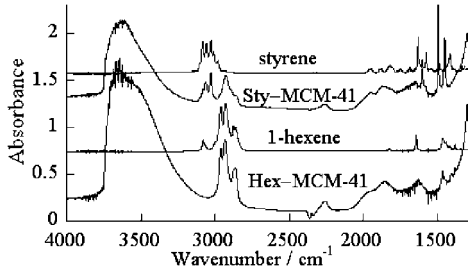

Figure 3. FT-IR spectra of Hex–MCM-41 Sty–MCM-41, 1-hexane, and styrene.

silanol group by LAH reduction and absorbed H_2O, respectively.[12] The amount of the Si–H group in the HSi–MCM-41 sample was calculated to be 2.5 mmol/g, and it revealed that ca. 86% of the BuO group was converted to the Si–H group. With this value and specific surface area of 709 m^2/g,[8] it can be estimated that ca. 2.0 Si–H groups exist per 1 nm^2 of the MCM-41 surface. When the reaction period is increased, the yield of HSi–MCM-41 would also increase. However, its periodic structure is gradually disordered because of the competitive dissociation reaction of Si–O–Si in the framework. Hence, more suitable reaction conditions should be investigated in order to obtain HSi–MCM-41 in high yield. As shown by the ^{29}Si CPMAS NMR of HSi–MCM-41 in Figure 2b, the signals of H–Si(OSi≡)$_3$ or H–Si(OBu)(OSi≡)$_2$ and H–Si(OH)(OSi≡)$_2$ were observed at −85 and −75 ppm, respectively.[5a]

The hydrosilylation reactions of HSi–MCM-41 with 1-hexene and styrene were carried out using the procedure described below. An excess amount of 1-hexene or styrene and a catalytic amount of hexachloroplatinic(IV) acid were added to a suspension of toluene containing HSi–MCM-41. After the mixture was heated at 353 K for 3 days, the resulting materials, designated as Hex and Sty–MCM-41, respectively, were filtered, washed several times with water and ethanol, and then dried at 473 K for 12 h under vacuum.

Figure 3 shows the FT-IR spectra of the samples obtained after the hydrosilylation reactions and their precursors. In the spectrum obtained by the reaction with 1-hexene, the vibration peaks at 2800–3000 cm^{-1}, corresponding to the C–H bond, were clearly observed and the vibration at 3080 or 1640 cm^{-1}, attributed to the terminal olefin, was not observed. Whereas, in the spectrum obtained by the reaction with styrene, the vibrations at 2800–3100 cm^{-1} and 1600, 1452, and 1492 cm^{-1} corresponding to C–H and C=C bond, respectively, were observed. In comparison with the spectrum for styrene, the peak pattern of the C–H vibration region (2800–3100 cm^{-1}) is much different and the new peaks attributed to the C–H vibration in the alkyl group (<3000 cm^{-1}) are observed. These results strongly suggest that the Si–H group adducts to the C=C bond in 1-hexene or styrene to form the Si–C bond (Figure 4). Although the Si–H bond still remained in the spectrum the Hex– and Sty–MCM-41, the intensities of the peaks attributed to the orgaic group were much higher than that attributed to the Si–H bond. Therefore, it is obvious that an adequate amount of the organic group was introduced onto MCM-41. However, a more suitable catalyst and reaction conditions should be investigated in order to obtain the functionalized MCM-41 in a higher yield.

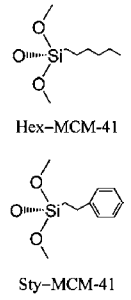

Figure 4.

The XRD patterns of the Hex– and Sty–MCM-41[8] indicate that the characteristic hexagonal structure was also maintained during the hydrosilylation step.

In this study, the Si–H group was introduced onto the surface of MCM-41 for the first time, and its density was directly measured by ^{1}H MAS NMR. Furthermore, the hydrosilylation reaction of HSi–MCM-41 with 1-hexene and styrene was carried out to produce the functionalized MCM-41 with pendant organic groups. Because the hydrosilylation reaction is a good method for the synthesis of various organosilyl compounds, hydrogenated mesoporous silica materials should be a new precursor for its functionalization.

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