Does Water Liquid Phase Intrude into Hydrophobic Nanospaces of Alkyl-grafted Mesoporous Silica Immersed in Water? Detection by ^{13}C CP-MAS NMR

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In situ ^{13}C CP-MAS NMR measurements enabled for the first time detection of the presence and absence of water liquid phase in nanospaces of alkyl-grafted mesoporous silicas through the signals of alkyl chains, when the materials were immersed in water. It was revealed that *n*-octyl-grafted mesoporous silica excluded liquid water from the hydrophobic nanospaces at least in an hour time scale while liquid water penetrated into *n*-pentyl-grafted material much faster. This is important for understanding the adsorbents in the working states in water.

The discovery of mesoporous silica[1–6] opened a research field of new organic–inorganic nanocomposites based on mesoporous silica toward various applications.[7–37] The grafting of organic groups onto the pore walls of the silica[11–15] has provided novel materials for catalysts,[16–18] heavy metal ion adsorption,[19–25] photocontrollable molecular storage,[26] gas separation,[27] and molecular recognition/molecular selective adsorption.[28–37]

We previously reported that alkyl-grafted mesoporous silica adsorbed nonylphenol in water with high molecular selectivity.[32–35] It was the first example of organo-grafted mesoporous silicas applied as adsorbents for organic molecules in water. To date many studies have been devoted to develop organo-functionalized mesoporous materials as adsorbents toward organic contaminations such as alkylphenols,[32] alkylanilines,[33,34] and chlorophenols[38–40] in water.

When alkyl-grafted mesoporous silicas are used as adsorbents in water, the states of the hydrophobic nanospaces are very important to understand behaviors of the adsorbents. It is not evident whether liquid water intrudes into the hydrophobic alkyl-grafted nanospaces or not, when the materials are immersed into liquid water. Recent solid-state NMR study has shown that chlorophenol, not amphiphilic molecule like nonylphenol, is highly mobile in the hydrophobic nanospaces of alkyl-grafted mesoporous silica, but the samples were measured after filtration.[38] That is, the behaviors of the materials in liquid water phase are still ambiguous. There is a report that alkyl-grafted mesoporous silica is usable as a pressure damper in water, indicating the liquid water is excluded from the nanospaces.[41] However, spectroscopic evidence is lacking, and the effect of alkyl chain length has not been reported.

Here we report that in situ NMR can detect the presence and absence of liquid water in the nanospaces through the changes in mobility of alkyl chains. This is very important for understanding the adsorbents in the working states in water.

Preparation of alkyl-grafted mesoporous silica is described elsewhere in detail.[34] In this study two kinds of mesoporous silica were used. One is mesoporous pure silica (pore diameter $d_p = 2.7$ nm, pore volume $V_p = 0.72$ cm^3 g^{-1} determined by N$_2$ adsorption at 77 K, designated as Si-M), and the other is aluminum-containing mesoporous silica (Si/Al = 100, $d_p = 2.6$ nm, $V_p = 0.61$ cm^3 g^{-1}, designated as M(100)). For the organo-functionalization, the mesoporous silica was refluxed in fresh distilled toluene with an excess amount of *n*-pentyltriethoxysilane or *n*-octyltriethoxysilane (from Tokyo Kasei Co.) for 48 h followed by washing with toluene and then with methanol. These samples were dried in vacuo at ambient temperature for ca. 2 h. These samples are designated as C5-Si-M, C5-M(100) (*n*-pentyl-grafted mesoporous silicas), and C8-M(100) (*n*-octyl-grafted mesoporous silica). Alkyl group surface densities were determined by TG-DTA to be 0.8, 1.5, and 1.0 molecule nm^{-2} for C5-Si-M, C5-M(100), and C8-M(100), respectively. Note that C5-Si-M had lower alkyl content than C5-M(100). In situ ^{13}C CP-MAS NMR spectra were measured with a Bruker AMX-400 spectrometer. O-ring-sealed zirconia rotors (7 mm in diameter) were used for the in situ measurements. Under N$_2$ atmosphere the powder sample (ca. half volume of the rotor) was introduced into the rotor followed by adding H$_2$O or D$_2$O to fill up the rotor (immersion into water). Then the rotor was sealed with a cap equipped with two O-rings. The rotation of the sample was gradually accelerated up to 3 kHz. The data was taken with a contact time of 1 ms and a pulse width of 1 μs.

Figure 1 shows ^{13}C CP-MAS spectra of C5-Si-M. The peak assignments are also shown as a–g. When C5-Si-M was immersed into H$_2$O (top spectrum of Figure 1), an intense methyl signal appeared (signal b). The peaks around 12 ppm were separated by curve fitting, and the intensity ratio of carbon b (methyl)/carbon a was determined to be 1.2. When
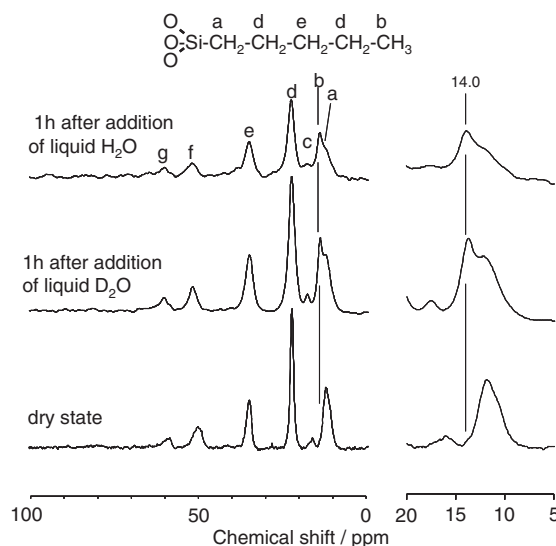

Figure 1. In situ ^{13}C CP-MAS NMR spectra of C5-Si-M. Carbons c and g were assigned to residual ethanol or ethoxide groups. Carbon f was residual methanol or methoxide groups.
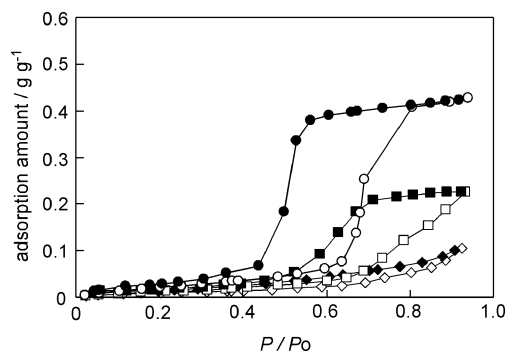
Figure 2. Water vapor adsorption isotherms of alkyl-grafted mesoporous silicas: Circles, C5-Si-M; squares, C5-M(100); diamonds, C8-M(100). Open symbols, adsorption blanch; solid symbols, desorption blanch.

D_2O was used instead of H_2O, similar signal was observed as shown in the middle spectrum of Figure 1. An intense methyl signal appeared, and the intensity ratio of carbon b (methyl)/carbon a became up to 0.58.

On the other hand, the signal of methyl carbon (carbon b) was apparently absent in the dry state (the bottom spectrum of Figure 1). It is well known that, in ^{13}C CP-MAS NMR spectra, highly mobile species give weak signal intensities because of the weakened dipole–dipole interactions between ^{13}C and ^1H. It is probable that the absence of the methyl signal is due to the high mobility of *n*-pentyl groups in the nanospaces of mesoporous silica in the dry state. Similar absence of a methyl carbon signal had been reported for as-synthesized MCM-41 mesoporous silica: In the case of surfactant molecules confined in the nanochannel of MCM-41, the alkyl chains are highly mobile so that the methyl carbon gives no signal in the ^{13}C CP-MAS NMR.[4] Another less likely possibility is that the methyl signal shifts and becomes hidden by a neighboring signal such as signal a.[42]

For better understanding of these NMR behaviors, water vapor adsorption isotherms for the alkyl-grafted samples are presented in Figure 2. It is clear that water condensed readily into the nanospaces of C5-Si-M. Comparing the data to the NMR results, it was demonstrated that the intense CP-MAS methyl signal can be used as a marker of liquid water intrusion into the alkyl-grafted nanospaces.

Similar experiments were carried out for C5-M(100), as the results are shown in Figure 3. The dry sample gave no methyl peak (the bottom spectrum of Figure 3). 1 h after the immersion of the sample into H_2O, a weak methyl peak was observed and the intensity ratio of carbon b (methyl)/carbon a was 0.17 (middle of Figure 3). After a supersonic treatment for 24 h with liquid H_2O in the rotor, the intensity ratio increased up to 0.75 (the top spectrum of Figure 3). These results show that penetration of liquid water is slower for C5-M(100) than for C5-Si-M. The difference is attributable to the different surface alkyl densities. The NMR results are also consistent with the fact that water vapor condenses into C5-M(100) (Figure 2).

Figure 4 shows the results of experiments for C8-M(100). Assignments of carbons were also presented in Figure 4. As shown in the bottom spectrum, dried C8-M(100) gave no methyl peak. 1 h after the immersion of the sample into water, only a
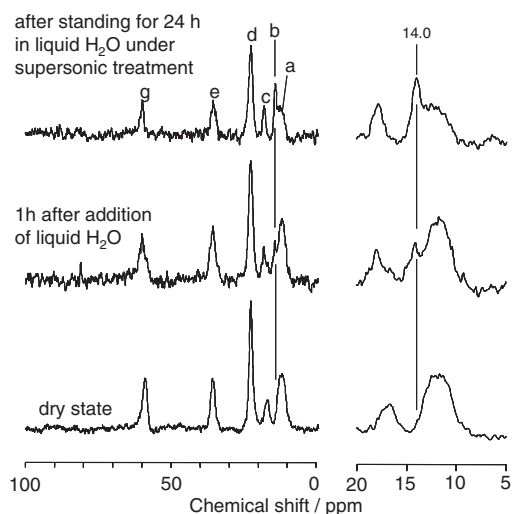

Figure 3. In situ ^{13}C CP-MAS NMR spectra of C5-M(100). The assignments of carbons are the same as those for Fig. 1.
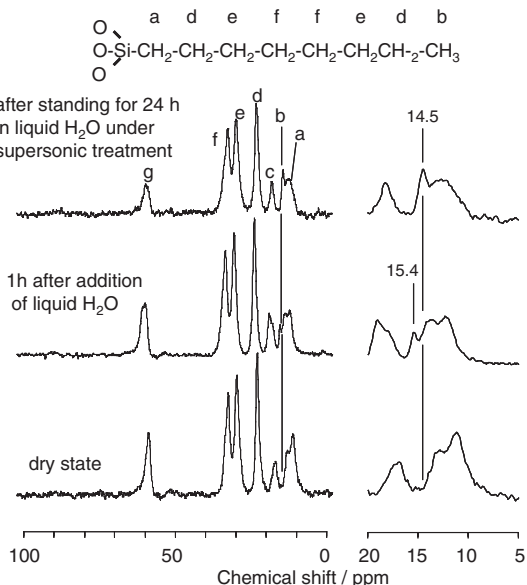

Figure 4. In situ ^{13}C CP-MAS NMR spectra of C8-M(100). Carbons c and g were assigned to residual ethanol or ethoxide groups.

very weak methyl peak was observed at 15.4 ppm, as shown in the middle spectrum of Figure 4. The intensity ratio carbon b (methyl)/carbon a was as small as 0.09. This demonstrates that liquid water did not penetrate into the hydrophobic nanospaces in this time scale. Since the outersurface area of the mesoporous silica used here is ca. one tenth of the total surface area, the observed methyl signal can be ascribed to that from alkyl groups grafted on outer surfaces of the mesoporous silica. As shown in the top spectrum in Figure 4, the methyl peak slightly shifted (14.5 ppm) and became stronger after 24 h of a supersonic treatment. The peak intensity ratio of carbon b (methyl)/carbon a was 0.32 after 24 h. The split of the carbon a signal may due to different environments of the neighboring Si having different number of OH groups or alkoxides.

The results in Figure 4 revealed that it is difficult for liquid water to intrude into the *n*-octyl-grafted hydrophobic nanospaces of C8-M(100). According to N_2 adsorption, C8-M(100) had pore spaces as large as $0.27\,cm^3\,g^{-1}$, and these spaces are available for molecular adsorption. We previously reported that C8-M(100) was a good adsorbent for alkylphenols or alkylanilines in water. The present results revealed the working state of the adsorbent in liquid water: The hydrophobic nanospaces of the adsorbent excluded liquid water, and the organic molecules penetrate into the free spaces between the grafted alkyl chains, even when the adsorbents were immersed into liquid water. This model explains well the high performance of the octyl-grafted mesoporous silica as adsorbents.[32–35] On the other hand, liquid water penetrated into C5-Si-M much faster. The differences are attributed to the different chain lengths. The data indicated that the large nanospaces of C5-Si-M ($0.55\,cm^3\,min^{-1}$) were filled by liquid water. This interpretation coincides well with the low performance of C5-Si-M as an adsorbent, as was reported by us in a previous study.[34]

There is a possibility that the exclusion of liquid water by the octyl-grafted sample is a kinetic phenomenon, because the methyl carbon relative intensity increased up to 0.23 after 24 h even for C8-M(100). In the time scale of adsorption experiments (1–2 h), the water remained and resulted in the high performance of C8-M(100). Another issue to be considered is a wetting process of the hydrophobic outer surfaces of the adsorbent. This factor may also affect the apparent adsorption performances.

In conclusion, our first NMR analysis revealed that liquid water was excluded by the hydrophobic nanospaces of the octyl-grafted mesoporous silica at least in a time scale of an hour when the sample was immersed into water, while liquid water intruded into the nanospaces much faster for pentyl-grafted mesoporous silicas. The results gave important information about the working states of the adsorbents and explained well the different performances of the adsorbents in water.

References and Notes

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42. In order to check how the methyl signal shifts when the alkyl chains are surrounded by water molecules, NMR spectra of neat and 1.7% aqueous solution of 1-pentanol were compared. Chemical shifts of carbon 1 were very close (61.99 and 62.06 ppm for the neat compound and aqueous solution, respectively). The methyl peak in aqueous solution gave a signal at slightly higher field (13.42 ppm) than that of neat compound (14.02 ppm). The peak shift was small and opposite to signal a.