Surface Modification of Ordered Mesoporous Silica with an Organosilane Containing Polyethylene Oxide Groups to Retain the Hydrophilic Nature

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The ability to adsorb water of ordered mesoporous silica was successfully controlled by organic modification with an organoalkoxysilane containing polyethylene oxide groups.

Surface modifications of ordered mesoporous silicas with metal oxides, organosilanes, alcohols, and organometallic compounds have developed new chemistry within the periodic mesopores including catalysis, separation, adsorption, and organometallic chemistry.[1,2] Organic modifications of ordered mesoporous silicas have been conducted by various methods to control the surface properties and functionalities.[3–5] However, surface properties of the organically modified materials reported so far have never been controlled. Because the surfaces of the silicate frameworks are mainly covered with alkyl chains, the derivative surfaces are extremely hydrophobic.[4,5] Here, the surface modification of ordered mesoporous silica to retain the hydrophilic nature is presented by utilizing an organosilane containing both alkyl and polyethylene oxide (PEO) groups. The presence of the hydrophilic PEO groups within mesopores is useful for controlling the hydrophilic nature.

According to the literature,[6] an ordered mesoporous silica (FSM-16) was prepared by using hexadecyltrimethylammonium chloride (C_{16}TMACl). The X-ray diffraction (XRD) pattern of the calcined FSM-16 showed four diffraction peaks in low scattering angles assignable to a 2-dimentional (2-d) hexagonal structure ($d_{100} = 3.9$ nm). The BET surface area, the pore volume, and the pore size were 1175 $m^2 g^{-1}$, 0.91 $cm^3 g^{-1}$, and 3.2 nm, respectively. The density of surface silanol (Si–OH) groups was estimated to be 2.0 groups nm^{-2} ($Q^3/Q^4 =$ ca. 0.3). The parent FSM-16 was dried at 110 °C over night prior to organic modification. During the drying process, the d_{100} value was decreased to 3.6 nm. After that, the dried FSM-16 (1 g) was dispersed in toluene (50 ml) containing different amounts of M(PEO)PrTMS ($(H_3CO)_3Si(CH_2)_3(OCH_2CH_2)_{6\text{–}9}OCH_3$, Azmax Co. Ltd.) (0.05–1.00 ml). The suspension was refluxed at 110 °C for 24 h and the resultants were washed 5 times with acetone to remove the unreacted M(PEO)PrTMS.

The XRD pattern of the parent FSM-16 hardly changed after silylation and the peak intensity was varied according to the added amount of M(PEO)PrTMS in the reaction mixtures. The ^{29}Si MAS NMR spectrum of the parent FSM-16 showed both Q^3 (-100 ppm) and Q^4 peaks (-109 ppm) due to the presence of HO*Si*(OSi)$_3$ and *Si*(OSi)$_4$ species, respectively. After silylation, additional peaks assignable to T^n (R–*Si*(OSi)$_n$(OH)$_{3-n}$, $n = 1$–3, R; organic group) environments appeared at -49 ppm, -56 ppm, and -65 ppm in the ^{29}Si MAS NMR spectra of all the silylated materials with the slight decrease of the Q^3 peak intesity. The degree of the decrease of the Q^3 peak intensity is related to the grafted number of the organosilica species. These results indicate that M(PEO)PrTMS is reacted with Si–OH groups at the surface of FSM-16 without structural change.

The carbon contents of the silylated FSM-16 were measured by elemental analysis (Table 1) and increased with the added amount of M(PEO)PrTMS in the reaction mixtures. The values are related to the grafted numbers of organosilica species. The grafted numbers of silylated materials (Table 1) are controllable by changing the added amount of M(PEO)PrTMS in the reaction mixtures. The N_2 adsorption isotherms of the silylated FSM-16 showed the variation of type IV to I behaviors, indicating that the pore size can be controlled by changing the grafted numbers. When FSM-16 was fully silylated, the obtained material became nonporous because organic groups in M(PEO)PrTMS are very large. The BET surface areas, the pore volumes, and the pore sizes of the silylated materials are shown in Table 1. Both the pore volumes and the pore sizes became smaller with the increase in the grafted numbers, revealing that organosilica species are fixed on the inner (and outer) surfaces.

The water adsorption-desorption isotherms of the silylated FSM-16 were measured to investigate the variation in the surface property and the isotherms are shown in Figure 1. The isotherm of parent FSM-16 showed type V behavior, indicating that the surface of the parent FSM-16 is hydrophobic. However, water molecules can be adsorbed on the surface of the silicate

Table 1. Characteristics of the silylated FSM-16

	Added amount of M(PEO)PrTMS /ml	Carbon content /mass %	Grafted number[a] /group nm^{-2}	BET surface area /$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	Pore size[b] /nm
Parent FSM-16	—	—	—	1175	0.91	3.2
Silylated FSM-16	0.05	4.3	0.2	1095	0.79	3.1
	0.25	8.5	0.4	837	0.57	2.7
	0.50	11.5	0.6	668	0.35	2.4
	0.75	14.7	0.7	449	0.27	2.2
	1.00	16.7	0.8	157	0.09	—

[a]The grafted numbers were calculated by using the grafted number of the fully silylated meterial investigated by ^{29}Si MAS NMR (T^n/Q^n ratio = ca. 0.1) on the basis of the carbon contents. [b]The pore sizes were calculated by the Holvth–Kawazoe method.[7]

framework and a capillary condensation occurred at around $P/P_0 = 0.5$–0.6. The water adsorption-desorption isotherms of FSM-16 modified with M(PEO)PrTMS were also type V and capillary condensations were observed in the range of $P/P_0 = 0.4$–0.6. All the organically modified mesoporous silicas reported so far have extreme hydrophobic surfaces.[4,5] In contrast, water molecules can be adsorbed on the modifed FSM-16 with M(PEO)PrTMS. The result suggests that the presence of hydrophilic PEO groups within the mesopores largely moderates the hydrophobicity due to the presence of hydrophobic alkyl groups at the surface of FSM-16. Then, the organic modification with M(PEO)PrTMS is quite efficient in retaining the ability to adsorb water molecules (hydrophilic nature) of ordered mesoporous silicas.

As reported previously,[5] water molecules hardly adsorbed on the surfaces of silylated FSM-16 with alkylsilanes because of the presence of alkyl ($-n$-C_nH_{2n+1}) groups at the surfaces of silicate frameworks. Even when aminopropyl ($-C_3H_6NH_2$) groups are fixed on the surface of the silicate framework, the amount of adsorbed water molecules is not increased so dramatically.[5] Similar results are obtained by esterification of FSM-16 with alcohols with long alkyl chains (butyl and octyl alcohols).[4] In the present system, organically modified pore spaces are accessible by water molecules even after organic modification though all the surfaces of silicate framework of FSM-16 was covered with organic groups.

Compared with the H_2O adsorption-desorption isotherm of parent FSM-16, almost of all the adsorbed water molecules were eliminated by the desorption process from the modified FSM-16 with M(PEO)PrTMS (Figure 1). This means that adsorbed water molecules are not consumed in order to hydrolyze the silicate frameworks. In addition, the XRD patterns of the modified materials hardly changed after the measurements, meaning that the stability of FSM-16 is improved by the organic modification as in the case of silylation of ordered mesoporous silicas with alkylsilanes.[8] Thus, the modified mesoporous silicas with M(PEO)PrTMS are expected for use in catalysts, catalyst supports, and adsorbents including sensors in the presence of, water vapor because of the retaining hydrophilic nature and the improved stability.

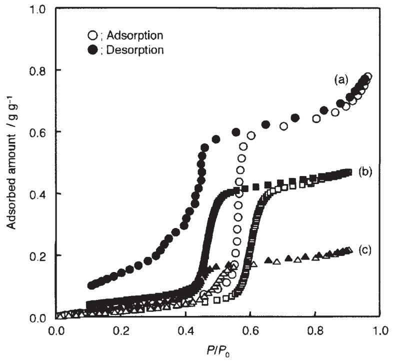

Figure 1. Water adsorption-desorption isotherms of (a) parent and modified FSM-16 with different amounts of M(PEO)PrTMS; (b) 0.25 ml and (c) 1.00 ml.

On the basis of the variation of pore sizes by the grafted number of the organosilica species, the structural models of organically modified FSM-16 with larger and smaller amounts are discussed. In the fully silylated material, hydrophobic alkyl groups are located near the silicate framework and hydrophilic PEO groups are filled residual spaces within mesopores. The pore spaces accommodate organic reactants near the silicate framework by the hydrophobic-hydrophobic interaction; effective reactions of the organic reactants are expected. In contrast, both alkyl chains and PEO groups are located on the surface of mesopores and exposed in the slightly silylated material. Because of the presence of large PEO chains on the surface of the silicate framework, alkyl groups are dispersed on the surface of the silicate framework. It is considered that relatively larger molecules such as dye molecules and photosynthetic pigments can be adsorb homogeneously within the mesopores.

In conclusion, organic modification of ordered mesoporous silicas was conducted by using M(PEO)PrTMS as a silylating agent. The hydrophilic nature of the mesoporous silicas was successfully retained after silylation because of the presence of hydrophilic PEO groups. The materials can be expected as novel reaction media according to the grafted number of organosilica species by utilizing the location and distribution of hydrophobic and hydrophilic moieties within mesopores.

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