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Fabrication of novel mesoporous dimethylsiloxane-incorporated silicas

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Mesoporous dimethylsiloxane-incorporated silica materials are synthesized which exhibit high surface areas, regular mesopores, thick walls, high hydrophobicity and high mechanical strength.

Since the discovery of the M41S mesoporous silica materials in 1992 by Mobil researchers,[1] various mesoporous materials have been developed.[2] Several organic-group modified mesoporous silica materials have been synthesized by the *in situ* co-condensation of organosilane precursors and tetraethyl orthosilicate (TEOS) in the presence of surfactant self-assemblies.[3] Recently, several groups reported the synthesis of mesoporous organic–inorganic hybrid materials with organic groups directly incorporated into the silicate framework using bis(alkoxysilyl)-functionalized precursors. Here, we present the synthesis of mesoporous dimethylsiloxane-incorporated silica materials from the co-condensation of TEOS and diethoxydimethylsilane (DEDMS) in the presence of surfactant self-assemblies.

In the multi-component sol–gel processes it is important to control the hydrolysis and condensation rates of the precursors.[6] If the hydrolysis rates of the precursors were considerably different, phase-separated mixtures would be produced instead of homogeneous hybrid materials.[7] It is well-known that the hydrolysis rate of DEDMS is nearly zero in basic medium and that it hydrolyzes much faster in acidic medium. In consequence, we chose the so-called $S^+X^-I^+$ route (S^+: cationic surfactant, X^-: halide ion, and I^+: cationic silicate oligomer) to synthesize MCM-41 type mesoporous dimethylsiloxane-incorporated silicas.[8]

TEOS and DEDMS were partially pre-hydrolyzed separately in acidic medium by stirring for 30 minutes in an ice bath with molar ratios of 1 TEOS : 2 H_2O : 0.04 HCl and 1 DEDMS : 1 H_2O : 0.04 HCl respectively. The resulting two clear solutions were mixed with vigorous stirring and were poured into a surfactant solution at 60 °C. The resulting gel mixture had a molar composition of 1 (TEOS + DEDMS) : 0.13 octadecyltrimethylammonium bromide (OCTAB) : 5.4 HCl : 150 H_2O. The mixture was aged for 5 d with vigorous stirring at 60 °C. The surfactant was removed by refluxing in ethanol for 3 h followed by refluxing for 6 h in 5 mol% HCl in ethanol. The resulting mesoporous materials were designated as mesoporous $(CH_3)_2SiO$-$a$$SiO_2$ materials (a = the molar ratios of DEDMS and TEOS in the initial reaction mixtures, and were set to 2, 3 and 4). For comparison, pure mesoporous MCM-41 silica was synthesized according to a similar procedure using TEOS as a precursor. The elemental analytical results of these mesoporous materials revealed that most of the surfactant was successfully removed (typical elemental results in wt%: C, 7.68; H, 1.84; N, 0 for $(CH_3)_2SiO$-4SiO_2. C, 9.36; H, 2.41; N, 0 for $(CH_3)_2SiO$-3SiO_2. C, 11.11; H, 2.76; N, 0 for $(CH_3)_2SiO$-2SiO_2). Solid-state ^{13}C NMR also confirmed the successful removal of surfactant.

The ordered mesoporous structure of the materials was investigated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and gas adsorption measurement. Powder X-ray diffraction patterns of mesoporous $(CH_3)_2SiO$-$a$$SiO_2$ materials and mesoporous silica are shown in Fig. 1. The XRD pattern of mesoporous silica [Fig. 1(*a*)] exhibited hexagonal MCM-41 pore arrangement, displaying one intense (100) reflection with d_{100} of 4.0 nm and smaller (110) and (200) reflections. On the other hand, the XRD patterns of dimethylsiloxane-incorporated silica materials shown in Fig. 1(*b*)–(*d*) revealed only a (100) reflection, demonstrating that they are less ordered in the long range than the pure silica material.

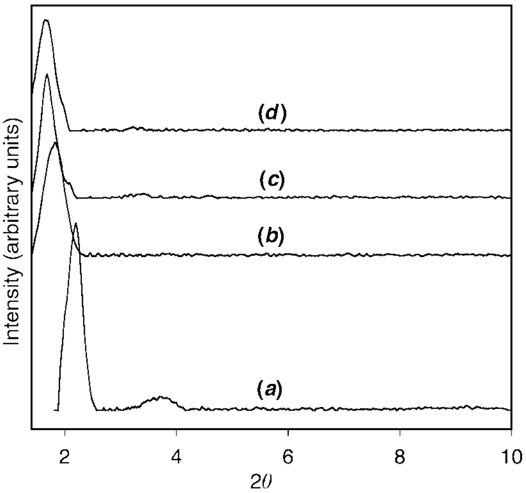

Fig. 1 X-Ray diffraction (XRD) patterns of mesoporous MCM-41 silica (trace *a*), mesoporous $(CH_3)_2SiO$-4SiO_2 (trace *b*), $(CH_3)_2SiO$-3SiO_2 (trace *c*) and $(CH_3)_2SiO$-2SiO_2 (trace *d*) materials. The patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and Cu-K_α radiation (λ = 0.15418 nm).

Table 1 shows the pore characteristics of these mesoporous materials. The BET surface areas of the dimethylsiloxane-incorporated silicas are slightly smaller than that of the pure silica material. Nitrogen adsorption/desorption isotherms of these materials exhibited type IV, which is characteristic of mesoporosity. The pore diameters of these materials were comparable to that of the pure mesoporous silica. The wall thickness was obtained by subtracting the BJH pore size from the unit cell parameter a_0 ($a_0 = 2d_{100}/\sqrt{3}$). The results revealed that the walls of these dimethylsiloxane-incorporated silicas were thicker than those of the pure silica derivative, which is very important for their future applications. A TEM image of

Table 1 Pore characteristics of mesoporous dimethylsiloxane-incorporated silicas[a]

Sample	Surface area/ $m^2\ g^{-1}$	Pore diameter/ nm	Pore volume/ $cm^3\ g^{-1}$	Wall thickness/ nm
MCM-41 SiO_2	1082	2.8	0.95	1.8
$(CH_3)_2SiO$-4SiO_2	1028	2.7	0.67	2.9
$(CH_3)_2SiO$-3SiO_2	980	2.4	0.62	3.6
$(CH_3)_2SiO$-2SiO_2	1029	2.3	0.73	3.8

[a] N_2 adsorption and desorption isotherms were collected on a Micromeritics ASAP2010 Gas Adsorption Analyzer after the materials were degassed at 150 °C at 30 μTorr for 5 h. The surface areas were calculated by the BET method and the pore size distributions were calculated from the adsorption branch of the nitrogen isotherm by the BJH method.

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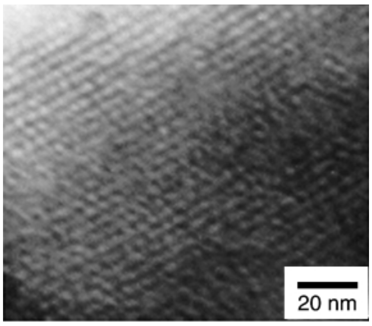

Fig. 2 Transmission electron micrograph (TEM) of mesoporous $(CH_3)_2SiO$-$4SiO_2$ material. The images were obtained with a Phillips CM-20 instrument.

the mesoporous $(CH_3)_2SiO$-$4SiO_2$ material showed a regular array of *ca.* 2.5 nm diameter holes separated by *ca.* 3 nm thick walls (Fig. 2).

One of the disadvantageous features of mesoporous silica materials for the applications is their poor mechanical stability.[9] In the present research, we have incorporated the dimethylsiloxane component into silica frameworks to increase the mechanical strength of the silica framework. The mechanical properties of these materials were evaluated by taking XRD patterns after compressing the materials. In the case of the pure silica mesoporous material, the XRD pattern after compressing at 104 MPa (15 000 psi) for 10 min showed no diffraction peak, revealing that the mesopores were completely collapsed. On the other hand, mesoporous $(CH_3)_2SiO$-$3SiO_2$ after compressing at 104 MPa exhibited a (100) reflection with slightly decreased intensity compared to the XRD pattern before the compression. The surface area and pore volume of the mesoporous material were kept nearly unchanged after compressing at 104 MPa. The results clearly demonstrated that these mesoporous dimethylsiloxane-incorporated silicas possess better mechanical stability compared to mesoporous silica materials.

The hydrophobicity of the mesoporous materials was tested by mixing with an immiscible mixture of water and methylene chloride. After shaking vigorously, the mesoporous $(CH_3)_2SiO$-$3SiO_2$ material resided exclusively in the methylene chloride layer. In contrast, the pure silica mesoporous material stayed in water layer. The same trend was observed when a mixture of diethyl ether and water was used as a partitioning medium. These results showed that these mesoporous materials are very hydrophobic. Thermogravimetric analysis (TGA) of mesoporous $(CH_3)_2SiO$-$3SiO_2$ revealed that the material decomposed around 300 °C.

The homogeneous distribution of the $(CH_3)_2Si$ moiety in the mesoporous material was investigated by FT-IR spectroscopy (Fig. 3). The successful incorporation of $(CH_3)_2Si$ groups in the silicate framework was confirmed by four peaks at *ca.* 2970, 1267, 850 and 800 cm^{-1}, which can be assigned as CH_3 asymmetric stretching, CH_3 deformation, CH_3 rocking and Si–C stretching mode, respectively. The Si–O–Si bending vibration mode was known to be sensitive to the chemical environment and was utilized as a fingerprint for the homogeneous incorporation of organic groups into the silicate framework.[10] In our samples, the Si–O–Si bending vibration mode was shifted from 467 cm^{-1} for pure silica mesoporous material to 454 cm^{-1} for $(CH_3)_2SiO$-$4SiO_2$ and $(CH_3)_2SiO$-$3SiO_2$, and 450 cm^{-1} for $(CH_3)_2SiO$-$2SiO_2$, demonstrating that the Si-$(CH_3)_2$ moieties are homogeneously distributed in the silicate framework structure.[10] The ^{13}C CP-MAS (cross polarization-magic angle spinning) NMR spectrum of mesoporous $(CH_3)_2SiO$-$3SiO_2$ material showed a single Si-$(CH_3)_2$ peak at δ −1.5. The ^{29}Si CP-MAS NMR spectrum of the material exhibited characteristic peaks attributed to $(CH_3)_2Si(OSi)_2$ (D_2 δ −15.7), $Si(OSi)_4$ (Q_4 δ −110), $(OH)Si(OSi)_3$ (Q_3 δ −103). These NMR results demonstrated that the $(CH_3)_2Si$ moiety was kept intact during the synthesis and was successfully incorporated into the silicate framework.

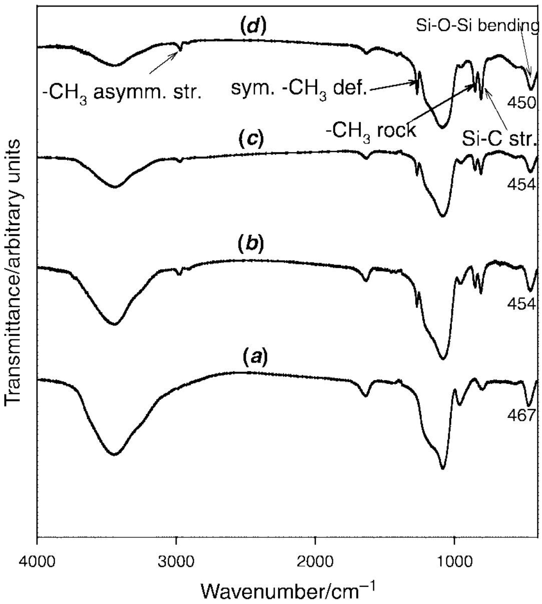

Fig. 3 FT-IR spectra of mesoporous MCM-41 silica (trace *a*), mesoporous $(CH_3)_2SiO$-$4SiO_2$ (trace *b*), $(CH_3)_2SiO$-$3SiO_2$ (trace *c*) and $(CH_3)_2SiO$-$2SiO_2$ (trace *d*) materials. The spectra were obtained with a Bomem MB-100 instrument.

These new mesoporous dimethylsiloxane-incorporated silica materials exhibit many interesting characteristics for future applications, including high surface areas, regular mesopores, thick walls, high mechanical strength and high hydrophobicity. We expect that these materials can find applications in catalysis, adsorption technology and the fabrication of low dielectric materials for ULSI (ultra large scale integration) devices.

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