Synthesis of Highly Ordered Hybrid Mesoporous Material Containing Etenylene (–CH=CH–) within the Silicate Framework

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A hybrid mesoporous material containing etenylene in a two-dimensional, hexagonally arranged mesoporous silicate framework with long-range symmetry is successfully synthesized. Quantitative analysis of the reactive etenylene groups within the silicate framework indicates that approximately 30% of the etenylene is exposed at the surface and is available for further modification.

Recently, hybrid mesoporous materials containing organic fragments within the silicate framework have been synthesized from bridged organosilane compounds as silica sources in the presence of a structure-directing agent.[1–6] Such materials have the potential to offer a wide range of functionality through appropriate selection of the organic group in the silicate framework. Several organic groups, such as $-CH_2-$,[5] $-CH_2CH_2-$,[1,2,4] $-CH=CH-$,[3,4] and $-C_6H_4-$[6] have been successfully incorporated into the pore walls. Notably, $-CH_2CH_2-$ and $-C_6H_4-$ bridged mesoporous organosilica affords a highly ordered, hexagonal mesoporous structure. A unique feature of these hybrid mesoporous materials is that organic moieties are homogeneously distributed at the molecular level within the silicate framework, and that both organic fragments and inorganic species are exposed at the surface. The smooth accessibility of organic groups introduced into the framework provides scope for further modification,[6] and the present authors have been investigating the incorporation of unsaturated hydrocarbon groups into the framework of highly ordered mesoporous silicate for the purpose of such chemical modification. To date, the only reported hybrid mesoporous material containing –CH=CH– has had a wormhole-like pore structure.[3,4] A hybrid material with a highly ordered mesoporous structure will have the advantages for analysis and modeling of organic groups after chemical modification. In this study, a highly ordered hybrid mesoporous material containing etenylene fragments in the framework is synthesized using $(C_2H_5O)_3Si–CH=CH–Si(OC_2H_5)_3$ as a silica source and octadecyltrimethylammonium chloride as a structure-directing agent in basic media.

$(C_2H_5O)_3Si–CH=CH–Si(OC_2H_5)_3$ was prepared according to the procedure in the literature.[7] A solution of vinyltriethoxysilane (50 mmol) and $RuCl_2(PPh_3)_3$ (0.05 mmol) was refluxed for 24 h, and the product was isolated by distillation (125 °C, 4 mmHg) with 80% yield. ^1H and ^{13}C nuclear magnetic resonance (NMR) analysis indicated that two isomers were mixed in the product, and the E/Z ratio was estimated to be 86/14.[7]

In the typical synthesis procedure for hybrid mesoporous ethylene-silica,[1] bis(triethoxysilyl)ethylene (5 mmol) was added to a mixture of octadecyltrimethylammonium chloride (2.9 mmol), sodium hydroxide (12 mmol), and water (1.8 mol) under vigorous stirring at 25 °C for 24 h. The introduction of the bridged organosilane precursor to the solution resulted in the immediate formation of a white precipitate. This solution was heated to 95 °C and maintained at that temperature for 72 h without stirring. The resulting precipitate was recovered by filtration, then cooled and washed with deionized water. Surfactant-extraction was performed by stirring 1.0 g of as-synthesized product into 150-mL of ethanol and 3.5 g of 36% HCl aqueous solution at 50 °C for 6 h. This treatment was then repeated twice more to obtain the hybrid mesoporous material.

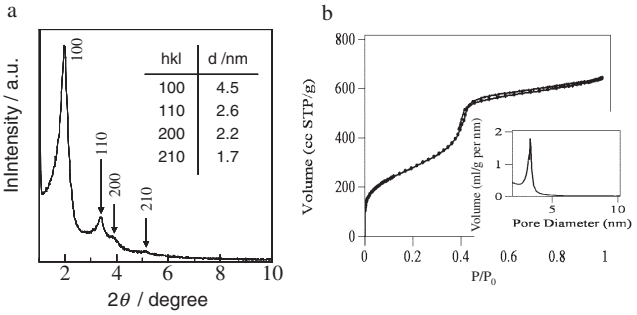

Figure 1. (a) XRD pattern, and (b) N_2 adsorption-desorption isotherm with pore-size distribution (inset) for hybrid mesoporous etenylene-silica.

The X-ray diffraction (XRD) pattern of ethylene containing hybrid mesoporous material (Figure 1a) exhibits four clear diffraction peaks with lattice spacing of $d = 4.5$, 2.6, 2.2, and 1.7 nm, assigned to two-dimensional (2D) hexagonal (*P6mm*) symmetry with a lattice constant of $a = 5.2$ nm, as determined from $d(100)$. The 2D-hexagonal pore structure is a typical symmetry observed in pure silica mesoporous materials and other inorganic mesoporous metal oxides. The similarity of the present XRD pattern to those of highly ordered pure-silica mesoporous materials such as MCM-41 and SBA-15 indicates that the present material exhibits a high degree of mesoscopic ordering. N_2-gas adsorption analysis revealed a typical type-IV isotherm, characteristic of mesoporous materials. The BET surface area, BJH pore diameter and pore volume were estimated to be 1040 m^2g^{-1}, 3.3 nm, and 1.35 mL g^{-1}, respectively. The narrow distribution of pore sizes reflects the uniformity of the mesoporous system (Figure 1b inset). The wall thickness estimated by the $d(100)$ spacing and the pore size is 1.9 nm assuming a 2D-hexagonal structure.

A typical transmission electron microscopy (TEM) image is shown in Figure 2. These images provide direct evidence of the

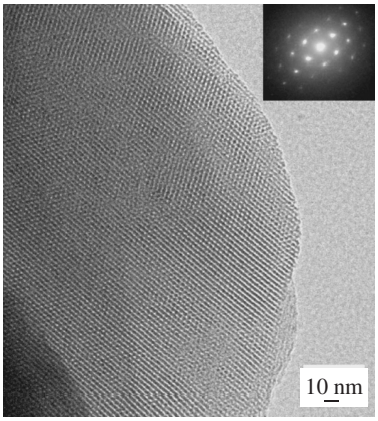

Figure 2. Typical TEM image of hybrid mesoporous etenylene-silica and the corresponding electron diffraction pattern (inset).

formation of a 2D-hexagonal arrangement of uniformly sized pores. It is also evidenced from the corresponding electron diffraction pattern (Figure 2 inset) that the product has well-ordered and long-range 2D-hexagonal symmetry.

The etenylene group incorporated into the silicate framework in the prepared sample was characterized by Raman spectroscopy and solid-state ^{13}C and ^{29}Si cross-polarization (CP) magic angle spinning (MAS) NMR. The Raman spectrum of the product exhibited characteristic bands at 1574, 1300, and 750 cm^{-1}, consistent with the bands for an etenylene fragment bridged by silicon (Si–CH=CH–Si) in the starting material $(C_2H_5O)_3Si–CH=CH–Si(OC_2H_5)_3$. These three peaks can be assigned to C=C stretching, =C–H deformation and Si–C stretching modes, respectively. The ^{13}C CP MAS NMR spectrum of the product (Figure 3) exhibited three strong resonances, at 146 ppm attributed to carbon in Si–CH=CH–Si, and at 59 and 19 ppm attributed to ethoxy groups. No carbon signal indicative of the ionic surfactant was observed by ^{13}C CP MAS NMR, in good agreement with the Raman spectroscopy results. These data demonstrate that the etenylene group was successfully incorporated into the silica framework and that the surfactant was completely removed.[10] The ^{29}Si CP MAS NMR spectrum reveals major resonances at approximately 73 and 83 ppm, assigned to C–Si(OH)$(OSi)_2$ (T_2 site) and C–Si$(OSi)_3$ (T_3 site), respectively. These peaks indicate the presence of the Si-bridged ethylene group in the silica walls.[11]

Thermogravimetric/differential thermal analysis (TG/DTA) of the product was carried out to examine the thermal stability of the etenylene group incorporated into the silica walls. A weight loss of about 20% was observed below 100 °C due to desorption of physisorbed water. This was followed by a gradual decrease in weight (30%) from 300 to 800 °C. Most of the etenylene groups were stably retained below 300 °C, as determined from the lower limit of the broad exothermic peak centered around 450 °C.

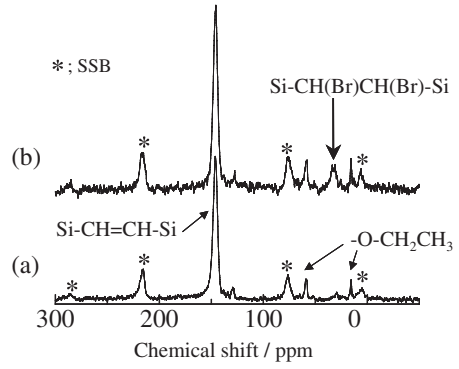

Figure 3. ^{13}C CP MAS NMR spectrum (50 MHz) of (a) hybrid mesoporous etenylene-silica, and (b) after bromination.

Quantitative analysis of the amount of etenylene incorporated within the silicate framework was carried out by liquid-phase bromination followed by iodometric titration.[12] Figure 3b shows the ^{13}C CP MAS NMR spectrum of etenylene-bridged mesoporous organosilica after bromination. The presence of brominated carbon at 33 ppm and unreacted ethylene group at 147 ppm can both be seen in the spectrum, indicating that complete bromination was not achieved. Assuming that the pore wall consists of a covalently bonded network of $O_{1.5}Si–CH=CH–SiO_{1.5}$, 30% of the ethylene group within the framework was therefore brominated, representing the proportion of etenylene moieties present on the surface and hence available for chemical modification.

A hybrid mesoporous material containing etenylene and having a well-defined 2D-hexagonal mesopore array with long-range symmetry was successfully synthesized for the first time using bis(triethoxysilyl)ethylene as a silica source and octadecyltrimethylammonium chloride as a structure-directing agent. The incorporation of etenylene groups into the framework was confirmed by Raman spectroscopy and ^{13}C and ^{29}Si CP MAS NMR, and the incorporated ethylene groups were demonstrated to be preserved during thermal treatment at up to 300 °C. Approximately 30% of the ethylene groups were present on the material surface as reactants for further modification.

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10 Although the signal of ethoxy group cannot be detected from the as-synthesized material, the existence of the ethoxy groups were shown by Raman and ^{13}C CP MAS NMR spectrum of product. This indicates the formation of ethoxy group with the silanol group during the removal of surfactant.
11 Minor resonances at 100 ppm (Q_3 site; Si(OH)$(OSi)_3$) and 108 ppm (Q_4 site; Si$(OSi)_4$) were observed (data not shown). The ^{29}Si CP MAS NMR spectrum of periodic mesoporous organosilica containing ethylene with a wormhole-like pore structure reported previously[4] also exhibits these resonances, considered to arise from slight hydrolysis of the ethylene-silicon bond.[8,9] Cleavage of the Si–C bond may therefore occur to some extent during the surfactant-extraction process.
12 The amount of reacted bromine was indirectly investigated by iodometric titration. A sample of hybrid mesoporous ethylene-silica (0.2 g) was suspended in 150 mL of $CHCl_3$. Br_2 (1.2 equiv.) was added drop-wise slowly to the reaction mixture under continuous stirring in an ice bath. After stirring for 30 min, unreacted bromine in the mixture was reacted with added KI to produce KBr and I_2. Titration of free I_2 was carried out using $Na_2S_2O_3$ aq. as the standard solution and starch as the indicator.

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