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Selective Incorporation of Inorganic Precursors into the Channels of MCM-41 by Molecular Assembly Template as a Hydrophobic Carrier

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Liquid crystal templating has been attracting wide interest since the condensation reaction of silica/silicate precursors in the presence of surfactants was reported to result in formation of a novel mesoporous oxide called MCM-41, which possesses a highly ordered pore structure established by hexagonally packed cylindrical channels.[1,2] It is generally recognized that the liquid crystal phase with a high spatial regularity formed by collaborative interactions of the oxide precursors and the surfactants serves as a self-organizing template and molds the resulting oxide framework into highly ordered mesopore structures.[3,4] It is hence expected that, if the templating molecular assemblies incorporate another (secondary) substance within their interior beforehand, they will carry the secondary substance selectively into the channels of the resulting mesoporous oxides. In fact, the original paper from Mobil reported expansion of the pore diameters of MCM-41 by using templating micelles incorporating large aromatic molecules.[1,2] Nevertheless, there has been no report in which the solubilization effect of templating molecular assemblies was applied for delivery of hydrophobic precursors for the secondary inorganic phase to be deposited in the channels of MCM-41. Moreover, the local environment of the solubilized species in the templating micelles would be of importance in order to fully utilize the interior of templating molecular assemblies. Here we report spectroscopic information on the location and local environment of hydrophobic substances incorporated in MCM-41 observed by in situ fluorescence probing and present an applicability of the templating micelles as a hydrophobic carrier for selective incorporation of inorganic precursors into the channels of MCM-41.

Silica MCM-41 was synthesized at room temperature by hydrolyzing 0.05 mol of $Si(OC_2H_5)_4$ (TEOS) in a liquid crystal template solution prepared by solubilizing 1 mL of a hydrophobic solution of secondary substance into 100 mL of a 0.2 M aqueous solution of $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) containing 5 wt % of $(CH_3)_4NOH$ (TMAH). Typical nominal molar ratio of the reactants was CTAB:TMAH:TEOS:H_2O = 0.4:1.0:1.0:110. As secondary substances to be solubilized into the templating micelles, *N*,*N*-dimethyl-1-naphthylamine (DMNA) was used as a hydrophobic fluorescence probe, and $(C_5H_5)_2Fe$ (ferrocene, Fc), $Pd(CH_3COCH_2COCH_3)_2$ (Pd-acac), and $Pd(NH_3)_2Cl_2$ were used as hydrophobic inorganic precursors.

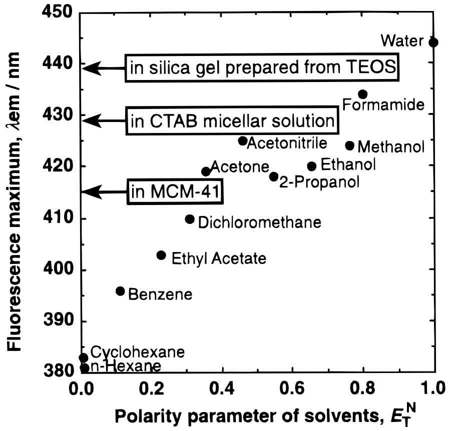

Figure 1. Fluorescence maxima of DMNA in various solvents as a function of the polarity parameter and those observed in some phases relevant to formation of MCM-41.

An acid chloride derivative (dansyl chloride) and water-soluble derivatives of DMNA have been widely used as a fluorescence labeling agent[5] and fluorescence probes to investigate local environment of proteins, polymers, and organic membranes.[6,7] The fluorescence maximum of DMNA shifts toward the longer wavelengths upon increasing the polarity of its surroundings.[8] As shown in Figure 1, the fluorescence maximum wavelength of DMNA, λ_{em}, varies from 381 nm in *n*-hexane to 444 nm in water, indicating a linear correlation to the polarity parameter, E_T^N, empirically defined as 0.0 for tetramethylsilane and 1.0 for water, so as to increase with increasing solvent polarity.[9,10] The CTAB micellar solution solubilizing DMNA showed λ_{em} at 428 nm, agreeing well with the previous report in which the hydrophobicity of the interior of the CTAB micelles was determined as nearly the same as that of acetonitrile.[11] Whereas λ_{em} was observed at 415 nm in MCM-41, that in amorphous SiO_2 gel obtained similarly but in the absence of CTAB was at 439 nm, indicating that DMNA was located in a much more hydrophobic environment in MCM-41 than in the SiO_2 gel, which is expected to be analogous to the amorphous SiO_2 framework of MCM-41. Moreover, the fluorescence quantum

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.

(4) Raman, K. R.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682.

(5) Gray, W. R. *Methods Enzymol.* **1967**, *11*, 139.

(6) Chen, R. F.; Kernohan, J. C. *J. Biol. Chem.* **1967**, *242*, 5813.

(7) Onodera, M.; Yagi, K. *Biochim. Biophys. Acta* **1971**, *253*, 254.

(8) Seliskar, C. J.; Brand, L. *J. Am. Chem. Soc.* **1971**, *93*, 5414.

(9) Dimroth, K.; Reichardt, C. *Ann. Chem.* **1963**, *661*, 1.

(10) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Verlag: Weinheim, 1988.

(11) Murakami, Y.; Hisaeda, Y.; Ohno, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2094.

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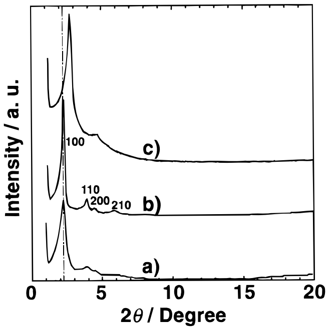

Figure 2. Powder X-ray diffraction patterns of (a) as-prepared MCM-41, (b) as-prepared Fc/MCM-41, and (c) stepwise-calcined Fc/MCM-41.

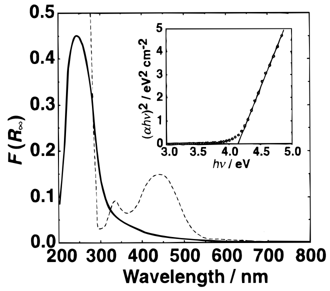

Figure 3. UV−vis absorption spectra of Fc/MCM-41 before (dashed line) and after (solid line) stepwise calcination at 600 °C. The inset shows the Tauc plotting for the calcined Fc/MCM-41.

efficiency of DMNA in the SiO_2 gel is 0.035 times that in MCM-41, endorsing a strongly hydrophilic environment in the SiO_2 gel.[8] Although the more rigid surroundings also cause a decrease in the fluorescence quantum efficiency, this would not be the case with the SiO_2 gel, because high rigidity should also result in a blue shift of λ_{em}. Accordingly, the shift of λ_{em} from 428 nm for the micellar solution to 415 nm via formation of an oxide framework of MCM-41 may reflect an increase in the rigidity around the templating micelles.

These results are demonstrative of the applicability of the templating micelles for charging hydrophobic substances selectively into the channels of MCM-41. We first investigated incorporation of ferrocene (Fc) into MCM-41. A clear yellow solution obtained by solubilizing 1 mL of 1 M $CHCl_3$ solution of Fc into 100 mL of the CTAB micellar solution showed intense optical absorption at 330 and 520 nm, which are characteristic of Fc. After room temperature hydrolysis of TEOS added to this solution, a yellow solid product and the completely colorless liquid phase resulted. The product was washed repeatedly with distilled water, recovered by centrifuge, and dried at room temperature. Comparing X-ray diffraction (XRD) patterns of the products shown in parts a and b of Figure 2 confirmed formation of the hexagonal phase regardless of the coexistence of Fc in the reaction system. The $d(100)$ values were determined as 39.9 Å for both neat MCM-41 and that containing Fc (Fc/MCM-41).

Calcination of the products was first carried out as described in the literature.[1,2] The temperature was kept at 540 °C for 1 h in flowing N_2, followed by another 5 h in air. The specific BET surface areas were determined as 940 and 350 m^2/g for the calcined samples of MCM-41 and Fc/MCM-41, respectively. The predominant pore volume of calcined MCM-41 around 20−30 Å with an extremely narrow distribution drastically decreased for calcined Fc/MCM-41. We considered that the drastic decrease in the pore volume would be due to collapse of the pore structure caused by abrupt decomposition of the inorganic precursors in the channels before firm SiO_2 pore walls were established, because employment of Pd-acac as another inorganic precursor resulted in more severe destruction of the pore structure. Moreover, the rather high vapor pressure of Fc was found to cause poor reproducibility of absorption spectra of the samples after calcination. Finally, we employed stepwise calcination in order to avoid unfavorable volatilization and abrupt decomposition of Fc. A powder of as-prepared Fc/MCM-41 was placed in a tubular furnace, smothered in static N_2 at 300 °C for 20 min, and cooled once. With slow introduction of O_2 at 5 cm^3/min, the sample was again heated at a rate of 2 °C/min, with an increase in the flow rate to 20 cm^3/min at 460 °C. The temperature was kept at 600 °C for 1 h, and the O_2 flow rate again increased to 100 cm^3/min, followed by holding at 600 °C for another 3 h. Figure 2c shows the XRD pattern of the sample after the stepwise calcination. Note that the calcined Fc/MCM-41 retained a fairly resolved profile characteristic of the hexagonal phase. The BET surface area of the calcined Fe/MCM-41 was determined as 820 m^2/g in this case, showing an only 13% decrease compared to calcined neat MCM-41.

The appearance of the calcined Fe/MCM-41 was virtually white. Figure 3 depicts UV−vis absorption spectra of as-prepared and stepwise-calcined Fc/MCM-41 obtained from diffuse reflectance measurements followed by the Kubelka−Munk transform. The absorption bands due to Fc observed for the as-prepared Fc/MCM-41 completely disappeared after calcination, and a sharp and very strong absorption appeared at 244 nm with excellent reproducibility over the samples. The Tauc plotting for semiconductors with the direct transitions[12] shown in the inset of Figure 3 clearly indicates a completely linear fitting, yielding a band gap energy of 4.15 eV. Assuming formation of Fe_2O_3 by firing the sample containing Fc, this result concludes a considerable blue shift of the band gap energy reported as 2.2 eV for bulk Fe_2O_3.[13] Abe et al. also reported a band gap energy of 4.1 eV for fine Fe_2O_3 particles deposited in the mesopores of MCM-41 by an incipient wetness method.[14] However, they claimed that a suspension treatment in water was necessary to eliminate Fe^{3+} ions deposited on the outer surfaces. One inherent advantage of using templating micelles as a carrier of the inorganic precursors is its strict selectivity of precursor charging only into the channels. The suggested very narrow size distribution of the particles in our sample would presumably be established by a homogeneous distribution of the inorganic precursors restricted within the uniform channels. Furthermore, the minimum reflectance of 40% at 244 nm on the basis of 95% reflectance at 800 nm implies a largely enhanced molar extinction coefficient of Fe_2O_3, such an enhancement of

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(12) Wang, Y.; Suna, A.; Mahler, M.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315.

(13) Miyoshi, H.; Yoneyama, H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1873.

(14) Abe, T.; Tachibana, Y.; Uematsu, T.; Iwamoto, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1617.

light absorption being theoretically predicted for quantum-sized semiconductors. On the basis of calculation of the extinction coefficients from the absorption intensities, the enhancement should be at least 23 times, assuming no volatilization of Fc during firing (this assumption yields the lower limit of enhancement).

Since the Fe_2O_3 particles were not observable via TEM, we tried to introduce a heavier metal element, Pd, into the channels via solubilization into the templating micelles. Since Pd-acac was revealed to be unsuitable, probably because of its low decomposition temperature, $Pd(NH_3)_2Cl_2$, which begins to decompose at 210 °C, was employed as a hydrophobic Pd precursor. This allowed us to find a Pd (or PdO) particle of ca. 3 nm in diameter located in the channel of MCM-41 observed from the direction perpendicular to the *c* axis. However, the Pd loading appears to be extremely small at present, suffering from the very limited solubility of $Pd(NH_3)_2Cl_2$ in the micellar solution. A study of the anisotropic growth of the secondary inorganic phase along the one-dimensional channels of MCM-41 is currently under way.

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