Metal Ion-Planted MCM-41. 1. Planting of Manganese(II) Ion into MCM-41 by a Newly Developed Template-Ion Exchange Method

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Much effort has been devoted to applying a new mesoporous material termed MCM-41 as catalysts,[1] since it has excellent features of well ordered hexagonal arrays of uniform channels with controllable nanoorder pore diameter and of high surface area.[2,3] The most significant disadvantage of the present MCM-41, however, is that there are few catalytically active sites on its amorphous SiO_2 wall. This is in contrast to the fact that zeolites usually possess a large number of isolated active sites. The introduction of metal ion other than Si^{4+} is thus required to use MCM-41 as a possible catalyst.

Many kinds of metal ions[4−19] have been tried to be incorporated into the wall of MCM-41 through hydrothermal syntheses with mixed gels of various silica sources and metal cations. In the case of Mn^{2+} two kinds of assembly systems, that is, surfactants (S^+) and silicate precursors (I^-) assembly (S^+I^-)[5,12] and counterion-mediated assembly ($S^+X^-I^+$, where $X^- = Cl^-$ or Br^-),[9] have been employed to prepare Mn−MCM-41. The Mn^{2+} species, however, is suggested not to locate within the silica wall on the basis of the pale-pink color of products[5] and the high mobility of the Mn^{2+} ions detected by ESR.[12] Another way to prepare Mn-containing MCM-41 is to use Al−MCM-41 because Al−MCM-41 has been clarified to have ion-exchange capacity.[6,7] Due to the amorphous SiO_2 wall, the acid strength of Al−MCM-41 is not so great[20] and therefore the Mn^{2+}−silica bonds produced through the ion exchange of surface hydroxyl groups would not be so strong. At present, thus no method has been reported to prepare MCM-41 containing Mn^{2+} ion stabilized on or in the inorganic wall. Our attention has been focused on development of a novel method to prepare metal-containing MCM-41 with convenience. We wish here to report a newly developed "template-ion exchange" (TIE) method, in which the template ions of as-synthesized MCM-41 can be exchanged for Mn^{2+} ions in an aqueous solution. Characterization of the resulting Mn−MCM-41 are also carried out.

The parent MCM-41 was prepared in the manner previously reported by using $C_{12}H_{25}N(CH_3)_3Br$ as the template.[21] The white solid product obtained was washed with deionized water at ambient temperature and dried at 353 K for 1 h. The as-synthesized MCM-41 consisted of 60 wt % of SiO_2 and 40 wt % of organic surfactant and underwent the following TIE treatment to yield manganese ion-containing MCM-41. The as-synthesized MCM-41 (2.00 g) was vigorously stirred in 40 mL of the aqueous solution of manganese(II) acetate tetrahydrate (5.0×10^{-2}−1.3×10^{-3} mol dm^{-3}) at ambient temperature for 1 h. The mixture was kept at 353 K in a water bath for 20 h without stirring, and then the resulting solid was filtered, washed with deionized water, and dried at 353 K for 1 h. The samples obtained (as-synthesized Mn−MCM-41) is faintly reddish white in color. Finally, to remove the remaining template ions, the sample was heated in air at a heating rate of 5 K min^{-1} to 423 K and then at a rate of 0.2 K min^{-1} to 873 K and calcined at the same temperature for 6 h. Pale-brownish gray Mn−MCM-41 was obtained. The pure-silica MCM-41 was prepared by calcining the as-synthesized MCM-41 at 873 K for 6 h in air and was white in color.

The content of manganese in Mn−MCM-41 was determined by inductively coupled plasma emission spectrometry (ICP; Perkin-Elmer, Optima 3000). The amount of template ions was evaluated by measuring weight loss at 410−683 K in thermogravimetry analysis (TG-DTA; MAC Science, TG-DTA 2000S). X-ray powder diffraction patterns (XRD; MAC Science, MXP3, Cu Kα), N_2 adsorption−desorption isotherms at 77 K (Quanta Chrome, Autosorb-1) and transmission electron micrograph images (TEM; JEOL, JEM-1200EXII) were also taken to characterize the materials obtained. Electron spin resonance spectra (ESR; JEOL, JES−FE1XG) were measured at ambient temperature in air to elucidate the state of Mn^{2+} ion on Mn−MCM-41.

Figure 1 shows XRD patterns of pure-silica MCM-41 and Mn−MCM-41 with various Si/Mn ratios. The patterns of Mn−MCM-41 are all similar to that of pure-silica MCM-41. The relative intensities of the (100) diffraction of Mn−MCM-41, listed in Table 1, indicate that no significant destruction occurred during the TIE treatment. This was also confirmed by BET surface

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Table 1. Physicochemical Properties of Prepared Mn−MCM-41 and Pure-Silica MCM-41

manganese content in solution (Si/Mn)	Mn^{2+} concn in solution (mol dm^{-3})	manganese content in Mn−MCM-41 obtained (Si/Mn[a])	rel intensity of (100) XRD diffraction	surface area (m^2 g^{-1})	pore diam (nm)
10	5.0×10^{-2}	20	96	949	2.24
25	2.0×10^{-2}	28	107	1020	2.24
50	1.0×10^{-2}	42	107	1100	2.24
75	6.7×10^{-3}	63	117	1100	2.24
100	5.0×10^{-3}	70	102	1090	2.24
125	4.0×10^{-3}	110	113	1060	2.24
150	3.3×10^{-3}	130	107	1080	2.25
200	2.5×10^{-3}	170	124	1130	2.24
400	1.3×10^{-3}	320	107	1120	2.24
pure-silica MCM−41			100	1070	2.24

[a] Determined by ICP analysis after each sample was dissolved into a HF solution.

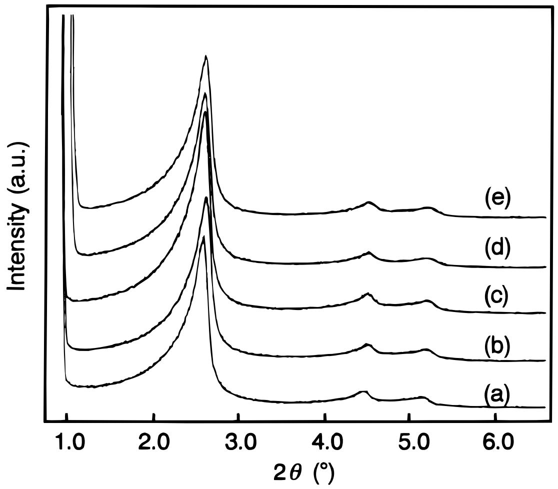

Figure 1. XRD patterns of (a) Mn−MCM-41 with Si/Mn = 28, (b) Si/Mn = 63, (c) Si/Mn = 170, (d) Si/Mn = 320, and (e) pure-silica MCM-41.

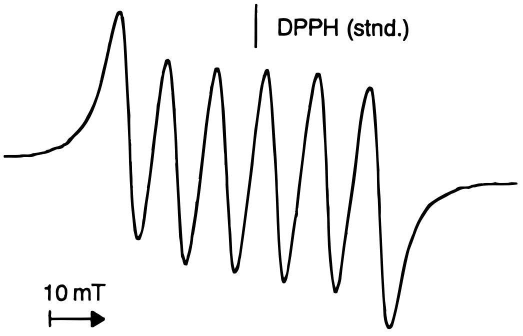

Figure 2. ESR spectrum of Mn−MCM-41 with Si/Mn = 20 measured at ambient temperature after the calcination at 873 K for 6 h.

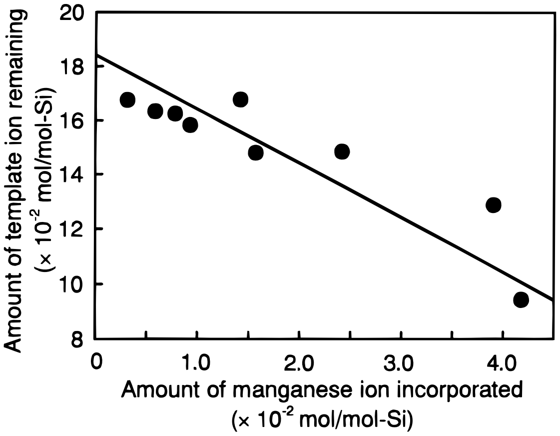

Figure 3. Relationship between the amounts of template ion remaining and of manganese ion incorporated.

areas and pore diameters as clearly shown in Table 1. All the samples, except for the sample of Si/Mn = 20, showed surface areas of about 1100 m^2 g^{-1}. The pore diameter distribution of each sample, which was determined from N_2 adsorption isotherm by BJH method, showed a narrow and single peak at 2.24 nm. The TEM measurements at the magnitude of 10^6 revealed the presence of hexagonal array of mesopores both in the pure-silica MCM-41 and in Mn−MCM-41. In addition, no particle of manganese oxide was able to be observed in any Mn−MCM-41. The ESR spectrum of Mn−MCM-41 (Si/Mn = 20, after calcination at 873 K), depicted in Figure 2, exhibits a typical Mn^{2+} signal with a hyperfine coupling constant of 9.4 mT and $g \approx 2.00$. Each sample prepared here gave the similar spectrum though its intensity is different. It should be noted that the spectrum in Figure 2 is similar to that reported by Zhao and Goldfarb.[12]

Table 1 clearly concludes that the amount of manganese in Mn−MCM-41 could be controlled by changing the concentration of Mn^{2+} ion in the solution. The maximum content of manganese was Si/Mn = 20 (Mn = 2.9 wt %) within the present experiments.

The amount of template ion remaining in the as-synthesized Mn−MCM-41, determined by TG-DTA, were compared with the amount of Mn^{2+} ion incorporated in Figure 3. The amount of Mn^{2+} ion planted on MCM-41 was in reverse proportion to that of template ion remaining. The slope of the line drawn in Figure 3 is −2, which concludes that there occurs the stoichiometric exchange between two template ions (+1 ion) and one Mn^{2+} ion (+2 ion), though the detail of the present exchange mechanism remains uncertain. The progress of the ion exchange between the template ions and the Mn^{2+} ions was further supported by the following experiments.

The present TIE method was compared with the traditional ion-exchange with surface hydroxyl groups of calcined MCM-41 in an aqueous solution. The pure-silica MCM-41 calcined at 873 K was suspended into the Mn^{2+} solutions (Si/Mn = 75 and 200) at ambient temperature for 1 h and then kept at 353 K for 20 h without stirring. The solids were subsequently filtered, washed, dried at 353 K for 1 h, and calcined at 873 K for 6 h. The respective Si/Mn ratio of the Mn−MCM-41 obtained were 500 and 540. The relative intensities of the (100) XRD diffraction of the resulting Mn−MCM-41 were decreased to 0.76 and 0.73 of that of the parent MCM-41. In addition, the (110) and (200) diffractions could scarcely be detected, in contrast to their clear appearance of TIE samples (Figure 1). The findings conclude that adsorption/absorption of Mn^{2+} ions onto the surface of MCM-41 or ion exchange between Mn^{2+} ion and surface hydroxyl group proceeds slightly under the present experimental conditions.

Finally the stability and location of Mn^{2+} ion in the calcined Mn−MCM-41 will be discussed. The calcined Mn−MCM-41 (Si/Mn = 77) was stirred in deionized water at ambient temperature for 1, 5, and 24 h. After filtration, the resultant Mn−MCM-41 showed the same Si/Mn ratios as that of parent Mn−MCM-41 within an experimental error and manganese and silicon were detected slightly in each filtrate. This indicates the great stability of manganese ions in Mn−MCM-41. In the ESR measurements of Mn^{2+}-substituted silicoaluminophosphates (SAPO), the spectra with the coupling constants of 6.5 and 9.0 mT have been assigned to Mn^{2+} in tetrahedral and octahedral coordination in the framework, respectively.[22,23] The present value of 9.4 mT is very close to the latter. These facts suggest that the Mn^{2+} ion is in an octahedral coordination and tightly bound to the framework of MCM-41, though it is uncertain whether Mn^{2+} is in the framework of MCM-41 or not.

It follows that Mn−MCM-41 can be effectively prepared through "template-ion exchange" method without any collapse of mesopore and the amounts of manganese ion planted can be controlled by the concentration of Mn^{2+} in the solution. The TIE method is expected to be employed for preparation of various metal ion-loaded MCM-41 with ease.

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