

A Novel Ion Exchange Method to Modify Mesoporous Molecular Sieve Al-FSM-16 by Cobalt-Complex

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A novel ion exchange method of modifying mesoporous material, Al-FSM-16, has been found and applied to preparation of functional Al-FSM-16 containing Co-Salen inside the pores. The method is characterized in that the Co^{2+} ion exchange, which is followed by chelation with Salen H_2 , is performed in a nonaqueous glacial acetic acid solution of cobalt(II) acetate. The lattice regularity and pore structure of Al-FSM-16 are retained through the modification as evidenced by XRD, TEM and N_2 adsorption measurements at 77 K. This non-destructive modification method is significant, since conventional ion exchange methods using aqueous solutions always cause severe damages to the framework structure of Al-FSM-16.

Mesoporous materials, the pore sizes of which are 2 to 50 nm, have become of interest in several applications such as selective separation of macromolecules and restricted reaction of large molecules which cannot enter the pores of conventional microporous zeolites. Since mesoporous material, FSM-16,^{1,2} has a regular hexagonal arrays of unidimensional pores similar to prominent mesoporous material MCM-41,³⁻⁵ it has been studied as model substance of gas adsorption in mesopores and catalysis support like other mesoporous analogues.⁶ However, because of the thinness of the wall, the mesoporous structure of FSM-16 easily collapses through hydrolysis of siloxane bonds in the presence of water.^{7,8} Thus a nonaqueous treating method is required to incorporate transition metals into the mesopores.

Co-Salen (*N,N*-disalicylalethylenediamine cobalt(II)), which is a reversible oxygen carrier at an ambient temperature, has been prepared in the supercages of microporous faujasite, by Co^{2+} ion exchange followed by chelation with Salen H_2 .⁹ Since the pore size of FSM-16 (for example 3.2 nm) is much larger than that of faujasite (0.7-1.3 nm), Co-Salen (0.6-0.9 nm) would be easily included in the pores of FSM-16 with enough space for diffusion of other molecules such as oxygen.

Here, we report a novel ion exchange of Al-containing FSM-16 (Al-FSM-16) using a nonaqueous glacial acetic acid solution of cobalt(II) acetate. This technique, followed by chelation with Salen H_2 , successfully retains the regular arrays of FSM-16 after a through Co-Salen modification.

Mesoporous Al-FSM-16 was synthesized from Al-containing kanemite using hexadecyltrimethylammonium chloride as a templating agent by known procedures.² The surfactant was burnt off in an air flow at 823 K for 5 h.

The modification of Al-FSM-16 with Co-Salen was performed as described below. In the first step, Al-FSM-16 was heated in vacuo at 773 K for 5 h, cooled to room temperature, immersed in a nonaqueous glacial acetic acid solution of cobalt(II) acetate, and stirred at room temperature for 2 h. The cobalt(II) acetate solution was prepared in advance by dissolving anhydrous cobalt(II) acetate in glacial acetic acid to

give 0.11 mol L^{-1} solution. This solution was clear and pale purple suggesting that Co^{2+} ions were dissolved without coordination with water.

The resulting suspension was filtered, washed with neat glacial acetic acid, dried, and the filtrate was, in the second step, dispersed into an excessive Salen H_2 /1-propanol solution (0.075 mol L^{-1}) with stirring at 333 K for 2 h. After cooled, thus formed orange-red suspension was filtered and the residual solid was washed with cyclohexane to remove excessive Salen H_2 . The sample was refluxed in 1-propanol at 353 K for 1 h to remove non-chelated Salen H_2 and non-fixed Co-Salen. Finally, these impurities were extracted with methylene chloride for 24 h. All procedures were carried out under a dry nitrogen atmosphere. The sample prepared by the novel method was colored deep orange and denoted as Co-Salen-Al-FSM-16.

Usual ion exchange procedure was comparatively carried out by use of an aqueous solution of cobalt(II) acetate. Al-FSM-16 was put in a 0.11 mol L^{-1} aqueous solution of cobalt(II) acetate, stirred at 313 K for 2 h, filtered and washed with distilled water. The ion exchanged sample was dried and then evacuated at 723 K for 5 h. The chelating procedures were the same as above. The sample obtained by this conventional method was colored deep orange and denoted as Co-Salen-Al-FSM-16-C.

The regularity of the mesoporous structure of the prepared samples was assessed by use of XRD and inspected. Chemical compositions were determined by ICP. Nitrogen adsorption isotherms at 77 K were volumetrically measured. Pore arrays of the samples were observed by TEM.

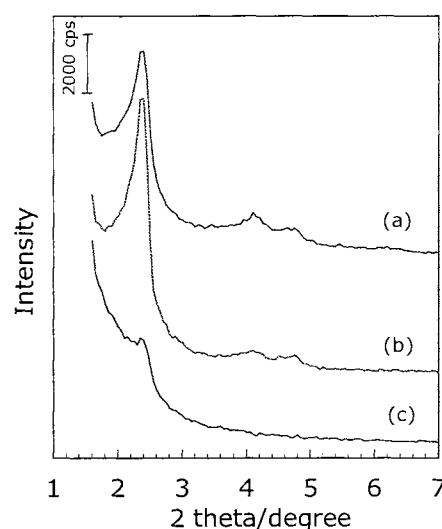


Figure 1. XRD patterns ($\text{CuK}\alpha$) of (a) Al-FSM-16, (b) Co-Salen-Al-FSM-16 and (c) Co-Salen-Al-FSM-16-C.

The amount of Co in Co-Salen-Al-FSM-16 was 0.22 mmol g^{-1} , corresponding to 43% of equivalents of exchangeable cation sites (1.02 mmol g^{-1}). The cobalt contents in the modified Al-FSM-16 were essentially the same irrespective of the ion exchange methods. The Co/Salen ratio in Co-Salen-Al-FSM-16 was 1, calculated from the carbon content determined by elemental analysis. Since an IR band around 1530 cm^{-1} disappeared on inclusion, the intramessoporous Co-Salen would be fixed to pore walls through some interactions of the aromatic rings with the walls, presumably with silanols.

The XRD pattern of Co-Salen-Al-FSM-16 shown in Figure 1 has Bragg peaks at $2\theta = 2.4, 4.1$ and 4.7° assigned to reflections from (100), (110) and (200) directions of hexagonal pore array, respectively. Since this resembles the features of the XRD pattern of Al-FSM-16, the hexagonal structure of Al-FSM-16 is considered to be retained after the modification by Co-Salen. No XRD peaks of Co-Salen crystals were observed. The XRD peaks of Co-Salen-Al-FSM-16-C were very weak, and even the main peak at $2\theta = 2.4^\circ$ could be hardly recognized. This result agrees with the finding by Tatsumi et al. that Si-O-Si bonds of FSM-16 were hydrolyzed by adsorbed water to lower the regularity of the mesoporous structure.^{7,8}

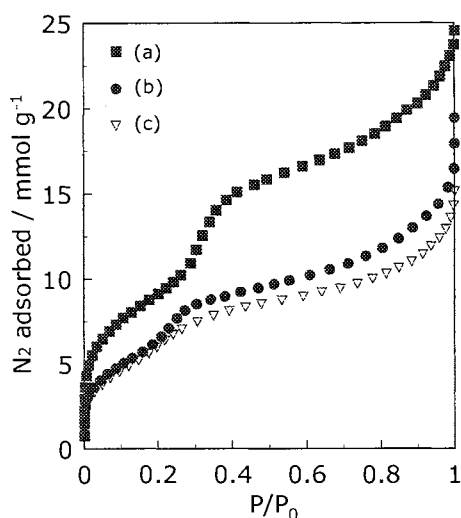


Figure 2. N_2 adsorption isotherms of nitrogen on (a) Al-FSM-16, (b) Co-Salen-Al-FSM-16 and (c) Co-Salen-Al-FSM-16-C at 77 K.

The adsorption isotherm for Al-FSM-16 shown in Figure 2, was of Type IV, typical for adsorption on mesoporous materials. A steep step at $P/P_0 = \text{ca. } 0.3 \sim 0.4$ due to capillary condensation of nitrogen in mesopores was clearly observed. In the case of Co-Salen-Al-FSM-16, the steep step at $P/P_0 = \text{ca. } 0.4$, became more gentle and slightly shifted to lower P/P_0 , but the Type IV character still remained. On the other hand, the comparative isotherm of Co-Salen-Al-FSM-16-C severely lost the Type IV character and rather showed Type II character often observed for non-porous solids.

Figure 3(A) shows the TEM image of Co-Salen-Al-FSM-16. Clear hexagonal arrays of mesopores are observed. This result suggests that the regular mesoporous structure is retained even after the Co-Salen modification. In the image of Co-Salen-Al-FSM-16-C, shown in Figure 3(B), additional fibrous structure is observed and the lowering of the regularity of the pore arrays is

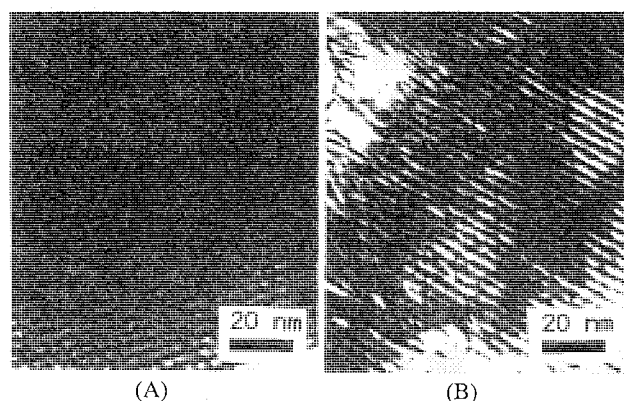


Figure 3. Transmission electron micrographs of (A) Co-Salen-Al-FSM-16 and (B) Co-Salen-Al-FSM-16-C.

detected. The conventional ion exchange procedure would have brought about the collapse of hexagonal arrays of mesopores along the c-axis to give the fibrous fragments. Such findings based upon the TEM images agree with the results of the nitrogen adsorption isotherms and XRD.

The regular mesoporous structure of FSM-16, is easily collapsed by water in an ambient atmosphere.⁷ In the novel ion exchange process, cobalt(II) acetate dissolved in glacial acetic acid releases Co^{2+} ions. At the moment, ligand species around Co^{2+} ions are unknown, but it is believed that they are not water, since the color of the solution is different from that of Co^{2+} ions coordinated with water. Thus the ion exchange by Co^{2+} ions would take place without hydrolysis of the walls of the mesoporous structure in the novel process. In the usual ion exchange process using an aqueous solution of cobalt(II) acetate, the siloxane bonds would be attacked by water molecules and the framework of Al-FSM-16 might be collapsed by the plausible hydrolysis.

In conclusion, we have established a novel ion exchange technique which provides modified Al-FSM-16 with its regular arrays of mesopores retained. Application of this technique to the preparation of Co-Salen-Al-FSM-16 was successful in retaining the siloxane bonds of Al-FSM-16. Characterization of selective adsorptivity of oxygen by well-constructed Co-Salen-Al-FSM-16 is in progress.

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