

Photoacoustic Spectroscopic Study on Cobalt Incorporation onto the Surface of Mesoporous Molecular Sieves

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The incorporation of cobalt into mesoporous molecular sieves MCM-41 and MCM-48 was carried out. Co-PO/MCM41 and Co-PO/MCM48 were prepared using Co(II) acetate solution adjusted to pH = 3.0 with phosphoric acid by the incipient wetness method. Photoacoustic spectroscopy (PAS) was used to study the local environments of Co(II) incorporated into mesopores. The band around 500 nm in PAS of as-prepared Co-PO/MCM41 and Co-PO/MCM48 with Co(II) acetate solution was changed to triplet bands around 600 nm. This could be assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of Co(II) surrounded tetrahedrally by oxygen ions after calcination. It may be attributable to that the octahedral cobalt species containing phosphate ligands in coordination sphere reacting with framework's silanol groups to be dispersed atomically onto the surface of mesoporous molecular sieves as a tetrahedral species. This is unlike that the Co in Co-Cl/MCM41 and direct-synthesized Co-MCM41 transforms to Co oxide phase upon calcination. Co-PO/MCM41 and Co-PO/MCM48 were stable while treated with water.

Introduction

Since the development of MCM-41, MCM-48, and MCM-50, which is designated as M41S by Mobil in 1992,¹ mesoporous materials permit new possibilities for the application as catalyst for bulky molecules, support for various transition metal compounds, and as host lattice for nanometer-sized materials. Molecular sieves containing redox active metals are used as active catalysts for the oxidative transformation of organic molecules. The incorporation of hetero-element into siliceous framework to modify the catalytic properties of the surface of mesoporous materials has been reported. MCM-41 exhibits a hexagonal array of one-dimensional uniform mesopores. The pore diameter can be tuned over 15-100 Å. Various metals such as B,² Al,³ Ga,⁴ Ti,⁵ V,⁶ Cr,⁷ Mn,⁸ Fe,⁹ Co,¹⁰ Sn,¹¹ and Zr¹² can be incorporated into the silica framework by the addition of metal sources. MCM-48 has a cubic $Ia\bar{3}d$ structure. MCM-48^{1b} has an advantage in catalytic application due to three-dimensionals in the cubic bicontinuous structure. The reports on MCM-48 are, however, very limited¹³ compared with MCM-41, probably due to the difficulty of its synthesis.

The quality of mesoporous materials is, in general, deteriorated by the addition of hetero-elements. Jentys *et al.*¹⁰ have reported the preparation of highly dispersed and stable Co clusters in MCM-41 using a direct synthesis method. A route to preparation of mesoporous metallosilicates via post-synthetic metal incorporation into frameworks of siliceous mesoporous materials has been suggested by Ryoo *et al.*, in order to overcome the quality deterioration.¹⁴ However the incorporation of Co into the MCM-41 lattice has not been observed.

The goal of this work is to incorporate atomically dispersed Co(II) onto the surface of high quality MCM-41 and MCM-48 using the incipient wetness with Co(II) aqueous solution containing phosphoric acid, similar to the post-syn-

thetic incorporation of Al, Zn and Sn by Ryoo *et al.*¹⁴ The samples thus prepared have been characterized using photoacoustic spectroscopy (PAS) for the local environment of Co, and X-ray diffraction (XRD), Brunauer-Emmett-Tellar (BET) surface area and pore size distribution.

Experimental Section

The chemicals used in the synthesis were fumed silica (99.8%, metal free, Sigma), cetyltrimethylammonium bromide (CTABr) (99%, Fisons) and tetramethylammonium (TMA) hydroxide (25 wt.% aqueous solution, Aldrich). Purely siliceous MCM-41 was synthesized following the literature procedure.¹⁵ TMAOH and CTABr were added to deionized water with stirring at 30 °C until the solution became clear. Then the fumed silica was added to the solution with stirring for 1 h. The molar composition of the final reaction gel, which is aged for 24 h at 20 °C, was 1.0 SiO₂ : 0.19 TMAOH : 0.27 CTABr : 40 H₂O. After aging, the mixture was reacted for 48 h at 150 °C in a Teflon-lined stainless steel autoclave. The product was filtered, washed with distilled water, dried in air at 60 °C and finally calcined at 550 °C for 8 h. MCM-41 from Co containing reaction mixture, which is designated by Co-MCM41, was synthesized by the same procedure as siliceous MCM-41 except for the addition of cobalt acetate as a source of cobalt.

Purely siliceous MCM-48 was synthesized following the literature procedure.^{13b} The sodium silicate solution was prepared using colloidal silica (Ludox HS40 (39.5 wt.% SiO₂, 0.4 wt.% Na₂O, and 60.1 wt.% H₂O), Aldrich) added to the heated NaOH solution, whose molar composition is 0.25 Na₂O : 1.0 SiO₂ : 12.5 H₂O. This solution was added to the autoclave containing the surfactant solution of a mixture of CTABr, ethanol, and H₂O. The molar composition of the resultant gel mixture was 1.4 SiO₂ : 1.0 CTABr : 0.35 Na₂O : 5.0 EtOH : 140 H₂O. The mixture was heated for 16 h at 413

K. After additional treatment with NaCl solution for improvement of hydrothermal stability, the product was then slurried in an ethanol-HCl mixture (0.1 mol of HCl per L of ethanol), filtered, washed with ethanol, dried in an oven, and calcined in air at 550 °C for 8 h.

XRD patterns were recorded using a Philips 1710 powder diffractometer with Cu K α radiation (40 kV, 40 mA), 0.02° step size and 1 s step time. N₂ adsorption isotherms were measured at -196 °C using a gas sorption analyzer (Quantachrome Corp., Nova-2000). Before the experiments, samples were dehydrated at 350 °C for 12 h. The volume of adsorbed N₂ was normalized to the standard temperature and pressure. The calculation of the pore size distribution (PSD) was performed using the Barrett-Joyner-Halenda (BJH) formula.¹⁶ The cumulative surface area of the mesopores was obtained from PSD curves.

To prepare Co-incorporated MCM-41, 0.1 g of MCM-41 was wetted and stirred for 5 h with 1 mL of cobalt(II) acetate (99%, Fluka) solution of pH = 3.0 controlled with phosphoric acid (85%, Junsei) or hydrochloric acid (35%, Osaka), and then dried at 313 K for 12 h, afterward calcined at 973 K for 3 h. The resultant sample treated with H₃PO₄ was designated Co-PO/MCM41 and another, treated with HCl, Co-Cl/MCM41. The concentration of cobalt acetate solution was varied from 0.01 M to 0.14 M. The Co-incorporated MCM-48 which is designated Co-PO/MCM48 was prepared using the same procedure as used for MCM-41.

The method for UV-Vis spectrum of a powdered sample using home-made photoacoustic spectrometer was described in more detail in other literature.¹⁷ PAS was recorded in the range of 350-800 nm and normalized by that of carbon black as a reference at the modulation frequency of 30 Hz.

Results and Discussion

The quality of MCM-41 and MCM-48 was confirmed by XRD and N₂ sorption measurement. The XRD pattern of

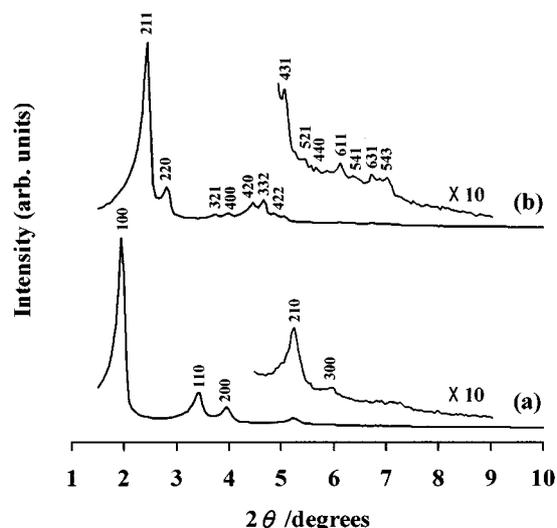


Figure 1. X-ray diffraction patterns of calcined (a) MCM-41 and (b) MCM-48.

MCM-41 (Figure 1(a)) reflects the high quality of the crystallites. The (100) peak is sharp and intensive. The (110) and (200) peaks are well resolved, and even the (300) peak is observed clearly. The calcined MCM-41 has a d_{100} value of 44.4 Å, a pore diameter of 32.5 Å, and a BET surface area of 1185 m²/g. The XRD pattern of MCM-48 (Figure 1(b)) shows typical peaks of the cubic crystallographic space group $Ia\bar{3}d$, which indicates that the crystallites are particularly well-developed. The calcined MCM-48 has a pore diameter of 26.4 Å and a BET surface area of 972 m²/g as shown in Figure 2.

Figure 3 shows photoacoustic spectra (PAS) for as-prepared Co-MCM-41 having Si/Co ratios of 50 and 100, respectively. The band at 500 nm which is characteristic of [Co(H₂O)₆]²⁺ could be assigned to the presence of cobalt in

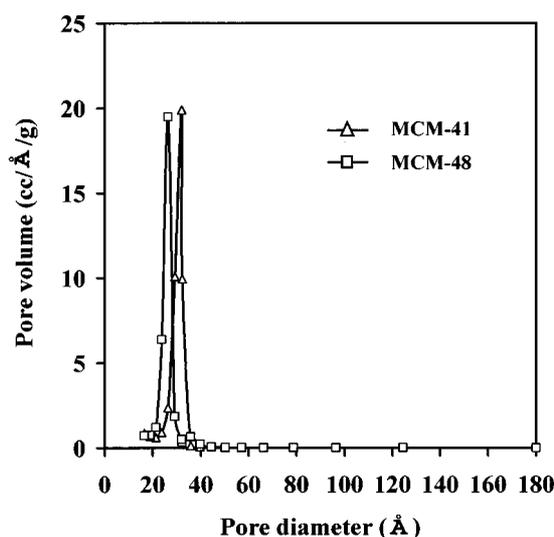


Figure 2. Pore size distribution curves for MCM-41 and MCM-48 calculated from the desorption branch of the nitrogen adsorption isotherm using the BJH formula.

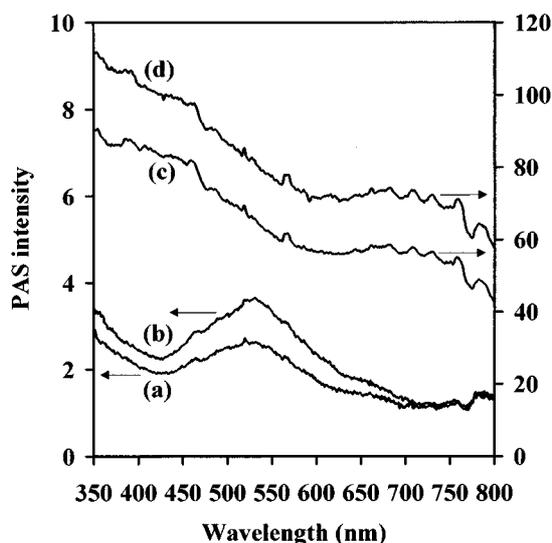


Figure 3. PA spectra of as-synthesized Co-MCM-41 from reaction gels with Si/Co molar ratios of (a) 100 and (b) 50 and calcined Co-MCM-41 with (c) 100 and (d) 50, respectively.

the octahedral environment.¹⁸ During calcination at 550 °C, the extraframework Co oxide species appeared, as reported by Jentys *et al.*¹⁶ The color of the sample changed to a light grey and the PAS intensity increased drastically for all ranges of 350–800 nm, which is similar to the spectra for the mechanically-mixed MCM-41 with Co oxide. These results indicate that Co in Co-MCM41 synthesized from a reaction gel containing a cobalt source was not incorporated in the framework of MCM-41.

Figure 4 shows PAS for Co-Cl/MCM41 treated with 0.04 M-cobalt acetate solution at pH = 3.0 controlled with HCl. The PAS for the dried sample (Figure 4(a)) exhibits a band around 520 nm, corresponding to an octahedral Co(II), and a triplet band around 650 nm, corresponding to a tetrahedral Co(II). Though both intensities are nearly the same value, the major portion of Co(II) is present at an octahedral environment since the molar absorptivity of the octahedral Co(II) is an order of magnitude lower than that of the tetrahedral species. After degassing in a vacuum of ca. 1×10^{-3} Torr. (Figure 4(b)), the intensity of the triple band, which is deconvoluted to three bands of $\lambda_{max} = 626$ nm, 669 nm, and 692 nm, increases significantly and the band around 521 nm is weakened. This can be attributed to the change to a tetrahedral geometry due to the removal of water molecules in octahedral complexes during degassing in vacuum. For a d^7 ion such as Co(II), ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent for weak field ligand such as Cl⁻. This triplet band, which is assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of Co(II) ion, is responsible for the formation of the chloride-containing tetrahedral complex.¹⁹ During calcination in air at 700 °C for 3 h (Figure 4(c)), the Co oxide

cluster resulted from the thermal transformation of cobalt complexes and tetrahedral Co(II) complexes grafted to the surface of MCM-41 appeared.

The increase of PAS intensity in all ranges is a result of the formation of extraframework Co oxide cluster and the broadened triplet band due to tetrahedral Co(II) complexes. This triplet band is deconvoluted to three bands of $\lambda_{max} = 519$ nm, 584 nm, and 640 nm, respectively, which is assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of Co(II) ion surrounded tetrahedrally by oxygen ions.¹⁹ This band is not symmetric and shows larger splitting on the high-energy side larger than on the low-energy side, similar to Co(II) in sodium silicate glass,²⁰ on Zeolite A,²¹ and on the surface of CoZSM-5.²² The ligating oxygen makes a stronger field than chloride, thus the triplet band of the calcined sample was blue-shifted and broadened compared with chloride-containing tetrahedral complexes. When the sample was suspended into water and then dried at 60 °C, the triplet band disappeared completely with retention of background, as shown in Figure 4(d). These results indicate that the tetrahedral complex formed is on the surface and is accessible for water adsorption. Subsequently, recalcination at 700 °C for 3 h, however, the triplet band recovered nearly completely with a slight increase in the background corresponding to the Co oxide cluster (Figure 4(e)).

Figure 5 shows PAS for Co-Cl/MCM41 samples treated with 0.02 M-, 0.04 M-, and 0.08 M-cobalt acetate solution under the same condition. The intensity of triplet band was remained nearly constant, indicating that the amount of tetrahedral Co(II) on the surface of MCM-41 is limited due to the silanol concentration. On the contrary, the background intensity increases proportionally with the concentration of cobalt source, which is attributable to the formation of the Co oxide cluster resulted from a residual Co.

In order to obtain the highly dispersed Co-containing MCM-41 without the formation of Co oxide clusters, we

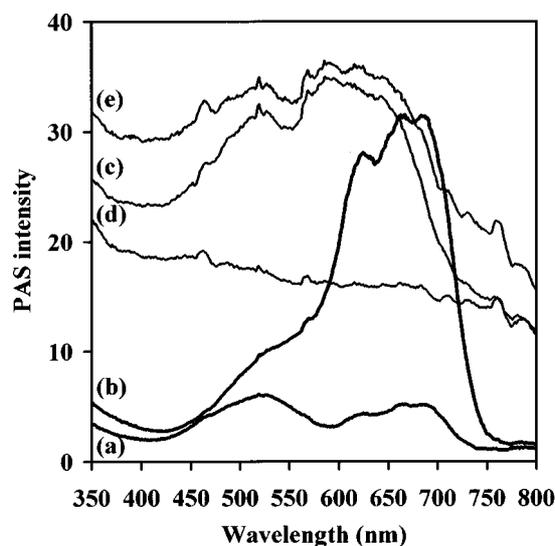


Figure 4. PA spectra of (a) Co-Cl/MCM41 treated with 0.04 M-Co acetate solution at pH = 3.0 controlled with HCl, and dried 40 °C for 12 h, (b) sample (a) placed in a vacuum (ca. 10^{-3} torr) at room temperature for 1.5 h, (c) sample (a) calcined in air at 700 °C for 3 h, (d) sample (c) placed in air at 80 °C for 12 h after suspending with H₂O at room temperature for 3 h, and (e) sample (d) recalcined in air at 700 °C for 3 h.

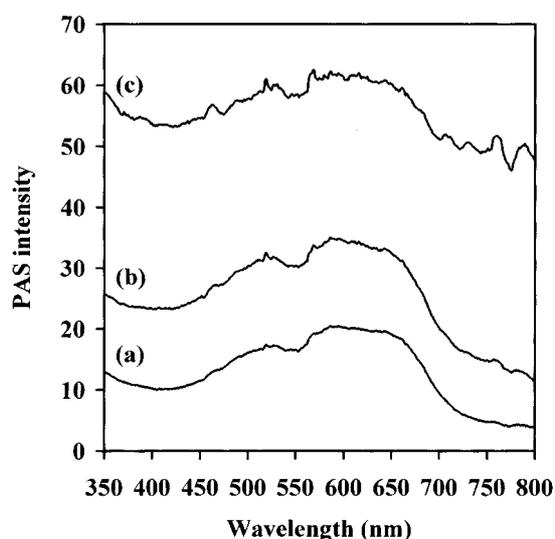


Figure 5. PA spectra of calcined Co-Cl/MCM41 in air at 700 °C for 3 h after treated with (a) 0.02 M-, (b) 0.04 M-, and (c) 0.08 M-Co acetate solution at pH = 3.0 controlled with HCl.

have investigated the effect of phosphoric acid, which not only can react with the silanol group on the surface of MCM-41, but also coordinate to cobalt ion simultaneously. Figure 6 shows PAS for Co-PO/MCM41 treated with 0.04 M-cobalt acetate solution at pH = 3.0 controlled with H₃PO₄. PAS's for a dried sample and a degassed one in a vacuum (Figures 6(a) and (b)) exhibit a band around 520 nm corresponding to an octahedral Co(II). The triplet band around 600 nm due to a tetrahedral one is absent. It seems that Co(II) is coordinated octahedrally by six ligating oxygen atoms in water molecules, silanol groups or phosphate ions. After calcination in air at 700 °C for 3 h (Figure 6(c)), the triplet band due to tetrahedral Co(II) complexes appeared without rising of background indicative of the Co oxide phase. This triplet band is also deconvoluted to three symmetrically spaced bands of $\lambda_{max} = 534$ nm, 582 nm, and 632 nm, which is assigned to the $^4A_2(F) \rightarrow ^4T_1(P)$ transition of Co(II) ion surrounded tetrahedrally by oxygen ions.¹⁹ This highly symmetric triplet band, as compared with that of HCl treatment sample, is similar to that of Co(II) isomorphously substituted to the framework of as-synthesized CoAPO-5²³ and CoAPO-39.²⁴ The narrowing of triplet band may be due to coordination by oxygens bonded to phosphorous, which is more electronegative than silicon, in a phosphate ion anchored on the surface of MCM-41. The symmetric triplet band was retained during recalcination after suspension in water at room temperature for 3 h. This indicates that most of Co in mesoporous MCM-41 is very stable and atomically dispersed without the formation of Co oxide cluster due to the phosphate ions, which are well known as ligands of monodentate, chelating, or bridging types. All Co-PO/MCM41 samples have a ratio of P to Co on the range of 2.8-3.7, which is measured using EDX(KEVEX Corp., KEVEX

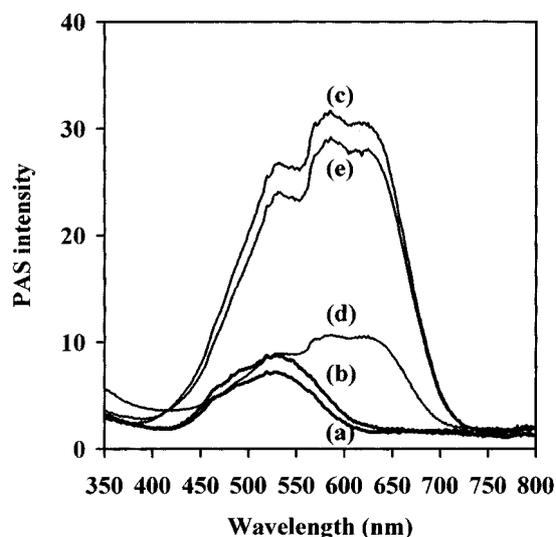


Figure 6. PA spectra of (a) Co-PO/MCM41 treated with 0.04 M-Co acetate solution at pH = 3.0 controlled with H₃PO₄, and dried 40 °C for 12 h, (b) sample (a) placed in a vacuum (ca. 10⁻³ torr) at room temperature for 1.5 h, (c) sample (a) calcined in air at 700 °C for 3 h, (d) sample (c) placed in air at 80 °C for 12 h after suspending with H₂O at room temperature for 3 h, and (e) sample (d) recalcined in air at 700 °C for 3 h.

superdry detector).

Figure 7 shows PAS for Co-PO/MCM41 samples treated with 0.01 M-, 0.02 M-, and 0.04 M-cobalt acetate solution under the same conditions. The intensity of PAS at 632 nm increases linearly with the content of Co in MCM-41 until being treated with 0.04 M-solution but remains constant at concentrations higher than 0.04 M (an inset in Figure 7), which can be taken as an additional evidence for the Co(II) in a tetrahedral coordination stabilized on the surface of MCM-41 by phosphate ligands. Kraushaar-Czarnetzki *et*

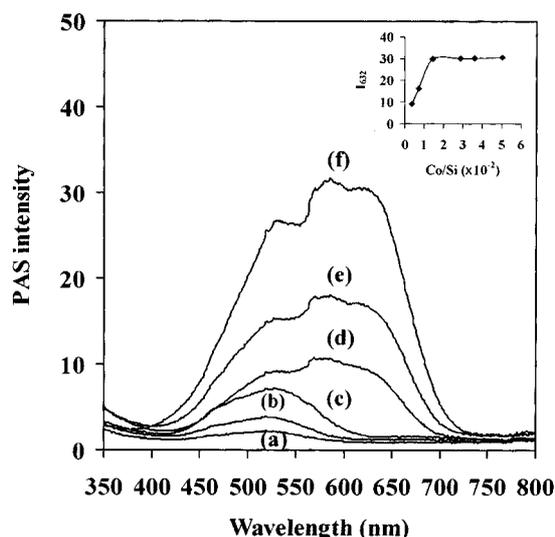


Figure 7. PA spectra of Co-PO/MCM41 treated with (a) 0.01 M-, (b) 0.02 M-, and (c) 0.04 M-Co acetate solution at pH = 3.0 controlled with H₃PO₄, and dried 40 °C for 12 h, and calcined Co-PO/MCM41's ((d), (e), and (f)) with sample (a), (b), and (c), respectively. The inset shows the intensity of the PAS band at 632 nm with the Co content in Co-PO/MCM-41.

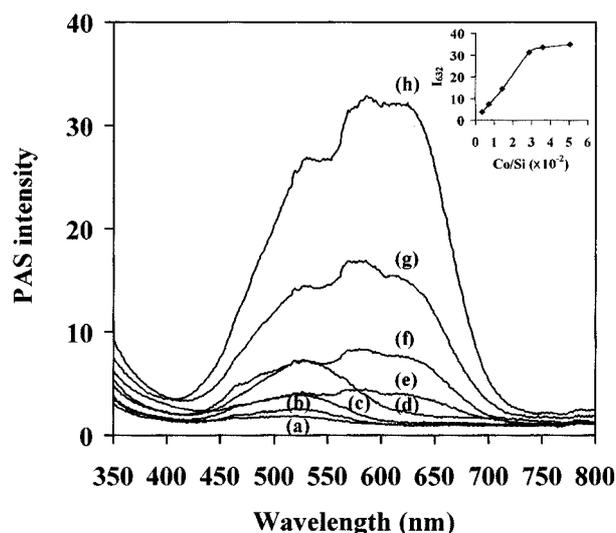


Figure 8. PA spectra of Co-PO/MCM48 treated with (a) 0.01 M-, (b) 0.02 M-, (c) 0.04 M-, and (d) 0.08 M-Co acetate solution at pH=3.0 controlled with H₃PO₄, and dried 40°C for 12 h, and calcined Co-PO/MCM48's ((e), (f), (g), and (h)) with sample (a), (b), (c), and (d), respectively. The inset shows the intensity of the PAS band at 632 nm with the Co content in Co-PO/MCM-48.

increased with the Co content and then remained constant after the metal incorporation in various CoAPOs ceased. The character of the residual Co species is not yet clear, but at least some may act as counter ions. Figure 8 shows PAS for Co-PO/MCM48 samples treated with 0.01 M-, 0.02 M-, 0.04 M-, and 0.08 M- cobalt acetate solution under the same condition as Co-PO/MCM41. The intensity of PAS at 632 nm increases linearly with the content of Co in MCM-48 until being treated with 0.08 M-solution but remains constant at concentrations higher than 0.08 M (an inset in Figure 8). The maximum level of PAS intensity of MCM-41 is lower than that of MCM-48, which seems to be characteristic of each structure type. Apparently, MCM-48 has a slightly higher Co acceptance than MCM-41. The PAS intensity of MCM-48, however, is lower than that of MCM-41 treated with the same concentration of cobalt acetate solution, which is probably due to the sodium ion added on the synthesis procedure for MCM-48.

Acknowledgment. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the Program Year 1997 and thank Prof. R. Ryoo at KAIST for MCM-48 samples.

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