

BULLETIN

OF THE
KOREAN CHEMICAL SOCIETY

VOLUME 19, NUMBER 4
APRIL 20, 1998

BKCS 19(4) 395-498
ISSN 0253-2964

Communications

The Photoacoustic Spectroscopic Study on Cobalt Coordinated by Aminosilanes Immobilized within Mesoporous Molecular Sieve MCM-41

Dong Ho Park*, Sung Soo Park, and Sang Joon Choe

Department of Chemistry, Inje University, Kimhae, Kyongnam 621-749, Korea
Received August 29, 1997

Mesoporous molecular sieve MCM-41, which was synthesized by Mobil group in 1992,^{1,2} has a space enough to provide new heterogeneous catalytic environment within regular mesopores due to the pore size having diameters of 20-100 Å and the silanol group consisting of significant portion of surface.²⁻⁴ The potential applicability of the functionalized of mesoporous silica surface has attracted considerable interest in recent years.⁵⁻⁷ Liu *et al.* reported the alkene oxidation by ruthenium porphyrin encapsulated MCM-41,⁵ Rao *et al.* achieved the immobilization of triazacyclononane ligands on a glycolated surface,⁶ and O'Brien *et al.* could modify the surface of MCM-41 via ring opening of a ferrocenophane.⁷ It is expected that the channel of MCM-41 can be modified to a nanometer-sized reactor with specific function and shape by immobilization of transition metal complexes on the wall. In this communication, we describe the characteristics of cobalt coordinated by aminosilanes (3-(2-aminoethylamino)propyltrimethoxysilane (APTMS, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$, 97%, Aldrich) and 3-(2-(2-aminoethyl)aminoethylamino)propyltrimethoxysilane (AAPTMS, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, tech, Aldrich) immobilized within the mesopore of MCM-41.

The chemicals used in the synthesis were fumed silica (99.8%, metal-free, Sigma), cetyltrimethylammonium bromide (CTABr, 99%, Aldrich) and tetramethylammonium hydroxide (TMAOH, 25 wt % aqueous solution, Aldrich). Purely siliceous MCM-41 was synthesized following a literature procedure.⁸ The molar composition of final gel mixture was 1.0 SiO_2 :0.27 CTABr:0.19 TMAOH:40 H_2O . High quality of MCM-41 was confirmed by X-ray diffraction pattern and N_2 sorption measurement. The calcined MCM-41

has d_{100} value of 44.4 Å, pore diameter of 32.5 Å, and high surface area (1185 m^2/g).

The procedure for immobilization of aminosilanes (APTMS and AAPTMS) was as follows: MCM-41 (0.1 g) degassed at 300 °C for 12 h in a vacuum (*ca.* 10^{-3} torr.) was saturated with a dry chloroform. The samples were stirred in a dry chloroform solution of aminosilanes (10 mL, 0.1 M) at room temperature for 12 h. After stirring, the samples were filtered and washed with chloroform and dichloromethane (1:1 (v/v)), dried at 40 °C for 12 h, and placed in an oven at 80 °C for 12 h to complete Si-O-Si formation, which were designated by APTMS/MCM-41 and AAPTMS/MCM-41, respectively. IR spectra were recorded on FT-IR spectrometer (Shimadzu Corp. FTIR-8201PC) with 2 cm^{-1} resolution and 100 scan times using the KBr pellet technique.

Figure 1 shows the IR spectra of (a) calcined MCM-41, (b) APTMS/MCM-41, and (c) AAPTMS/MCM-41. As compared with the IR spectra of calcined MCM-41 (Fig. 1(a)), some characteristic peaks for the immobilization of aminosilanes appeared as denoted by solid circle in Figures 1(b) and 1(c). Both 2870 cm^{-1} and 2960 cm^{-1} for aliphatic CH stretching, 1558 cm^{-1} for NH scissoring, 1473 cm^{-1} for CH_2 bending and 1329 cm^{-1} for CH_3 bending can be assigned. The 960 cm^{-1} peak for silanol group of MCM-41 was weakened possibly due to the formation of Si-O-Si linkage between aminosilane and MCM-41 with demethanolization. The presence of CH_3 bending peak associated with 1329 cm^{-1} shoulder in Figure 1(b) and 1(c) indicates that all the methoxy groups in aminosilane do not participate the Si-O-Si linkage with surface silanol group of MCM-41. Chen *et al.* reported that there are at least four distinguish-

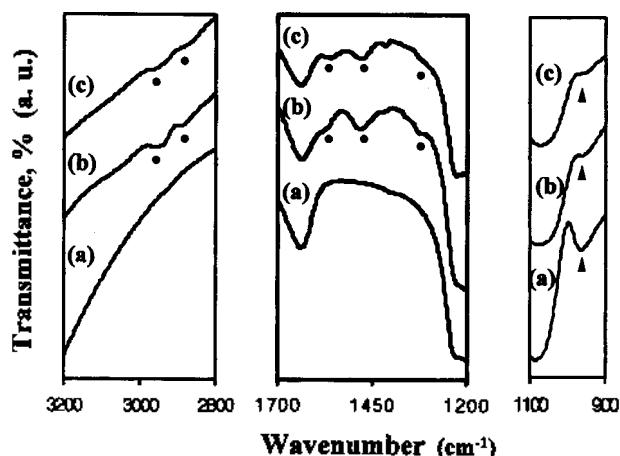


Figure 1. IR spectra of (a) calcined MCM-41, (b) APTMS/MCM-41, and (c) AAPTMS/MCM-41.

able types of silanol groups in MCM-41.⁹ Depending on the local environment of silanol group, all or part of methoxy groups in aminosilane could be removed by the linkage formation.

In order to demonstrate the immobilization of aminosilanes, Raman spectrometer (Bruker Analytische Messtechnik GMBH) with InGaAs detector has been also used. There is no peak in Raman spectrum of calcined MCM-41 resulting from the amorphous silica wall (Figure 2(a)). On the other hand, the characteristic peaks of aminosilanes, except of the peaks in the spectra of APTMS and AAPTMS which are denoted by triangle (Figure 2(c) and 2(e)), have appeared on treatment of MCM-41 with aminosilane solutions (Figure 2(b) and 2(d)), indicating that aminosilanes immobilized on the surface of MCM-41. The disappeared 2839 cm^{-1} peak could be assigned to C-H stretching mode of aminosilane's CH_3 removed during demethanolization.

According to Rosenzweig-Gersho theory for the photoacoustic effect,¹⁰ the acoustic signal in optically opaque and thermally thick solids such as silicate including metal is proportional to the optical absorption coefficient of the solid sample for the wavelength and varies as (the chopping fre-

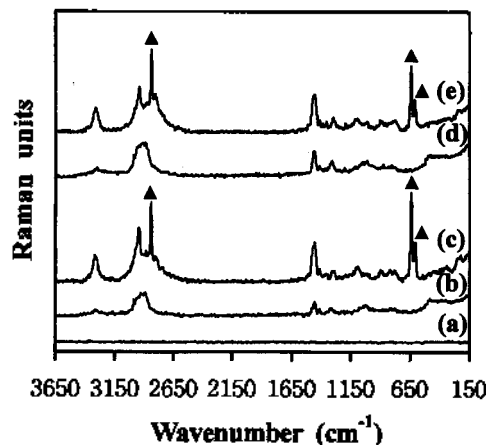


Figure 2. Raman spectra of (a) calcined MCM-41, (b) APTMS/MCM-41, (c) APTMS, (d) AAPTMS/MCM-41, and (e) AAPTMS.

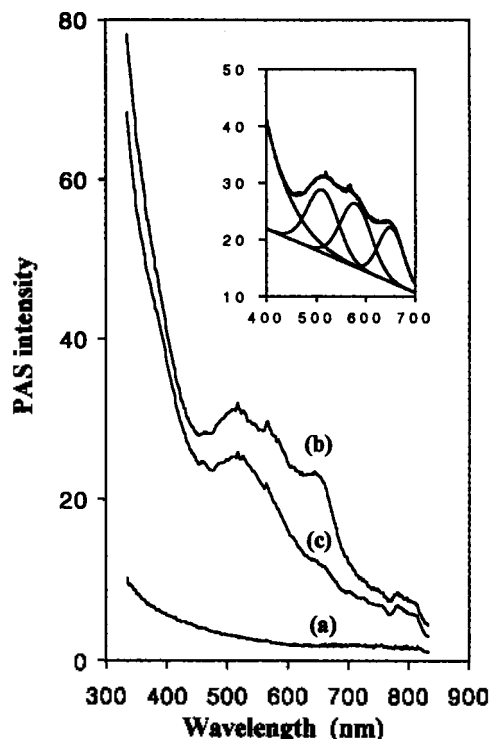
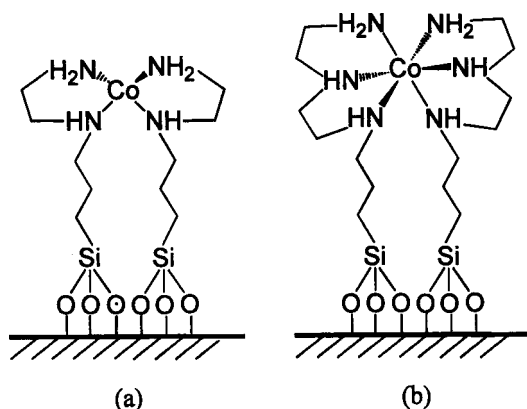


Figure 3. Photoacoustic spectra of (a) APTMS/MCM-41, (b) Co/APTMS/MCM-41, and (c) Co/AAPTMS/MCM-41. Inset shows the deconvoluted curves of PAS for Co/APTMS/MCM-41 by curve-fitting calculation.

quency)^{-3/2}. PAS technique made it possible to detect quantitatively the Co(II) complexes coordinated by aminosilanes immobilized on the wall of MCM-41. PAS spectra were obtained using a home-made photoacoustic spectrometer as illustrated in other literature.¹¹

The APTMS/MCM-41 and AAPTMS/MCM-41 were immersed in a aqueous solution of cobaltous acetate tetrahydrate (10 mL, 0.04 M) at room temperature for 2 h, respectively. The samples were filtered and washed with a deionized water, and dried at 80 °C for 12 h, which were designated by Co/APTMS/MCM-41 and Co/AAPTMS/MCM-41. Figure 3 shows the photoacoustic spectra of (a) APTMS/MCM-41, (b) Co/APTMS/MCM-41, and (c) Co/AAPTMS/MCM-41. Figure 3(a) shows the PAS spectrum of APTMS/MCM-41. There is no absorption band in this wavelength range. After treatment with Co(II) solution, the triplet bands around 600 nm and very intensive charge transfer band below 400 nm appeared as shown in Figure 3(b). In a crystal field environment of T_d symmetry, the ground-state energy level 4F of Co(II) is split into three level, 4A_2 , 4T_2 , and $^4T_1(F)$, respectively.¹² Electronic transition among these and the next higher level $^4T_1(P)$ in a same spin state is allowed according to the selection rule for the electronic transition. The band due to the transition ($^4T_1(P) \leftarrow ^4A_2$) occurs in the range of visible and is split into triplet bands due to spin-orbit coupling. Therefore, the triplet band around 600 nm can be responsible for the Co(II) complex coordinated tetrahedrally by two ATPMS/MCM-41. Scheme 1(a) shows Co(II) coordinated by four ligating N atoms of two neighboring immobilized ATPMS. Especially, λ_{max} values for triplet bands deconvoluted by curve-fitting calculation are 512



Scheme 1.

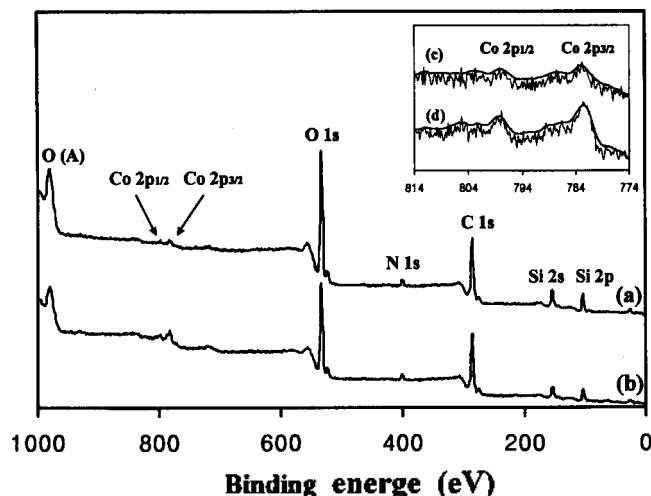


Figure 4. X-ray photoelectron spectra of (a) Co/APTMS/MCM-41 and (b) Co/AAPTMS/MCM-41. Inset shows the smoothed and enlarged XPS spectra of the cobalt 2p photoelectron region of (c) spectrum (a) and (d) spectrum (b).

nm, 579 nm, and 650 nm, respectively, at almost same space (an inset in Figure 3); which is attributable to high tetrahedral symmetry of Co(II) complex. However, it is difficult to rule out completely the presence of Co(II) in octahedral environment since the intensity of the corresponding bands will be an order of magnitude lower and hence will be masked by the intense bands of the tetrahedral Co(II). In the case of Co/AAPTMS/MCM-41, PAS spectrum (Figure 3(c)) characteristic of octahedral structure, as shown in scheme 1(b), was obtained. It is attributable to coordination of Co(II) by six ligating N atoms of two neighboring immobilized AAPTMS. The band around 500 nm is a characteristic one for the octahedral complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.^{13,14} The weak band around 650 nm due to some tetrahedral structure, which is possibly related to Co(II) coordinated by the single AAPTMS, was showed.

Another evidence for the oxidation state of cobalt ion was obtained using VG Microtech. MT500 model electron spectrometer with X-ray excitation from $\text{MgK}\alpha$. Figure 4 illustrates the XPS spectra of Co/APTMS/MCM-41 and Co/

AAPTMS/MCM-41. Smoothed curves of spectra in Co 2p energy region as shown in an inset in Figure 4 have satellite peaks on high binding energy side of $2p_{1/2}$ and $2p_{3/2}$ peaks, even though some obscurity due to low signal/noise ratio. Frost *et al.* have reported that Co(II) complexes have satellite peaks while low spin Co(III) complexes do not.¹⁵

Co(II) impregnated within MCM-41 without immobilized aminosilane was removed completely with stirring in water for 2 h at room temperature. On the contrary, Co/ATPMS/MCM-41 and Co/AAPTMS/MCM-41 were stable while treatment with water. This result reflect that most of Co(II) within MCM-41 are coordinated by ligating N atoms of aminosilanes without the impregnation on the surface of MCM-41.

In this short report, we have tried to reveal that it is possible for siliceous MCM-41 to be functionalized by the formation of tetrahedral or octahedral Co(II) complexes by immobilized aminosilanes. Studies are in progress to investigate the catalytic properties of Co(II) complexes within regular space of MCM-41 unlike that on the amorphous silica support.

Acknowledgment. The financial support for this work by Grant from InJe University (1997) is greatly acknowledged.

References

- Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vaturi, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- 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.
- Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159.
- Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.
- Liu, C.-J.; Li, S.-G.; Pang, W.-Q.; Che, C.-M. *Chem. Commun.* **1997**, 65.
- Rao, Y. V. S.; Vos, D. E. D.; Bein, T.; Jacobs, P. A. *Chem. Commun.* **1997**, 335.
- O'Brien, S.; Tudor, J.; Barlow, S.; Drewitt, M. J.; Heyes, S. T.; O'Hare, D. *Chem. Commun.* **1997**, 641.
- Cheng, C.-F.; Park, D. H.; Klinowski, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*(1), 193.
- Chen, J.; Li, Q.; Xu, R.; Xiao, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2694.
- Rosenzweig, A.; Gersho, A. *J. Appl. Phys.* **1976**, *47*, 64.
- Park, D. H.; Lee, K. W.; Choe, S. J. *Bull. Korean Chem. Soc.* **1995**, *16*, 469.
- Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M. J. *Amer. Chem. Soc.* **1961**, *83*, 4690.
- Anderson, J. H. Jr. *J. Catal.* **1973**, *28*, 76.
- Cotton, F. A.; Wilkenson, G. A. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, U. S. A., 1988; p 730.
- Frost, D. C.; McDowell, C. A.; Woolsey, I. S. *Mol. Phys.* **1974**, *27*, 1473.