Stabilization of Cobalt Complexes by Functionalized Silanes in Inorganic-Organic Hybrid Materials

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The surrounding fields around cobalt ions in the pore-free inorganic-organic hybrid materials were controlled through coordination bonds by various functional groups directly bonded to the silica framework. Tetrachloro cobalt (II) ion $[CoCl_4]^{2-}$ was also stabilized for a period of over one month in the pore-free materials, whereas it was gradually transformed to $[Co(H_2O)_6]^{2+}$ in the porous ones. The pore volume of the hybrid materials was changed against the methyltrimethoxysilane to total silane ratio.

There is a growing interest in inorganic-organic hybrid materials which consist of Si-O-Si linkage chemically bonding to organic groups.[1] These materials are expected to be comparable to inorganics and organics.[2] Moreover, they are in particular demand for use in optical devices due to their superior transparency in the near UV and visible regions, their ease of preparation of crack-free materials and their high heat resistance compared with that of common organic polymers.[3-5] Doped hybrid materials have been intensively investigated for a wide variety of dopants ; rare earth ions,[4] metal particles,[5] dyes,[3-4] ect. It is essential that such materials are able to control the surroundings of dopants and stabilize them in the host.

In this paper, we report the control of the ligand fields around cobalt ions by functional groups of silane coupling agents and the stabilization of water-sensitive complex in pore-free inorganic-organic hybrid materials.

Prehydrolized silica sol was prepared by 1-hour stirring of tetramenthoxysilane ($(CH_3O)_4Si$: TMOS), methyltrimethoxy silane ($(CH_3O)_3SiCH_3$: MTMS), and distilled water adjusted to pH=3. The molar ratio of MTMS/(MTMS+TMOS), which was defined as R, was changed from 0 to 1. The water to total silane ratio in mole was 2. The prehydrolized sol was added to methanol containing cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$). After stirring for 1 hour, methanol was evaporated from the mixture at 50 ℃ in 0.01 atm for 30 min. Finally, the sol was poured into teflon containers of 30 mm in diameter. Co-doped inorganic-organic hybrid materials were obtained by drying sols at 60 °C for 1 week. In some cases, 3-(2-aminoethylaminopropyl)-trimethoxysilane ($(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$: AATM) was used instead of MTMS. The absorption spectra for the Co-containing solutions and hybrid materials were measured in the UV/Vis region using a Hitachi U-4000. Binding energy of $Co_{2p1/2}$ spectra for the hybrid materials was monitored by X-ray photoelectron spectroscopy (XPS) using a Shimadzu ESCA-850. The specific surface area of the materials was calculated by the BET method.

Figure 1 shows the absorption spectra for Co-containing methanolic solution (3.3×10^{-3} mol dm^{-3}) (a), and with AATM (1.65×10^{-1} mol dm^{-3}; Co/AATM =1/50 in mole) (b) in the near UV and visible range. AATM-containing solution was diluted to 1/5 of its initial concentration. In the absorption spectrum (a), a broad peak is seen at around 525 nm in wavelength, and the solution was colored pink. This peak is characteristic of an octahedral complex $[Co(H_2O)_6]^{2+}$.[6] In curve (b), the peak is not seen at 525 nm, but the shoulder peaks appear at around 395 nm, and a tiny broad peak at 540 nm. These peak positions are the same as those of the complex [*cis*-$CoCl_2(en)_2$]Cl.[7] Because AATM does not have any absorption peak above 250 nm at this concentration, complex ions such as $[Co(AATM)_2Cl_2]^+$ seem to be formed in the Co-doped methanolic solution.

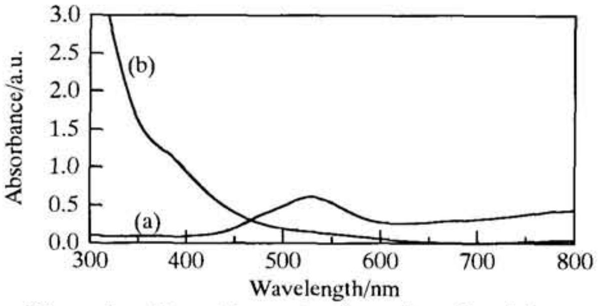

Figure 1. Absorption spectra for methanolic solution with $CoCl_2$ (a), and with $CoCl_2$ and AATM (b).

Co-doped inorganic-organic hybrid materials obtained from $CoCl_2$ and silica sol were transparent, and were *ca.* 25 mm in diameter and 3 mm in thickness. The specific surface area (S_g) of the hybrid materials as a function of R is shown in Fig.2. The specific surface area decreased with the increase of R regardless of the substitution of MTMS to AATM, and S_g became less than 2 m^{2}g^{-1} at and above R=0.8, indicating that the materials have few open pores. The addition of PDMS (polydimethysiloxane) to silica gel generated rubber behavior.[2] Because the use of MTMS also reduced network formation, more micro pores are collapsed by capillary force during drying of hybrid materials containing higher levels of methyl groups. Monolith was easily obtained above R=0.5, suggesting that a terminal CH_3-Si bond causes structure relaxation.

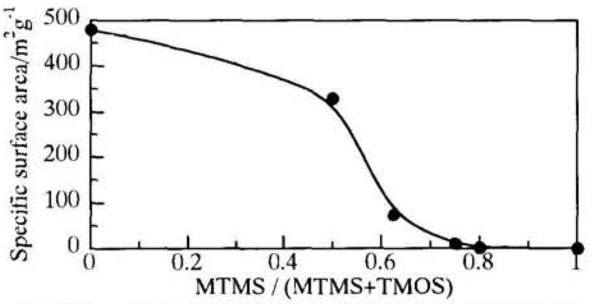

Figure 2. Change in specific surface area of the inorganic-organic hybrid materials against MTMS to total silane ratio.

Figure 3 shows the diffuse reflection spectra for the hybrid materials prepared from TMOS and MTMS at R=0.5 (a), R=0.8 (b), and from TMOS, MTMS and AATM (R=0.8) (c). In curve (a), an absorption peak at 525 nm, which was due to the complex ion $[Co(H_2O)_6]^{2+}$, is observed, and this peak is the same as that of the Co^{2+}-contaning methanolic solution without functionalized silane (Figure1 (a)). In curve (b), however, a broad absorption peak assured at around 665 nm, and is attributed to the complex anion $[CoCl_4]^{2-}$. The complex $[Co(H_2O)_6]^{2+}$ was converted to $[CoCl_4]^{2-}$ in nearly pore-free material (R=0.8) during gelation and drying, whereas $[Co(H_2O)_6]^{2+}$ remained in porous materials (R=0.5) because water can attach to Co^{2+} ions through pores. In curve (c), the absorption peaks located at 368 and 530 nm, which are very similar to those of the complex ions $[Co(NH_3)_5Cl]^{2+}$, are observed.[8] In the hybrid material, therefore, cobalt ions are provably bonded to two *en*, one terminal NH_2 of 3-(2-aminoethyl-aminopropyl) group and one of Cl^-. The formation of the complex ions like $[Co(NH_3)_5Cl]^{2+}$ compared with $[CoCl_4^{2-}]$ in the hybrid materials prepared from AATM suggests that cobalt ion preferred to amino groups against chloride ions. Because the binding energies of $Co_{2p_{1/2}}$ for the samples (b) and (c) were almost same as those of $CoCl_2$ and $[Co(NH_3)_6]Cl_3$, respectively,[9] the dominant first neighbor of cobalt ions in the hybrid materials is Cl and N for samples (b) and (c), respectively. Moreover, gem type OH- and mercapto (SH-) groups were also coordinated with Co ion in the materials by using glycidyloxypropyl- and mercaptopropyl-containing silanes, respectively.[10]

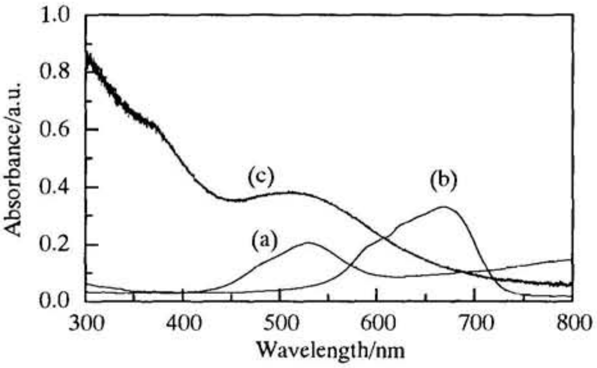

Figure 3. Diffuse reflection spectra for the hybrid materials prepared from TMOS and MTMS at R=0.5 (a), 0.8 (b), and from TMOS, MTMS and AATM at R=0.8 (c).

Figure 4 shows the stability of $[CoCl_4]^{2-}$ in the materials prepared at R=0.5 (a) and 0.8 (b) as a function of standing time. After almost all the $[Co(H_2O)_6]^{2+}$ was changed to $[CoCl_4]^{2-}$ by heating at 100 °C overnight *in vacuo* for sample (a), the stability of the complex $[CoCl_4]^{2-}$ was measured. The peak intensity dramatically decreases with standing time for sample (a), whereas it is steady for sample (b). Fujii et al. reported that $[Co(H_2O)_6]^{2+}$ was precipitated in Co-doped SiO_2 gel having a high specific surface area.[11] Water attacked $[CoCl_4]^{2-}$ to form $[Co(H_2O)_6]^{2+}$ for sample (a). These results suggest $[CoCl_4]^{2-}$, which was reactive against the ambient atmosphere, were produced in a pore-free host. In the case of the materials prepared from AATM, the peak intensity attributed to $[Co(NH_3)_5Cl]^{2+}$ was not changed for the period over one month in the pore-free hybrid materials.

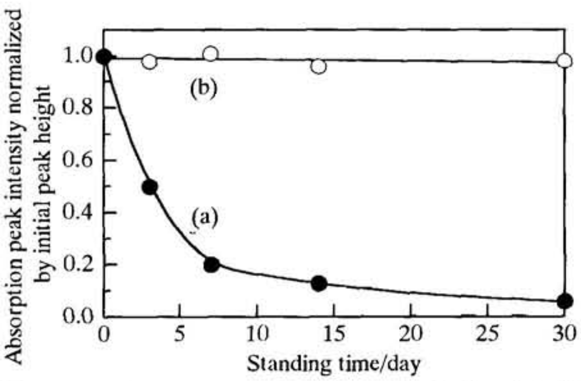

Figure 4. Change in peak intensity of $[CoCl_4]^{2-}$ for hybrid materials prepared at R =0.5 (a), and 0.8 (b).

In conclusion, the specific surface area of inorganic-organic hybrid materials were changed from almost 0 to 450 m^2g^{-1} against the methyltrimethoxysilane to total silane ratio. Water sensitive complexes such as $[CoCl_4]^{2-}$ were stabilized in pore-free hybrid materials. Functional groups that were chemically bonded to the silica framework coordinated with cobalt ions to form complexes. This preparation method may constitute a new doping technique, especially for atmospheric sensitive dopants with low solubility in media such as metal fluorides or organometallics. The authors are grateful to Kinki University for its financial support.

References and Notes

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10 Co-doped inorganic-organic hybrid materials prepared from glycidyloxypropyltrimethoxysilane and mercaptopropyltrimethoxysilane were yellow and brown, respectively. The absorption spectra for them in the UV/Vis region were also different from those of the Co-doped material without functional groups.

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