NOTE

Shape-Selective Copper-Loaded Imogolite Catalyst

Imogolite with a chemical composition of $[SiO_2Al_2O_3 \cdot 2H_2O]_n$ is a tubular clay mineral which is found in naturally occurring weathered pumice beds of volcanic ash (1). It can also be synthesized from hydroxyaluminum cation and orthosilicic acid (2–4). The outer diameter of an imogolite tube is approximately 24 Å and the length is several thousand angstroms (5, 6). The inner layer is composed of silica tetrahedra pointing their silanol groups toward the inside, and this silica layer is covered with a gibbsite-like aluminum hydroxide layer. It has a rigid rod nature which causes the formation of a lyotropic liquid crystal mesophase (7). One of the authors investigated the suprastructure formed in the mesophase of imogolite (8–12). Imogolite retains its tubular structure with an average inner diameter of 6.5 Å when calcined at temperatures up to 750°C and exhibits shape-selective adsorption behavior in the vapor phase (13). The inner silanol groups are expected to exchange metal ions, and the metal-loaded imogolite can be used as a shape-selective catalyst. No investigation, however, has been carried out to utilize metal-loaded imogolite as a catalyst. This work deals with the shape selective behavior of Cu-loaded imogolite. EXAFS analysis clarified the state of the loaded Cu, and the decomposition of two peroxides with different molecular sizes was carried out as a monitoring reaction for the shape-selective behavior of imogolite.

Imogolite was obtained from the soil of the weathered pumice beds of volcanic ash of Murasakino, Iwate Prefecture, and was purified as described previously (13). Copper was loaded on imogolite as follows. A 3 g sample of imogolite was dispersed in 200 ml of 0.2 *M* aqueous copper(II) nitrate (the pH of the solution was 3.5) and was stirred overnight at a room temperature. Then the imogolite was filtered and washed with water three times, followed by calcination at 500°C in air for 3 h. The amount of Cu loaded was 2.59 wt%. Copper loaded silica gel was obtained by dispersing 3 g of a silica gel (Yamani Chemical Co., BET surface area of 499.6 m^2/g) in 100 ml of an aqueous copper(II) nitrate (with an amount corresponding to 2.59 wt% loading), followed by evaporation to dryness at 60°C with an evaporator. It was also calcined at 500°C in air for 3 h. This sample was designated as Cu–SiO₂.

A closed-circulation reactor was used for the isomerization of 1-butene at 50°C, and the decomposition of *tert*-butyl hydroperoxide and 1,1-bis(*tert*-butyldioxy)cyclododecane

(Nihon Yushi Co.) was carried out in a 100 ml three-necked flask under a nitrogen atmosphere.

EXAFS spectra were obtained for Cu K-edge at the beam line 10 B station of the Photon Factory in the National Laboratory for High Energy Physics (Tsukuba) with a ring energy of 2.5 GeV and a ring current of 290–350 mA.

The saturated amount of nitrogen adsorbed on the imogolite calcined at 500°C was 80.7 ml/g; the adsorption isotherm followed the Langmuir-type equation better than the BET equation. The value of 80.7 ml/g roughly corresponds to the BET surface area of 343.0 m^2/g, if we assume that 80.7 ml of nitrogen covers the surface of imogolite in a monolayer. As the amount of adsorbed nitrogen for Cu–imogolite was 83.7 ml/g, no decrease in the surface area occurred after Cu loading. The effect of Cu on the acid sites of imogolite was monitored by measuring the heat evolved on an adsorption of ammonia (100 Torr: 1 Torr = 133.3 N/m^2) with a Tokyo Riko TCC 21 micro-calorimeter at 20°C. The samples (0.1 g) were evacuated at 80°C before analysis. The heat evolved with a unit amount of unloaded imogolite was 108.4 J/g. The imogolite (0.1 g) was treated with 5 ml of dry cyclohexene containing 0.05 g of triphenylamine to cover the acid site present outside the tube (alumina layer). Since the smallest molecular diameter of triphenylamine is 10.2 Å, it cannot penetrate inside the tube of imogolite. Despite this treatment the heat evolved did not change (111.4 J/g). Thus the acid sites were mainly present inside the tube. Copper loading (2.59 wt%) decreased the amount of evolved heat to 43.0 J/mol; Cu decreased the accessible acid sites although the reason is not known. Isomerization of 1-butene (100 Torr) was carried out at 50°C with 0.1 g of the catalysts. The rate constants were 4.81×10^{-2} min^{-1} g^{-1} for unloaded imogolite and 2.76×10^{-2} min^{-1} g^{-1} for Cu–imogolite. The lower activity of the latter was due to its decreased acidity.

As shown in Fig. 1, the Cu–imogolite had higher activity in the decomposition of *tert*-butyl hydroperoxide than unloaded imogolite and Cu–SiO₂. The rather high activity of the unloaded imogolite was assumed to be due to the presence of iron; 0.17 wt% iron was detected in the imogolite as determined by an atomic adsorption spectroscopy. Figure 2 shows the decomposition of 1,1-bis(*tert*-butyldioxy)cyclododecane. In this case the activities of unloaded imogolite and Cu–imogolite were not so differ-
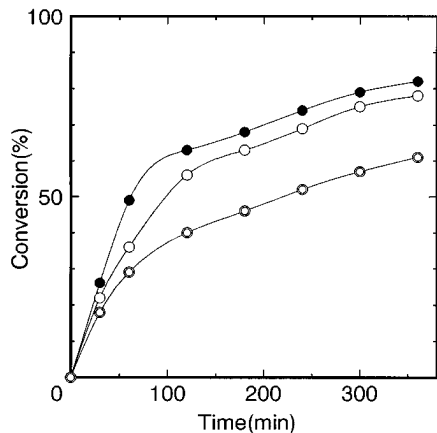
FIG. 1. Decomposition of *tert*-butyl hydroperoxide at 90°C. *tert*-butyl hydroperoxide: 0.1 M, catalyst: 0.1 g, solvent: chlorobenzene (50 ml). The amount of Cu loaded is 2.59 wt%. (◎) imogolite, (●) Cu–imogolite, and (○) Cu–SiO₂.

ent, the former being slightly more active. The reaction proceeded most effectively on Cu–SiO₂. These phenomena can be understood if we assume that the Cu is located mainly inside the tube of imogolite. As the smallest molecular diameter of *tert*-butyl hydroperoxide is ca. 5 Å, it can easily diffuse inside the tube of imogolite and is decomposed by the Cu. However, the size of 1,1-bis(*tert*-butyldioxy) cyclododecane is too large (the smallest diameter of ca. 7 Å) for this peroxide to access the Cu. Thus the Cu did not work. The reason why the activity of Cu–imogolite was a little lower than that of the pure imogolite is not known. The Cu–SiO₂ exhibited the highest activity. As SiO₂ has surface open spaces with no restriction for this peroxide to access the Cu loaded on it, the Cu can be effectively used in the reaction.
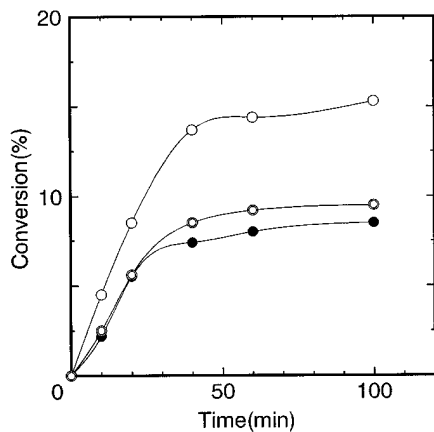

FIG. 2. Decomposition of 1,1-bis(*tert*-butyldioxy)cyclododecane at 70°C. 1,1-bis(*tert*-butyldioxy)cyclododecane: 0.05 M, catalyst: 0.1 g, solvent: chlorobenzene (50 ml). (◎) imogolite, (●) Cu–imogolite, and (○) Cu–SiO₂.
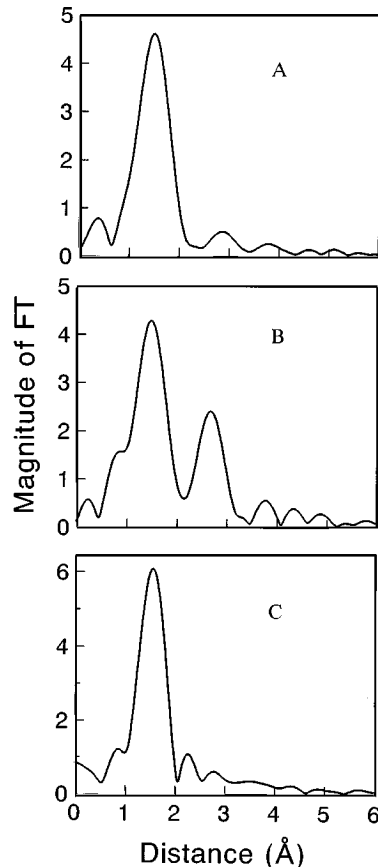

FIG. 3. Fourier transform of k^3-weighted EXAFS. (A) Cu–imogolite, (B) Cu–SiO₂, and (C) Cu(NO₃)₂ · 3H₂O.

EXAFS analysis was carried out in order to support the above assumption that the Cu is inside the tube of imogolite. Figure 3 shows the Fourier transforms of K^3-weighted EXAFS spectra of Cu K-edge measured in the transmission mode. Only one shell is observed for Cu–imogolite, which is similar to the case of Cu(NO₃)₂ · 3H₂O. The peak should be due to the Cu–O bond. Two peaks are present for Cu–SiO₂; the first peak should be due to Cu–O while the second peak to Cu–Cu.

The curve fitting was carried out for Cu–imogolite and Cu–SiO₂, and the result is shown in Table 1. The functions of back-scattering amplitude and phase shift for Cu–O and Cu–Cu were extracted from EXAFS oscillations of Cu(NO₃)₂ · 3H₂O and Cu foil. The fitting for Cu–imogolite was suitably performed with one shell of nearly four Cu–O bonds of 1.97 Å in length which is very close to that of the Cu–O bond in Cu(NO₃)₂ · 3H₂O (14). Two shells of Cu–SiO₂ were fitted with Cu–O and Cu–Cu interactions, and the former bond length (1.95 Å) is a little shorter than that in Cu–imogolite. It is rather similar to the bond length of Cu–O in CuO (15). The length of the Cu–Cu bond in the second shell also corresponds to the averaged Cu–Cu length

TABLE 1

Structural Parameters for Cu–O Bond in the First Shell

Sample	Bond length (Å)	CN[a]	Debye–Waller factor (Å^2)
Cu–imogolite	1.97	3.62	0.0025
Cu–SiO$_2$	1.95	3.99	0.0045
	$(2.94)^b$	$(2.26)^b$	$(0.0019)^b$
Cu(NO$_3$)$_2$ · 3 H$_2$O	1.97	3.98	0.0004

[a] Coordination number.
[b] Cu–Cu bond in the 2nd shell.

in CuO (15). Thus, there were copper species structurally similar to CuO; copper aggregated on the surface of SiO$_2$.

The presence of only one shell in the FT spectrum of Cu–imogolite shows that the copper ions (metal ions) are Coulombically bonded to Si–O$^-$ groups inside the tube of imogolite and are isolated. Metal-loaded imogolites are expected to act as shape selective catalysts as shown by the decomposition of two peroxides with different molecular sizes. As imogolite can be synthesized artificially (2–4), its use can be practical. However, attempts should be made for its practical use, for example, decreasing the tube length to eliminate the diffusional limitation of the reactants and so forth.

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