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Transition Metal Ions on Molecular Sieves. I. Complexes of Copper(II) on Y Molecular Sieves and Their Catalytic Activities

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An isolated metal ion attached to a molecular sieve would be expected to behave quite differently from a metal ion or atom in an ordinary metal oxide. In the latter case, the metal atoms are located that their interaction is possible, while on a molecular sieve the metal ions or atoms are more isolated and tend to behave as their homogeneous analogues even though they are located on a solid surface. Catalytic activities of transition metal ions bound to molecular sieves have been reported for the oxidation of propylene.[1,2)

Molecular sieve-bound metal ions have been extensively studied.[3) However, the interactions of a metal ion with polydentate chelating agents have scarcely been investigated in spite of the fact that such a system can be compared with that of an analogous homogeneous case. Burwell *et al.*[4) studied the exchange of complex metal ions with the hydroxide group of silica gel.

We have investigated the adsorption of bidentate chelating reagents such as ethylenediamine on isolated cupric ions by visible and infrared spectroscopy and also the heterogeneous catalytic activities of these compounds for the decomposition of hydrogen peroxide.

Experimental

Chemicals. Ethylenediamine(en) was obtained from Tokyo Kasei Co, ethanedithiol and dimethylglyoxime from Nakarai Chemicals Co. They were used without further purification.

The Cu(II)-form of the Y molecular sieves (Linde) was obtained by the exchange of sodium ion with aqueous cupprammonium ion. This treatment was followed by a thorough washing with deionized water and calcined at 400°C in the atmosphere. Details have been reported.[1) Cu(II)-Y, saturated with atmospheric water vapor, was found to contain 5.2% copper by weight.

Adsorption of Chelating Reagents. Cu(II)-Y was stirred for 2 days with aqueous diamine or ethanedithiol solution and washed with dry ethanol to yield the chelate-impregnated material. The dimethylglyoxime complex was similarly prepared using ethanol as a solvent.

Spectroscopic Analysis. Electronic spectra were obtained by the decalin mull method in a quartz cell on a Hitachi Type 124 Double Beam Spectrophotometer. The original Y sieve in decalin was used as a reference. Infrared spectra were measured in KBr on a IR-G double beam spectrophotometer of the Nippon Bunko Co.

Decomposition of Hydrogen Peroxide. The rates of decomposition of hydrogen peroxide were determined by the manometric measurement of oxygen evolved. After the reaction flask (containg 50 cc of aqueous NaOH solution of pH 11.8 and the catalyst) was immersed in a constant temperature bath for 2 hr, 1 cc of 30% aqueous hydrogen peroxide was added. After the reaction, the pH of the reaction media was found to be 9.8 for each catalyst.

Results and Discussion

Adsorption of Chelating Agents on Cu(II)-Y. Impregnation of Cu(II)-Y with ethylenediamine turned the sieve deep blue with heat evolution. The complex of the sieve Y-Cu(II)-en kept its color (visible absorption maximum, 660 mμ) in dry air, but turned purple (visible absorption maximum, 550 mμ) in contact with moisture. Similar values were reported for bisethylenediaminecopper(II) complexes.[4,5,6)

Y-Cu(II)-en had an infrared absorption band at 1048 cm^{-1} in addition to those at 1573, 1475, and 1318 cm^{-1} due to the adsorption of ethylenediamine on Cu(II)–Y. The absorption at 1048 cm^{-1} was overlapped by a strong band due to the molecular sieve, but was resolved by using a molecular sieve-containing KBr reference plate. Formation of chelates is indicated by the presence of this band which was assigned to the ring skeletal vibration by Powell and Sheppard.[7)

Ethanedithiol and dimethylglyoxime formed light green complexes on the sieve. These colors coincide with those of the corresponding sulfate complexes. In the case of ethenedithiol, the conformation of the coordinating ethanedithiol rings was determined by inspection of the infrared spectrum. This solid showed a weak absorption band at 1280 cm^{-1} (lit, 1275 cm^{-1})[8) which suggests that the rings are in a gauche form.

Thus, all the results indicate that cupric ions on molecular sieves have an affinity for chelating agents. The affinity suggests a new type of catalytically active sites which are expected to behave much like the usual coordination compound, but kept on the rigid surface.

Decomposition of Hydrogen Peroxide. Various copper compounds have been investigated as models for the

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enzyme by testing their ability to decompose hydrogen peroxide in basic aqueous solution.[9] The catalytic activity of ethylenediaminecopper(II) complex for this reaction was reported.[10] Jacobson and Smith[11] reported on the catalytic activities of ammine and diamine complexes of metal ions on silica gel.

The catalytic activities of Cu(II)–Y, Y–Cu(II)-en, and Y–Cu(II)-dimethylglyoxime toward the decomposition of hydrogen peroxide were observed in aqueous sodium hydroxide. In this pH region, no measurable decomposition of hydrogen peroxide could be observed without catalyst in the sodium hydroxide solution. For Y–Cu(II)-en, the decomposition rate was proportional to the weight of the catalyst. It was found that one molecule of the complex on the surface decomposed more than four hundred molecules of hydrogen peroxide. The reaction seemed to proceed in the first order with 90% decomposition.

Y–Cu(II)-en had a five times larger catalytic activity than Cu(II)–Y at the same pH region as shown in Fig. 1. The fact that catalytic activity of the dimethylglyoximato-complex is significantly less than that of Y–Cu(II)-en (Fig. 1) shows that the catalysis strongly depends on the type of chelating ligand employed. Such catalytic activity enhanced by chelation is of interest as an example of a complex catalyst on the rigid surface.

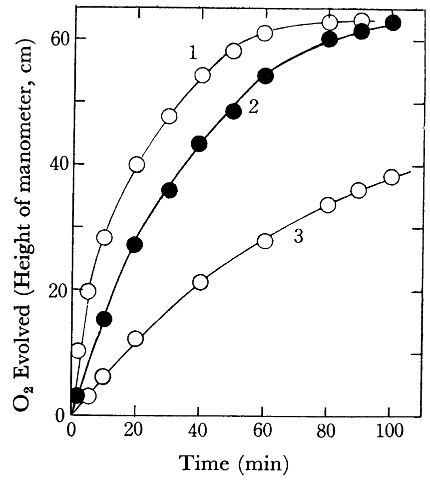

Fig. 1. Decomposition of hydrogen peroxide catalyzed by cupric ions on the molecular sieve at 26°C. The relative activities are calculated 4.6 (Y–Cu(II)-en), 1.0 (Cu(II)–Y), and 0.93 (Y–Cu(II)-dimethylglioxime).
1: Y–Cu(II)-en, 82 mg. 2: Cu(II)–Y, 132 mg.
3: Y–Cu(II)-dimethylglyoxime, 52.5 mg.

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