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PREPARATION OF METAL SUPPORTED MONTMORILLONITE CATALYST: A NEW APPROACH

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A new approach for the preparation of metal supported montmorillonite catalyst is reported here for the first time. The polyol process in which ethylene glycol is used as reducing agent was employed for the preparation of uniformly distributed copper metal particles on and within the montmorillonite matrix. A hydroxy copper acetate intercalated form of montmorillonite was refluxed at 195°C with liquid ethylene glycol for 6 h. The reduction of copper acetate to copper metal was apparent from the red color of the reduced product. An X-ray powder diffraction pattern showed the deposition of copper metal on the external surface of montmorillonite and scanning electron micrographs exhibited uniformly distributed spherical copper metal particles of about 0.5 μm size. This process may also be extended for the preparation of other fine metal particles supported on montmorillonite catalysts.

1. Introduction

Montmorillonite, a 2:1 type layer silicate, is a crystalline hydrated aluminosilicate with a 2-dimensional layer strucuture. Each layer is composed of one octahedral sheet sandwiched between two tetrahedral sheets with an interlayer space. In the structure, the higher valence metal cation, typically Al^{3+}, is partially substituted by lower valence cations, such as Mg^{2+}, in the octahedral sheet, and occasionally Si^{4+} is partially substituted by Al^{3+} in the tetrahedral sheet, thereby developing a net negative charge. The negative charge thus created is normally balanced by hydrated cations which occupy the interlayer spaces. The charge balancing cations of one kind can be replaced by another making this mineral a cation exchanger.

The application and properties of Cu^{2+}-exchanged smectites have been studied extensively for the last 20 years [1–3]. Conversions of hydrocarbons containing olefinic double bond to dimers and trimers were done in Cu^{2+}-montmorillonite interlayers by heating them together [4]. Thomas et al. [5] reviewed other unusual chemical conversions of organic molecules using Cu^{2+}-montmorillonite. Yamanaka et al. [6,7] studied the behavior of Cu^{2+} and Ni^{2+} ion exchanged montmorillonite in excess of the cation exchange capacity (CEC).

Recently pillared clays gained importance in the area of catalysis. For example alumina and zirconia pillared clays are highly selective catalysts for the dehydration of alcohols, cracking of petroleum and also in various acid-catalysed reactions [8–11]. These pillared clays are prepared by the calcination of intercalates containing the corresponding polyoxometal ions. Christiano et al. reported [12,13] clays interlayered with metal cluster complexes, such as those containing $M_6X_{12}n^+$ ($M = Nb$, Ta; $n = 2–4$) and $M_6X_8n^+$ ($M = Mo$; $n = 4$) cores, which after calcination form pillared clays and have been used as oxidation catalysts.

A potentially more versatile approach would be to introduce transition metal centers into clays, or pillared clays with a thermally stable oxide. The conventional impregnation method involves treating the clays with metal nitrate solution and reducing the metal in an inert atmosphere. This method generally lacks the specificity offered by molecular pathways. Giannelis et al. [14] reported the preparation of Ru metal supported on alumina pillared montmorillonite (APM) by reducing $HRu_3(CO_{12}^+$-APM in a hydrogen atmosphere. This catalyst was used in Fisher-Tropsch catalysis.

Generally, metal fine particles are prepared by the reduction of a Cu^{2+} salt with organic compounds or by heating in a reducing atmosphere using H_2 gas. Fievet et al. [15] reported the preparation of submicron copper metal particles by the polyol process. The chemical reduction approach to prepare metal powders has several advantages over other synthetic routes such as evaporation [16], irradiation [17], thermal decomposition [18] and particle beam methods [19] in terms of higher yield, narrower size distribution and chemical flexibility. The objective of this communication is to report our preliminary results on the preparation of finely divided Cu metal which is dispersed in montmorillonite.

2. Experimental

A natural Na-montmorillonite from Tsukinuno district, Yamagata Prefecture, Japan, (courtesy, Dr. S. Yamanaka) was used in this study. The elemental formula of this mineral was reported to be $(Na_{0.35}K_{0.01}Ca_{0.02})(Si_{3.89}Al_{0.11})(Al_{1.6}Fe_{0.08}Mg_{0.32})\ O_{10}(OH)_2.nH_2O$, and its cation exchange capacity (CEC) was measured to be 100 meq/100 g [7]. Four hundred milligrams of Na-montmorillonite (105°C dried basis) was dispersed in 25 mL of 0.1 M copper acetate $[Cu(CH_3COO)_2.H_2O]$ solution, and 30 mL of 0.1 M NaOH was added to the dispersion. The mixture was stored in an air-tight polypropylene bottle under constant stirring for 6 days [7]. After 6 days, the pH of the mixture was measured ($pH = 5.78$), and the solid was separated by centrifugation. Excess salts were removed by washing three times with deionized water followed by two washings with methanol. A few drops of clay-methanol suspension were allowed to dry on a glass slide for X-ray powder diffraction (XRD) analysis.

About 200 mg of basic copper acetate intercalated montmorillonite was suspended in 100 mL ethylene glycol in a two neck round bottom flask and refluxed (195 °C) for 6 h in an inert environment (Ar atmosphere). The above procedure was also repeated for Na-montmorillonite for comparison. After 6 h, the solid was separated by centrifugation and excess ethylene glycol was removed by repeated washing with methanol. Samples were then stored in a desiccator. Slide mounts for XRD analysis were prepared as described above.

The XRD analyses were performed with a Scintag diffractometer using Ni-filtered CuKα radiation. Sample morphology and particle/aggregate size were studied by scanning electron microscope (SEM) using an ISI DS 130 instrument.

3. Results and discussion

The XRD patterns of Na-, and hydroxy copper acetate intercalated montmorillonite before and after ethylene glycol treatment (reflux) are given in figs. 1 and 2.

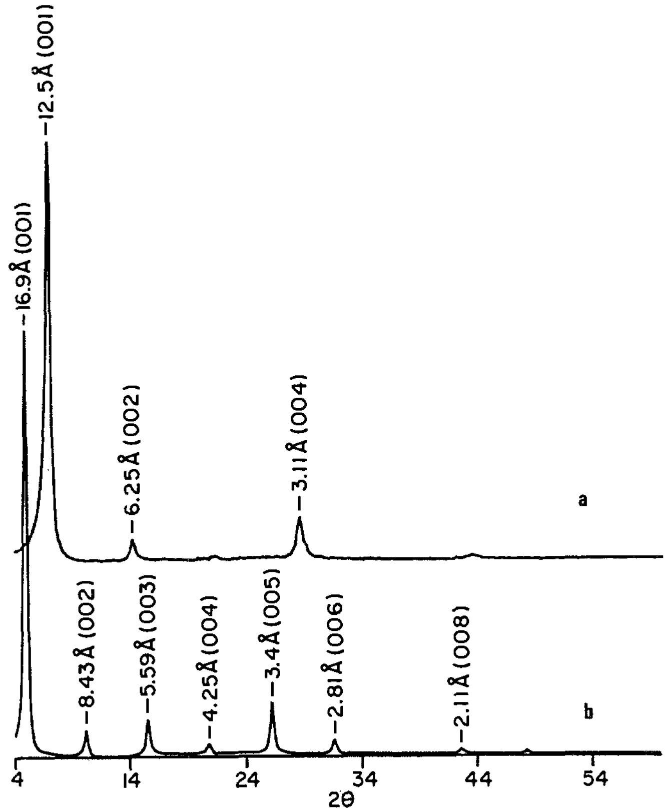

Fig. 1. X-ray powder diffraction patterns of Na-montmorillonite: (a) before and (b) after refluxing in ethylene glycol.

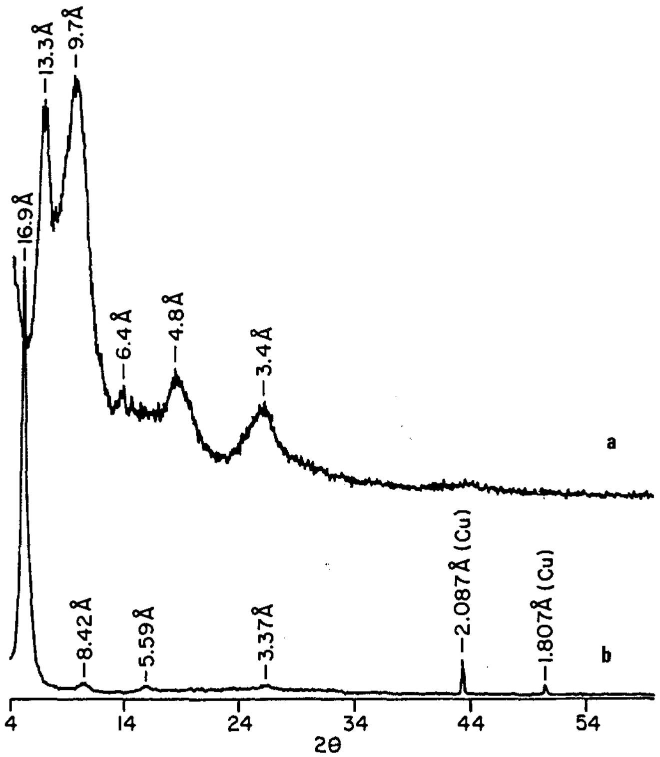

Fig. 2. X-ray powder diffraction patterns of montmorillonite treated with hydroxy copper acetate for 6 days: (a) before and (b) after refluxing in ethylene glycol.

The 12.5 Å and 16.9 Å d(001) peaks are typical of Na-saturated (fig. 1a) and ethylene glycol treated (fig. 1b) montmorillonite [20]. The 12.5 Å peak (fig. 1a) arose from 9.6 Å, the thickness of the basic silicate layer plus about 3 Å of the Na^+ ions coordinated with one layer of water molecules. Similarity, the 16.9 Å peak (fig. 1b) was due to the intercalation of Na^+ ion solvated with two layers of ethylene glycol molecules.

Intercalation of montmorillonite with hydroxy copper acetate showed two d(001) reflections, 9.7 and 13.3 Å (fig. 2a). The 9.7 Å peak is the d(002) reflection of 19.4 Å (001) hydroxy copper acetate intercalated phase of montmorillonite which is slightly smaller than the value reported by Yamanaka et al. [7] who reported a d(001) spacing of 20.2 Å. Yamanaka et al. [21] synthesized the basic copper acetate separately in the absence of montmorillonite and found that it had a layer structure of the botallackite type. The d(001) reflection of this compound was found to be 9.3 Å. The 19.4 Å phase of basic copper acetate intercalated montmorillonite may be attributed to the intercalation of 9.3 Å layers of basic copper acetate parallel to the layers of montmorillonite plus the thickness of basic silicate layer of montmorillonite which is 9.6 Å. The 13.3 Å peak can be attributed to some of the layers which are exchanged with Cu^{2+} and copper complexes other than the "robust" hydroxy copper acetate. After refluxing the hydroxy copper acetate intercalated montmorillonite with ethylene glycol (polyol process) for 6 h, the color of the montmorillonite changed from bluish green to

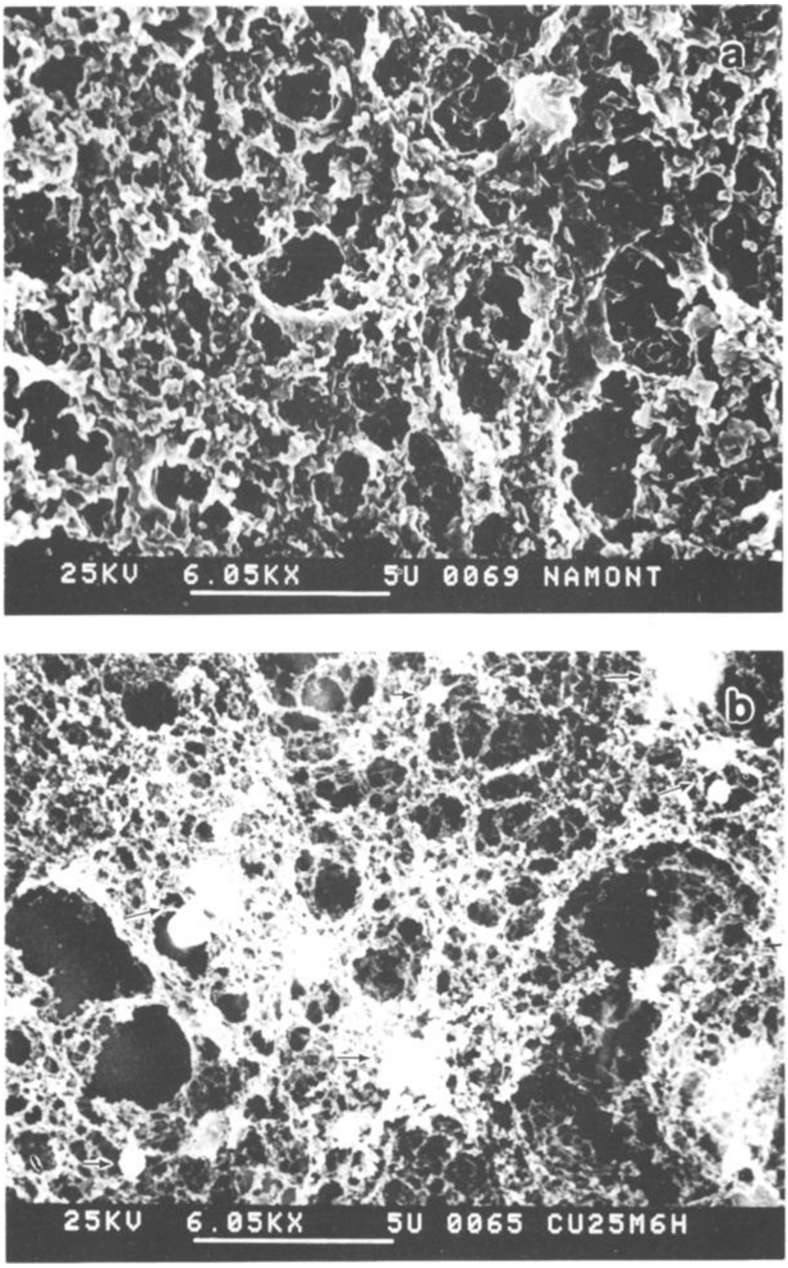

Fig. 3. Scanning electron micrographs of montmorillonite: (a) Na-exchanged, (b) hydroxy copper acetate intercalated and refluxed in ethylene glycol, and (c) X-ray map of the micrograph shown in (b). Copper metal particles are indicated with arrows.

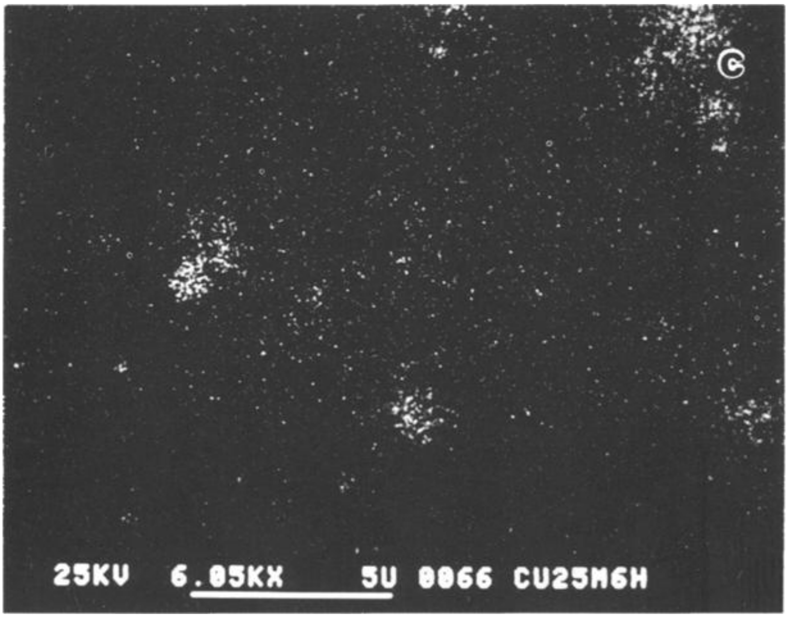

Fig. 3 (continued).

red indicating the reduction of copper acetate to copper metal. The XRD pattern, in fact, showed copper metal peaks at 2.087 (111) and 1.807 Å (200) (fig. 2b). There was, however, another intense peak at 16.9 Å along with its integral reflections. This peak, as in Na-montmorillonite, was due to the solvation of two molecular layers of ethylene glycol. At this point, however, it is not clear whether ethylene glycol is coordinated with Cu^{2+} ion or copper metal. It is highly unlikely that the ethylene glycol molecules are coordinated with neutral copper metal and ethylene glycol appears to coordinate Cu^{2+} ions which are balancing the negative charge of the montmorillonite. The presence of interlayer Cu^{2+} ions and possibly some copper metal are substantiated by the fact that the copper metal peaks observed are too small to account for the expulsion of all the copper from the interlayers.

The scanning electron micrograph of Na-montmorillonite shows a typical honeycomb-type morphology (fig. 3a). The micrograph of hydroxy copper acetate intercalated montmorillonite after polyol process showed well distributed copper metal particles (~ 0.5 μm) on the montmorillonite matrix (fig. 3b). The X-ray dot mapping of copper is presented in fig. 3c. During the conventional impregnation process, there is a chance of aggreggation of metal particles as islands, whereas in the polyol process uniform distribution of metal particles is possible. In the specific case of montmorillonite, the additional advantage of the polyol process is the ability of ethylene glycol (being polar) to penetrate effectively into the interlayers of montmorillonite. The amount of intercalation of hydroxy-copper acetate can systematically be varied by changing the amount and ratio of OH/Cu, thereby allowing the desired amount of copper metal on the montmorillonite matrix. Yamanaka et al. [7] reported that about 25% of Cu can be intercalated without precipitating the hydroxy copper acetate outside the interlayers. The study of basic copper acetate-montmorillonite complex in which all the layers of montmorillonite are intercalated with basic copper acetate would be very interesting and such a study is under way. This process may also be extended for the preparation of metal supported montmorillonite catalysts with other metals such as Ni, Co, Ru, Pt etc. These studies are also under way.

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