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Reaction of Molecular Hydrogen with Tetraaminecopper(II) Sulfate Monohydrate

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The reaction of tetraammincopper(II) sulfate monohydrate in a solid state with H_2 (10 MPa) was studied. The Cu(II) ion in the complex was reduced to Cu(0). The final product was a mixture of $(NH_4)_2SO_4$ and colloidal black Cu(0) which showed a remarkable reactivity as follows. In thermogravimetric analysis up to 440°C under nitrogen atmosphere, the above product reacted between the components very much differently from a control sample with the same composition. The six intermediate samples, taken at successive reaction times, were examined by powder diffraction method. As one of the intermediates, the copper double salt, $(NH_4)_2Cu(SO_4)_2$, was identified. © 1994 Academic Press, Inc.

INTRODUCTION

The reactions between molecular hydrogen and transition metal complexes have been studied in view of their importance in catalytic reactions and synthesis of hydride complexes. In these reactions hydrogen molecules may dissociate homolytically or heterolytically depending on the polarity of solvent and strength of hydrogen–metal bond. Direct reactions of metal complexes in the solid state with molecular hydrogen are advantageous in obtaining results without taking solvent effects into consideration, in spite of the limitation in inhomogeneous reaction. One of the present authors (Kanda) reported that the proton conductivity of a copper coordination polymer was increased $10^{5\sim6}$ times by treating it with molecular hydrogen (1). This was attributed to the yielding of protons from the hydrogen molecules absorbed in the polymer. Furthermore, he showed that the electrolysis of water by use of platinum or glassy carbon cathode coated with the coordination polymer yielded molecular hydrogen, and transformed the coating polymer on the cathode into a fairly stable reduced form (2), which could reduce organic compounds nonelectrolytically (3). The kinetic analyses of these reactions were based on the assumption of formation of copper hydride as an intermediate of the reactions catalyzed by a copper salt (4).

Copper hydrides have been known since 1884 (5). A number of ternary hydride complexes have been reported in recent years (6, 7). In view of these facts, in this study, molecular hydrogen (2–10 MPa) was reacted with several copper(II) salts in order to elucidate the final and intermediate reaction products and reaction mechanisms. However, we have been unsuccessful in obtaining reproducible results for the reactions with simple salts such as sulfate, chloride, and acetate, although the fact that hydrogen is absorbed to some degree was confirmed in each case by observing a weight increase of the salts and a decrease of hydrogen pressure. Thus, we report here the results of the reaction of tetraamminecopper(II) sulfate monohydrate with molecular hydrogen.

EXPERIMENTAL

Material. Tetraamminecopper(II) sulfate monohydrate, (abbreviated as **1**), was prepared by the conventional method (8). All other materials were commercially obtained, guaranteed grade reagents.

Reaction apparatus. Stainless steel reaction vessels, TVS type (50 cm^3 and 150 cm^3, safety pressure <1000 kg/cm^2) made by Taiatsugarasu Co., equipped with a Bourdon type pressure gauge, were used.

Reaction procedures. The copper complex, in a weighing bottle, was placed in the reaction vessel. The air in the vessel was replaced with hydrogen after evacuation. The vessel was kept in a thermostat and the hydrogen pressure was raised to 10 MPa. The decrease of hydrogen pressure during a reaction period of up to 1000 hr was around 20 kPa, which was comparable to or less than the observed error.

Physical measurements. X-ray powder diffraction was measured with a Rigaku Rint X-ray diffractometer (Cu$K\alpha$) and identified with JCPDS file with the aid of the

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Johnson/Vand method. Thermogravimetric analyses and differential thermal analyses were carried out with a Shimazu TG-50 and DTA-50.

RESULTS AND DISCUSSION

Procedure 1. When the complex salt **1** (1825 mg) was kept in the reaction vessel with concentrated sulfuric acid placed in a weighing bottle at the bottom of the vessel for 21 days under 2 MPa hydrogen at 80°C, the sulfuric acid gained 121.4 mg in weight, absorbing water and ammonia, while the sample lost 110.3 mg. This result suggests that 11 mg of molecular hydrogen was absorbed in the complex **1**. The atomic ratio of absorbed hydrogen to copper was 1.5.

Procedure 2. Powdered samples of **1** were kept in the reaction vessel with a sulfonic type cation exchanger (AMBERLYST-15, Rhom and Haas) instead of concentrated sulfuric acid in order to eliminate vapor from sulfuric acid under 9 to 10 MPa hydrogen atmosphere or nitrogen atmosphere (for blank test). In the process of the reaction, for each 3 ~ 4 days after weighing the whole sample, a slight amount of dark colored sample on a portion of the surface (note that the sample was no longer homogeneous due to the solid–gas reaction) was taken out for X-ray and thermal analyses. After the sampling, the remaining product was weighed again, mixed well to make it as homogeneous as possible, pumped, filled with hydrogen, and heated at 85°C. Such procedures were carried out nine times so that the total reaction time was 900 hr.

The reaction of complex **1** with molecular hydrogen caused a weight loss of the sample, described here by two parameters, ω and ϕ, which are defined by $\omega = 245.5 \times W/W_0$, where W_0 is the initial weight of **1** (FW = 245.5) used for the reaction, and W is the weight of the whole solid sample in the process of the reaction; and $\phi = 159.6 \times m_0/m$, where m_0 is the weight of the portioned sample just after separation from the reaction system during the process of the reaction with hydrogen, and m is the weight of the sample at the final stage of thermoanalysis (440°C) where the solid sample was thoroughly converted to $CuSO_4$ (FW = 159.6). In other words, these parameters are "mean formula weight" of the copper complex for the whole reaction solid product, and for a small portioned sample submitted to the X-ray and thermal analyses, respectively. The reaction can be monitored by the variation of the whole weight of the solid sample, which is shown in Fig. 1 (plotted by □) and Table 1. These data clearly show that the weight decreases gradually until the reaction time reaches 600 hr, and then rapidly in the 600–800 hr range. The behavior is reproducible when the same adsorbent is used as shown in Fig. 1 (plotted by △). This result may be interpreted by assuming that in the first stage of the reaction the water molecule in the complex went off gradually but hydrogenation reaction was very slow, whereas in the second stage the hydrogenation proceeded rapidly causing dissociation of two molecules of ammonia. This assumption is compatible with the weight loss data as a function of reaction time in the last three columns of Table 1. This view is also supported by the experimental result that when **1** was kept in the reaction vessel under 7 MPa nitrogen atmosphere at 85°C for 600 hr, the weight loss was only 0.4% (corresponding to 0.06 H_2O), as shown in Fig. 1 (plotted by ○), and no color change was recognized.

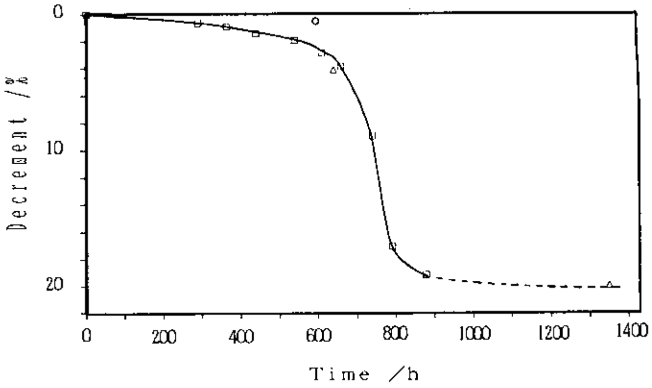


FIG. 1. Weight loss of $[Cu(NH_3)_4]SO_4 \cdot H_2O$ as a function of reaction time. □: data from procedure 2 with nine times sampling in 880 hr as shown in Tables 1 and 2A, see text. △: data from the same type procedure with two times sampling in 1350 hr. ○: data from the same type procedure under 7 MPa nitrogen.

Powder X-ray diffraction patterns at various reaction times are shown in Fig. 2. The main feature of the results may be described as follows: (1) all main peaks of the starting material, **1**, remained until sample 7 (740 hr), when an intensity decrease and a slight increase in parallel plane separations were observed; (2) in samples 7–9 more than 10 peaks due to ammonium sulfate (denoted as A in Fig. 2) appeared; (3) the black samples, 7–9, showed peaks due to metallic copper (denoted as Cu in Fig. 2), the intensities of which were markedly increased and the peak widths were narrowed with time, implying the progress of crystallization; (4) in samples 4–8 more than 10 peaks due to the double salt, $(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$ (JCPDS card 14-548, 25-1486) (abbreviated as **2**) were observed (denoted as D in Fig. 2); (5) there were several peaks which cannot be assigned to any registered compound, suggesting the presence of some unregistered or unknown compounds (denoted as U in Fig. 2); (6) the intensity ratios may differ from the JCPDS data due to the superposition of the peaks and the preferential crystallographic orientation of the small crystallite in the specimen; (7) sample 9 (880 hr) shows only peaks of ammonium sulfate and metallic copper except for a weak undefined peak (d = 0.252 nm); and (8) the registered main peaks for CuH in JCPDS(8-255) are d = 0.253, 0.231, and 0.222

TABLE 1

Change in Mean Formula Weights in the Reaction of $[Cu(NH_3)_4]SO_4 \cdot H_2O$ (**1**) with Hydrogen

Sampling no.	0	1	2	3	4	5	6	7	8	9
Reaction time/hr	0	290	340	415	540	610	660	740	790	880
MFW ω[a]	245.5	244	243	242	241	239	236	223	204	198
MFW ϕ[b]	245.5	229	235	232	235	238	236	224	204.6	200.5

[a] Mean formula weight $\omega = 245.5 \times W/W_0$, W_0 = the initial weight of **1**, and W = the weight of the *whole* solid sample in the process of the reaction with hydrogen. 245.5 = the formula weight of **1**.

[b] Mean formula weight $\phi = 159.6 \times m_0/m$, m_0 = the weight of a *portioned* sample just after taken out from the surface of the reaction product in the process of the reaction with hydrogen, and m = the weight of the sample at the final stage of thermoanalysis (440°C), where the solid samples were thoroughly converted into $CuSO_4$ (FW = 159.6).

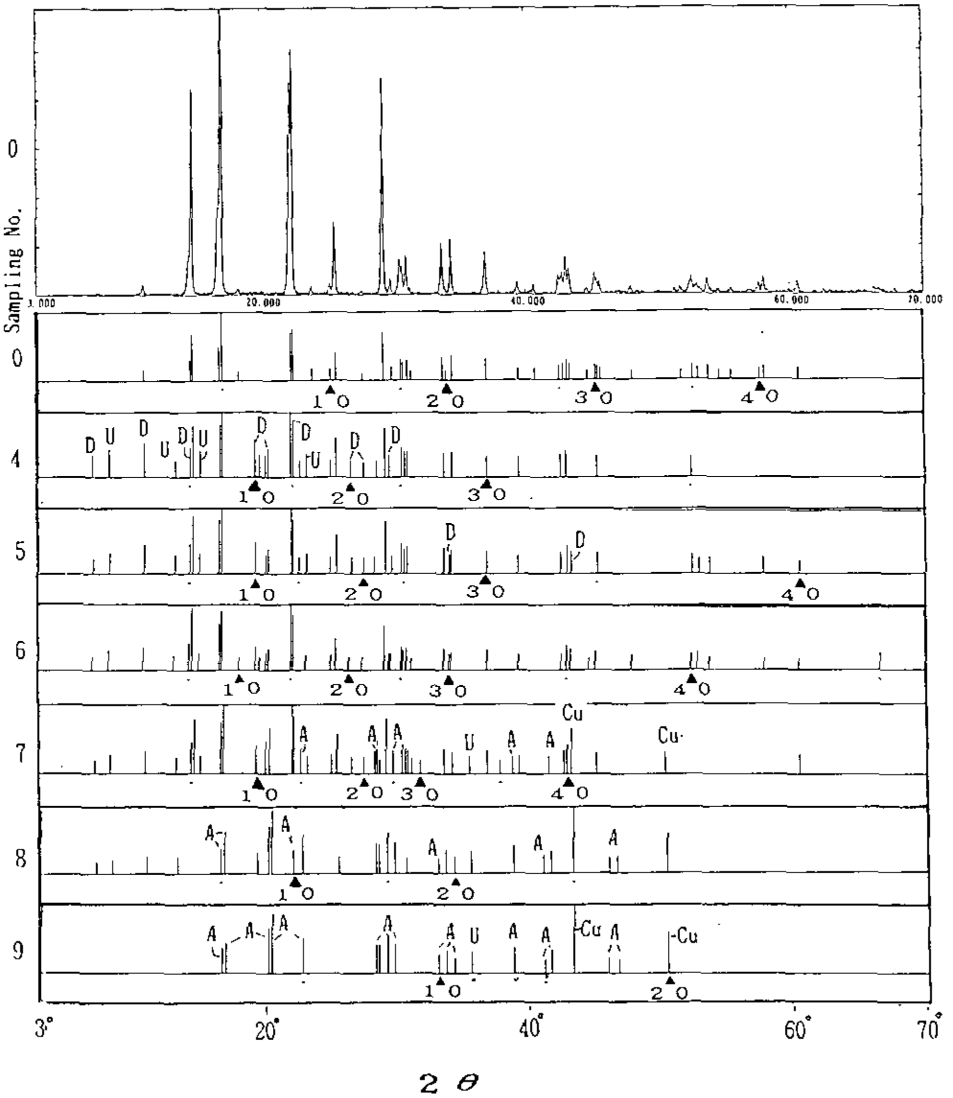


FIG. 2. Variation of X-ray diffraction pattern of $[Cu(NH_3)_4]SO_4 \cdot H_2O$ by reaction with hydrogen. The abscissa indicates 2θ from 3 to 70°, and the numbers marked ▲ indicate the ordinal numbers of the diffraction peaks in each pattern. The sampling numbers on the left ends are common with those in Tables 1 and 2A. The characters, *D*, *Cu*, *A* and *U*, denote the double salt, **2**, metallic copper, ammonium sulfate and unidentified peaks. These signs are attached at the first appearance of each identified main peak, from insufficiency of the space. For sample 9, the signs are attached at all the peaks. For more precise identification a supplemental material is available.

TABLE 2A
Characterization of the Reduction Products with H_2

Sampling no.	0	1	2	3	4	5	6	7	8	9
reaction time	0	290	340	415	540	610	660	740	792	880
MFW ϕ	245.5	229	235	232	235	238	236	224	204.6	200.5
MW Loss[a]	0	16.5	10.5	13.5	10.5	7.5	9.5	21.5	40.9	45.0
Loss of H_2O[b]	0	0.92	0.58	0.76	0.58	0.41	0.53	1	1	1
Loss of NH_3[b]	0	0	0	0	0	0	0	0.2	1.34	1.58
				From 100°C						
Loss H_2O/mole	1	0.08	0.42	0.23	0.33	0.60	0.47			
Loss of MW	50.3	36.6	40.9	38.3	22.48	44	21.7	27.7	5.89	
Loss %	20.5	16	17.4	16.5	9.57	18.48	9.2	12.4	2.88	
Loss NH_3/mole	2	2.07	2	2	0.98	2	0.77	1.63	0.34	
				From 160°C						
Loss of MW	#[c]	↓[d]	↓	↓	17.4	↓	20.4	↓	#	
Loss %					7.4		8.66			
Loss NH_3/mole					1.0		1.2			
				From 200°C						
Loss of MW	9.6	11.5	10.9	13	13.4	13.5	12.4	19.5	22	25.2
Loss %	3.9	5	4.67	5.5	5.7	5.7	5.27	8.7	11	12.6
Loss NH_3/mole	0.56	0.68	0.64	0.75	0.8	0.8	0.72	1.15	1.29	1.48
				From 270°C						
Loss of MW	6.4	#	#	#	3.57	↓	2.8	↓	↓	↓
Loss %	2.6				1.52		1.2			
Loss NH_3/mole	0.38				0.21		0.16			
				From 330°C						
Loss of MW	17.3	21.3	23.7	21.5	18.3	21.3	19	16.9	17	15.6
Loss %	7	9.3	10.1	9.2	7.77	8.94	8	7.54	8.33	7.7
Loss NH_3/mole	1.0	1.25	1.39	1.25	1.07	1.25	1.1	1.0	1.0	0.91
				Sum (observed)						
Loss of MW	83.5	69.4	75.6	74	75.5	78.4	76.3	64.1	45	40.9
Loss %	34	30.3	32.2	31	32.1	32.9	32.3	28.6	22	20.3

[a] Molecular weight loss from 1 = 245.5 − ϕ. The losses are attributed to the reaction with high pressure hydrogen.

[b] The number of the lost molecules of H_2O or NH_3. Here we presume that the weight loss occurs in the first stage (up to 700 hr) was mainly due to H_2O.

[c] # denotes no decrease in weight in this temperature range.

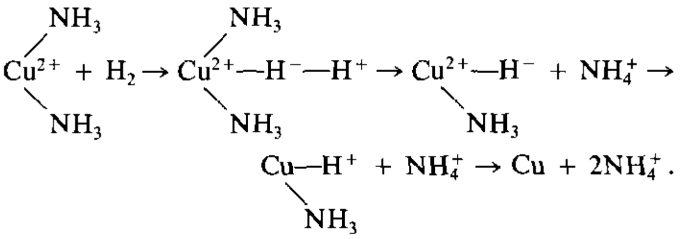
[d] The arrow denotes gradual decrease in weight in this temperature range. It is difficult to divide the curve at a certain temperature. The loss is involved in the value of a preceding temperature range. The No. 4 and No. 6 samples have a definite change of slope on the curve.

nm with the relative intensities 30, 30, and 100 respectively. In the same range the samples showed very weak peaks: 0.252 nm (unidentified, above), 0.232 nm (overlapping with that of $(NH_4)_2SO_4$) and 0.222 nm (only samples 5, 6, and 7). These peaks are not strong enough to confirm the generation of the copper hydride.

From the above data the total reaction may be expressed by the following equation:

$$\begin{aligned} &Cu(NH_3)_4SO_4 \cdot H_2O + H_2 \rightarrow \\ &\qquad (NH_4)_2SO_4 + Cu + 2NH_3 + N_2O. \end{aligned} \qquad [1]$$

The following mechanism can be proposed for this reaction as the most probable one. The reaction is initiated by the attack of H_2 on the copper(II) center followed by the elimination of one of the hydrogen atoms as a proton to bind neighboring ammonia molecules forming ammonium ion. The hydridocopper(II) thus formed readily dissociates into copper(0) and H^+ as the result of an intramolecular two-electron transfer accompanied by the incorporation of H^+ into another neighboring NH_3, i.e.,



$$(NH_3)_2Cu^{2+} + H_2 \rightarrow (NH_3)_2Cu^{2+}\text{—}H^-\text{—}H^+ \rightarrow (NH_3)Cu^{2+}\text{—}H^- + NH_4^+ \rightarrow (NH_3)Cu\text{—}H^+ + NH_4^+ \rightarrow Cu + 2NH_4^+.$$

TABLE 2B
Thermoanalysis of Authentic Samples

Sample mole weight	$(NH_4)_2SO_4$ 98.1	Control sample[a] 195.63	$(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$ 327.7
		From 100°C	
Loss of MW	#[b]	#	25.2
Loss %			7.7
Loss H_2O/mole			1.4
		From 160°C	
Loss of MW	#	#	10.6
Loss %			3.24
Loss H_2O/mole			0.6
		From 200°C	
Loss of MW	#	#	#
Loss %			
Loss NH_3/mole			
		From 270°C	
Loss of MW	27	29–34[c]	14
Loss %	20	15–17	4.4
Loss NH_3/mole	1.6	1.7–2.0	0.8
		From 330°C	
Loss of MW	106	39–44	121
Loss %	80	20–22	36.9
Loss NH_3/mole	0.4	0.3–0	1.2
Loss H_2SO_4/mole	1	0.35–0.45	1
		Sum (observed)	
Loss of MW	132	68–78	170.8
Loss %	100	35–40	52
Residue	nil	CuO, $CuSO_4$	$CuSO_4$

[a] The control sample is a mixture of finely powdered metallic copper and ammonium sulfate in 1 : 1 molar ratio with metallic luster.

[b] # denotes no decrease in weight in this temperature range.

[c] Decrement in weight in the control sample is sensitive to the experimental conditions; the values vary in the range shown. The weight loss sets in at 270°C and continues to 440°C with slight change of slope at 350°C in the weight-temperature curve.

Thus, the presence of ammonia at the reaction site seems essential for this reaction. The ammonium ions yielded in the reaction readily form ammonium sulfate or further react with an unreacted **1** to form a more stable double salt, $(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$, the presence of which was detected by the X-ray diffraction study, according to the reaction,

$$Cu(NH_3)_4SO_4 \cdot H_2O + (NH_4)_2SO_4 + H_2O \rightarrow (NH_4)_2Cu(SO_4)_2 \cdot 2H_2O + 4NH_3. \quad [2]$$

A part of the ammonia in [2] may still remain in the solid probably being trapped in the coordination sphere, and participates in the reduction of the double salt to give the final product, i.e.,

$$(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O + H_2 + 2NH_3 \rightarrow 2(NH_4)_2SO_4 + Cu + 2H_2O. \quad [3]$$

Thermogravimetric analyses were performed under nitrogen atmosphere from room temperature to 440°C at the ascending rate of 10°C/min on the samples taken out at various reaction times (samples 0–9 in Table 1). The result is summarized in Table 2A. The data show that all of the samples lost two molecules of NH_3 below 200°C in spite of the difference in their history, i.e., the weight losses of samples 0–6 in the reduction process, $(245.5 - \omega)$, were rather small, whereas samples **7–9** lost a considerable amount of weight (corresponding to 0.2–1.6 molecules of NH_3) during the reduction process. The third NH_3 molecule was lost in the 200–330°C range and the last NH_3 was given off above 330°C in the thermal analysis.

An interesting feature of the thermolysis is that all samples were converted into unhydrated copper(II) sulfate at the final stage of the thermal process. This implies that the metallic copper yielded by the reduction with hydrogen was oxidized during the thermal analysis, which was run in an nitrogen atmosphere. The probable oxidizing agent seems to be a slight amount of molecular oxygen present presumably due to incomplete substitution of nitrogen for air and/or adsorption on the surface of colloidal copper. A reaction without dioxygen such as, $Cu + (NH_4)_2SO_4 \rightarrow CuSO_4 + 2NH_3 + H_2$, might be considered as an alternative explanation at a high temperature. In any case no definite conclusion can be drawn at the present stage. In order to gain more insight into the reaction, a control sample consisting of a mixture of finely powdered lustrous metallic copper and ammonium sulfate in a 1 : 1 molar ratio, was treated under the same conditions up to 440°C. The result was definitely different from that of sample taken from the final reaction product (sample 9 in Tables 1 and 2A) as shown in Tables 2A and 2B; i.e., the weight loss of the control sample in the thermolysis was more than 35% ($2NH_3$ from 270°C and a part of H_2SO_4 from 310°C), whereas that of sample 9 was 20% (starting from 200°C of NH_3 loss). The latter value is compatible with the reaction,

$$Cu + (NH_4)_2SO_4 + O_2 \rightarrow CuSO_4 + 2NH_3 + 2H_2O, \quad [4]$$

where the decrease of weight is calculated at 18.4%. The final residues of the control sample, in which the losses ranged between 35 and 40%, seem to be mixtures of CuO and $CuSO_4$ in variable molar ratios. The difference in reactivity between sample 9 and the control sample could be attributed to the difference in surface conditions between the powdered (lustrous) and the colloidal (black) coppers.

The double salt, **2**, showed a behavior similar to the ammonium sulfate in the thermogravimetric analysis, that is, the loss of ammonia occurred at higher temperature than in the case of **1**. As shown in Table 2A, the ammonia loss of samples 1 through 5 at temperatures >330°C, 1 ~ 5, is significantly larger than that (= 1.0) for sample 0 (**1**). These facts indicate that the intermediate samples contain the double salt. This is compatible with the X-ray data in Fig. 2.

CONCLUSION

$Cu(NH_3)_4SO_4 \cdot 2H_2O$ reacts with 9.5 ± 0.5 MPa molecular hydrogen at 85°C giving $(NH_4)_2SO_4$ and colloidal copper as a final product. During the reaction the presence of $(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$ as a transient intermediate was detected by powder X-ray analysis. The presence of ammonia seems to be important to promote the reduction of Cu(II) to Cu(0).

The colloidal copper formed in the above reaction showed a remarkable reactivity to form a copper(II) compound.

SUPPLEMENTAL MATERIALS

A table of Numerical Values of 2θ in X-Ray Diffraction of the Reaction Products is available from one of the authors (Kanda).

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