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The Study of Metal Colloids Produced by Means of Gas Evaporation Technique. II. Reaction of Metal Sols in Organic Solvents

Keisaku Kimura
Instrument Center, Institute for Molecular Science, Myodaiji, Okazaki 444

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Synopsis. The reaction of copper colloid in ethanol was studied. In the beginning of the reaction, very small particles reacted with ethanol producing ethoxide. With the proceeding of the reaction, the 577-nm characteristic copper band showed a red shift together with the broadening of the line width. This was explaind by the size dependence of the particles on the spectrum. Lead colloid was also examined.

We have recently proposed a new technique to prepare metal colloids in organic solvents.[1] It was found that the colloid stability was dependent on the kinds of metal; In, Al, Ag, and Au were stable and Pb, Sn, Ca, and Cu were unstable. In the latter case, the color of the metal colloid solution changed with time. An absorption peak was found at 213 nm, irrespective of the metal species which suggested a formation of alkoxide anion.[2] The color change was particularly prominent in copper colloid, the color of which changed from wine red to yellow within 30 min under aerobic conditions while within one day under anaerobic conditions. In the present paper, we have studied this reaction in order to clarify the cause of the time dependence of the spectrum and the origin of the 213-nm peak.

Experimental

The metal colloids were prepared by the method described in the previous report.[1] Ethanol (99.5%) was used without further purification. Hexane was distilled *in vacuo* from CaH_2 to completely exclude traces of oxygen and water. An authentic sample of ethoxide was prepared by dissolving a small grain of sodium metal in ethanol.

The time development of the spectra (room temperature) was recorded by a Hitachi 556 spectrophotometer just after the preparation of the sol in an Ar atmosphere.

Results and Discussion

Figure 1 shows the time course of the spectra of copper–ethanol colloid. The existence of an isosbestic point at 296 nm shows that the reacting system contains two components. In this system, the metal fine particles change to a single unknown product, because the 577-nm peak, which is characteristic in fine copper particles,[3] gradually decreased as time passed. The increase of the peak height of the 213-nm absorption band is suggestive of the formation of the ethoxide ion.

In the previous paper, we postulated a formation of metal ethoxide. In order to confirm this conjecture, we measured the optical absorption spectrum of the colloid in hexane solution in which no alkoxide can form. Although the fine metal particles have a tendency to coagulate in alkanes, it is possible to measure the absorption spectrum if it is immediately after the preparation of the sample. In Fig.2 is shown the absorption spectra of copper colloid in ethanol (a), and in hexane (b) together with that of ethoxide ion (c). It is clear that there is no 213-nm peak in hexane. Therefore, the 213-nm peak in ethanol is concluded as coming from ethoxide ion.

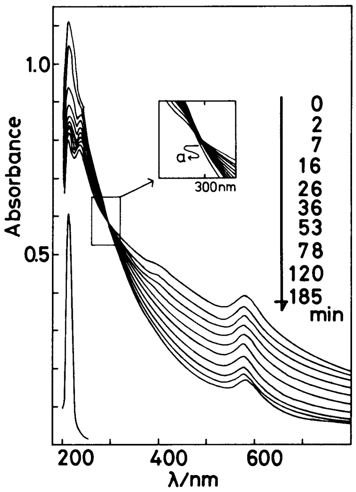

Fig. 1. Optical absorption spectra of copper colloid as a function of time. The number in the figure are the time after the preparation of the sample. The spectrum of sodium ethoxide in ethanol is also shown in the same figure. The insertion is the expansion of the region of isosbestic point. The deviation from the isosbestic point at 10 h after the preparation is shown by a.

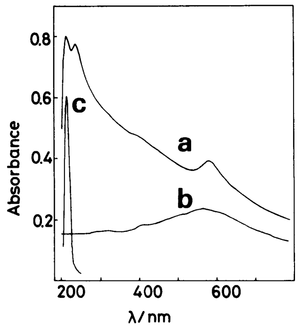

Fig. 2. Absorption spectra of copper colloid in ethanol (a) and in hexane (b). The spectrum of sodium ethoxide in ethanol is shown in c.

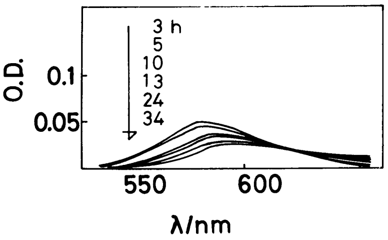

Fig. 3. Optical absorption spectra of copper colloid in the visible region as a function of time later than 3 h. Spectra are drawn after subtraction of the background slope.

Returning now to Fig.1, we notice that the 577-nm peak shifts to longer wavelength at 185 min and that the spectrum does not pass through the isosbestic point at 185 min and at 10 h after the preparation of the sample (see the expanded spectra in the insert). This peak shift is more noticeable after longer periods of time as seen in Fig. 3. After such a long reaction time, all spectra did not pass through the isosbestic point at 296 nm. These findings show that a new reaction phase has progressed. In this stage, the color of the solution gradually changed to yellow from wine red. It should also be noted in the same figure that the band width is broadened with the peak shift. The time dependences of the peak shift, of the band width at the half maxima, and of the absorption intensity are shown in Fig. 4 after correction for background absorption.

As mentioned before, the position of the absorption band of the copper colloid does not vary for the first couple of hours. When it is over 180 min, the peak gradually shifts to longer wavelength. Initially the band width decreases with time, but then it increases later than 180 min with the concurrent shifting of the peak as seen in Fig. 4. As for the intensity, it monotonously decreases with time, corresponding to the decrease of particle size. These findings show that the colloid system changes in the size distribution and in the average diameter and that this change becomes prominent at 180 min. The electron micrographs of the colloids were taken at 7 min and at 180 min after the preparation. The size distributions of the colloids at the different time are shown in Fig.5. Just after the preparation, the average diameter of the colloids was 53 Å and the width at the half maxima of the distribution was 60 Å. These values changed to 26 Å and 30 Å respectively at 180 min after. This finding shows that the size distribution becomes narrower and the average diameter also decreases after longer periods.

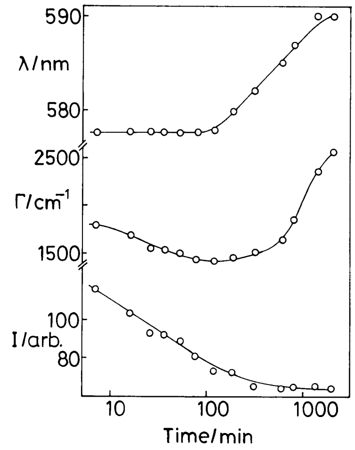

Fig. 4. The absorption peak, the band width and the absorption intensity as a function of time. These were calculated from the spectra in Fig. 3. Solid lines are for eye guide.

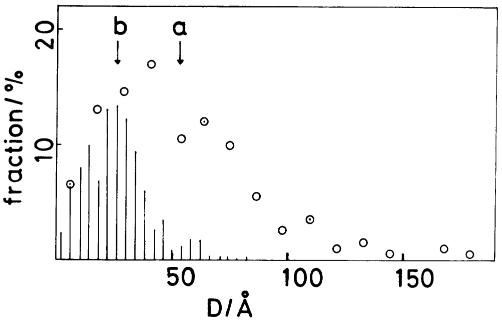

Fig. 5. The distribution of the particle size of colloids. The diameter distribution of the sample, 7 min after the preparation, is shown by circles. The average diameter is indicated by the arrow a. The histogram shows the distribution of the sample at 3 hr after the preparation. The average diameter of this sample is shown by b.

Based on these observations, we can explain the time dependence of the band width and the position of the absorption peak shown in Fig.4. In the first stage, ultrafine particles diminish rapidly because very small particles easily react with ethanol forming ethoxide. Therefore, the distribution of particle size becomes narrower, resulting in the decrement of the band width, because the absorption band is a superposition of many bands of the particles with different sizes. In the second stage, many particles reduce their radii, resulting in the reduction of the average particle size which may cause the change in the peak position and the band width.

It is well known that the spectrum of fine particles depends on the particle size. Quantum mechanical calculation shows that the band width of the surface plasmon is broadened and the peak shifts to higher energy with a decrease in the radius.[4,5] These results conflict with the present observations, if we explain the peak shift and broadening as a size dependence of a plasmon band. On the other hand, Abe *et al.* reported that the 577-nm band should not be regarded to a pure plasmon band but to interband transitions mixed with plasmon band.[3] Kreibig reported the size dependence of the interband transition edge in gold particles in which the band edge shifts toward lower energy with a decrease in size.[6] If this tendency also holds for the peak position, the peak shift is explaind by the size dependence of the interband transition of copper colloid. The 214-nm peak found in the lead–ethanol system also disappeared in the lead–hexane system. This finding is also consistent with the results of copper described above.

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References

1) K. Kimura and S. Bandow, *Bull. Chem. Soc. Jpn.*,**56**, 3578 (1983).

2) E. F. Caldin and G. Lang, *J. Chem. Soc.*, **1954**, 3737.

3) H. Abe, K. P. Charle, B. Tesche, and W. Schulze, *Chem. Phys.*, **68**, 137 (1982).

4) A. Kawabata and R. Kubo, *J. Phys. Soc. Jpn.*, **21**, 1765 (1966).

5) L. Genzel, T. P. Martin, and U. Kreibig, *Z. Phys.*, **21**, 339 (1975).

6) U. Kreibig, *J. Phys. (Paris), Colloq.*, **C2**, 97 (1977).