Formation of Ruthenium Colloid in Ethylene Glycol

Akane Miyazaki,* Kenji Takeshita, Ken-ichi Aika, and Yoshio Nakano
Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received December 9, 1997; CL-970933)

Ruthenium metal colloid was produced by the reduction of $RuCl_3$ in ethylene glycol. The metal particles observed by TEM had uniform shape and size, less than 5 nm in diameter. The particles agglomerated easily at pH higher than 3. When the pH value of the solution was decreased to 2, the colloidal particles were dispersed well due to the increase of the surface charge.

Ruthenium has been known to show very unique and interesting activity as a catalyst, for example in ammonia synthesis.[1] At the present stage, supported ruthenium catalysts are prepared mainly by impregnation. Metal particles supported by impregnation are commonly nonuniform in size and shape,[2] though the catalytic activity depends on the size and the shape of metal particles.[3] Catalyst preparation using metal colloid is known to be useful to obtain monodispersed supported metal catalysts, for example Rh[4] and Pt.[5] However, there is very few method to prepare ruthenium metal colloid. It is reported that ruthenium is unusual noble metal which cannot be reduced in methanol.[6,7] The purpose of this paper is to synthesize fine, well-dispersed ruthenium metal colloid by the polyol method. The polyol method is a way to prepare nano-scale metal powder.[8,9] This method can be applied for various metals, and size control of the powder is also possible. We tried to apply this polyol method to prepare the metal colloid of ruthenium.

Ruthenium (III) chloride, the precursor, was dissolved into ethylene glycol to obtain 0.3 mM of solution. This concentration corresponds to 1/100 of that reported by Kurihara *et al.*[9] The solution was maintained at 453 K in an oil bath. In the course of reaction, a few milliliter of the reacting solution was sampled every few minutes, and the sample solution was cooled down immediately in an ice-water bath.

In the polyol method, it is reported that the metal particles are formed by reduction of metal ions and nucleation of them in the solution.[8] In order to reveal the stage of particle formation, we observed the reacting solution by a transmission electron microscopy (TEM, Hitachi H8100). A series of color change observed in the course of reaction is shown in Figure 1 together with the TEM micrographs. Up to 8 min of heating, the color of the reacting solution changed to transparent, and then became pink. However, we could not observe any particles in these stages. After 11 min of heating, the solution acquired brownish color and clusters of small particles could be observed in this stage. The primary small particles had uniform ellipse shape and size of less than 5 nm in diameter. X-ray probe micro analysis (EPMA) suggested that the component of the particles was ruthenium, and electron beam diffraction pattern indicated that the particles had a crystal structure. Therefore, it was found out that the crystalline particles of ruthenium appeared after heating for 11 min.

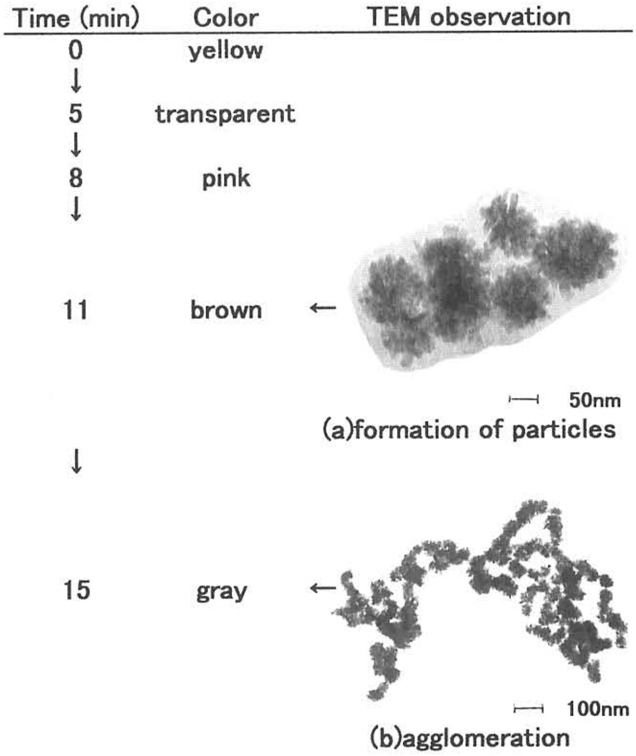


Figure 1. Schematic time course of the reaction and TEM observation of the solution.

After heating for 15 min, the solution became gray and the particles seemed to agglomerate intensively to form larger cluster around 1 μm as shown in Figure 1(b). Further heating, for 30 min, resulted in forming fine black precipitate. Powder x-ray diffraction analysis (Rigaku Gaigerflex RAD-B) was carried out for the precipitate collected by filtration. The diffraction pattern shown in Figure 2 corresponds well to that of ruthenium metal as depicted by bars. This result shows that the ruthenium (III) chloride was reduced almost completely to ruthenium metal through the above reaction by the polyol method. Therefore, it can be said that after 11 min of heating, we could obtain monodisperse ruthenium metal colloid.

The ruthenium colloid obtained above tends to agglomerate easily after the nucleation as shown in Figure 1. We tried to disperse the ruthenium colloidal particles by controlling the pH of the solution. Sulfuric acid or aqueous solution of sodium hydroxide was used to

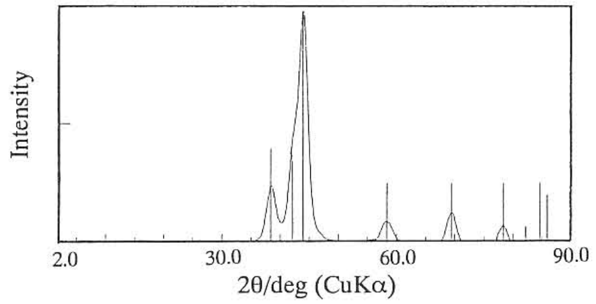


Figure 2. XRD pattern of the black precipitate.

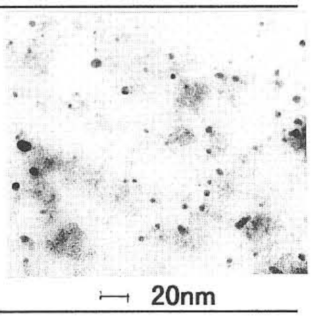
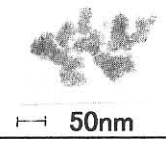
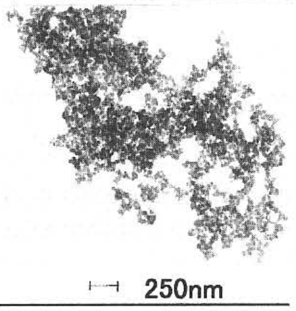
Zeta potential (mV)	pH	TEM observation
44.62	2.2	
23.58	2.8	
−7.96	4.1	
−25.13	8.3	

Figure 3. TEM observation of the colloidal solution at different pH values.

vary the pH value of the ruthenium colloidal solution, which was obtained after heating for 11 min. In order to evaluate the surface charge of the colloid, zeta potential was measured by an electrophoretic light scattering spectrophotometer (Otsuka Electronics ELS-800). Figure 3 shows TEM micrographs of the colloidal solution of different pH together with their zeta potential. It can be seen that the colloidal particles were dispersed better when the pH value of the solution was lower. Without the pH adjustment, the ruthenium colloidal solution had a pH value of around 3, and at this pH value the colloid charged slightly positive. When pH value of the solution was decreased around 2, the zeta potential increased to around 50 mV. It is said that the particles agglomerate easily when the absolute value of the zeta potential is lower than 50 mV.[10] As we can see in the TEM micrograph in Figure 3, the dispersion was improved very much when the pH value of the colloidal solution was around 2. The increase of acidity was found out to be effective to increase the surface charge of the ruthenium metal colloid and to improve its dispersion remarkably. The ruthenium metal colloid obtained in this study would help to prepare the supported ruthenium catalysis with fine and uniform shape.

References and Notes

1 K. Aika, *Petrotech*, **17**, 127 (1994).
2 B. C. Gates, *Chem. Rev.*, **95**, 511 (1995).
3 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. El-Sayed, *Science*, **272**, 1924 (1924).
4 M. Kishida, T. Fujita, K. Umakashi, J. Ishiyama, H. Nagata, and K. Wakabayashi, *J. Chem. Soc., Chem. Commun.*, **1995**, 763.
5 K. Aika. L. L. Ban, I. Okura, S. Namba, and J. Turkevich, *J. Res. Inst. Catalysis Hokkaido Univ.*, **24**, 54 (1976).
6 H. Hirai, *J. Macromol. Sci.-Chem.*, **A13(5)**, 633 (1979).
7 H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. *Sci.-Chem.*, **A13(6)**, 727 (1979).
8 F. Fievet, J. P. Lagier, B. Blin, B. Beaudoin, and M. Figlarz, *Solid State Ionics*, **32/33**, 198 (1989).
9 L. K. Kurihara, G. M. Chow, and P. E. Schoen, *Nano Structured Materials*, **5**, 607 (1995).
10 K. Furusawa, in "Zeta Potential," by A. Kitahara, K. Furusawa, M. Ozaki, and H. Ohshima, Scientist, Tokyo (1995), Chap. 3, P.105.