Characterization of Fine Particles of Ruthenium–Alumina Composites Prepared by Different Methods

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Fine particles of ruthenium-alumina composites were prepared by three different methods, i.e., direct synthesis, reduction of mixed oxide and impregnation methods. In the direct synthesis method, the sample was prepared by hydrogenolysis of a mist of a mixed solution of ruthenium chloride and aluminium nitrate. Transmission electron microscopy as well as electron and X-ray diffraction measurements showed that amorphous ruthenium clusters (<2 nm) dispersed in an amorphous alumina particle were prepared by this method. Reduction of the mixed oxide prepared in the same way in a stream of air produced the particles undistinguishable from the above sample by X-ray diffraction and transmission electron microscopy, whereas the conventional impregnation method gave crystalline ruthenium clusters dispersed on the alumina surface. The infrared spectrum of adsorbed carbon monoxide showed three characteristic absorption bands at about 2000, 2070 and 2140 cm\(^{-1}\) in all samples, but their frequencies and relative intensities were different, depending upon the method of preparation. In the sample prepared by the direct synthesis method, the frequencies and relative intensities of these bands changed during crystallization of the ruthenium clusters by firing at high temperatures. It is concluded that the most highly dispersed metal-ceramics composite was prepared by the direct synthesis method.

Key-words: Fine particles, Ru–Al\(_2\)O\(_3\) composites, Metal-ceramics composite, CO adsorption

1. Introduction

Metal–ceramics composite particles have a number of potential applications in many fields of materials technology such as cermets, hybrid materials, sensors and catalysts. High dispersion of metal clusters into ceramics is preferable in order to improve both mechanical and chemical properties. Metal–ceramics composite particles can be prepared by several methods. One of the most convenient method is the impregnation method. More finely dispersed metal clusters can be prepared by superficial reduction of dilute mixed metal oxide solid solution.\(^{1)}\) Recently, we reported a direct preparation method of ruthenium–alumina composite by reduction of the mist of a mixed solution of ruthenium chloride and aluminium nitrate.\(^{2)}\)

In the present paper, ruthenium–alumina composite particles are prepared by three different methods, and characterized in order to find how metal dispersion is influenced by the method of preparation.

2. Experimental

2.1 Materials

Ruthenium (III) chloride (99.9%) and aluminium nitrate (S grade) were obtained from Wako Pure Chemical. Hydrogen (7 nine) was obtained from Nippon Oxygen Co. and used through a dry ice trap. Carbon monoxide (99.5%) was obtained from Takachiho Chemical, and purified by distillation at liquid nitrogen temperature. Helium was obtained from Japan Helium Center and purified through a Molecular Sieve 5 A column and a rare gas purifier (Model RT–3, Japan Pure Hydrogen Co.), successively.

2.2 Preparation of composite particles

The samples (A, B and C) containing 3.0 wt% of ruthenium were prepared by following three different methods.

1) Direct synthesis method.\(^{2)}\) A mist of a mixed aqueous solution (5 wt%) of RuCl\(_3\) and Al(NO\(_3\))\(_3\) was generated into a stream of hydrogen by a ultrasonic atomizer, the diameter of the droplet being ca. 5 \(\mu\)m. The mist was heat-treated successively through three furnaces. Temperatures of the furnaces were adjusted for evaporation of water (443 K), hydrogenolysis of the mixed metal salts (573 K), and further reduction of the particles (773 K), respectively. The flow rate was controlled at 1 l/min by a control valve. The particles were collected by a glass filter at 393 K (sample A).

2) Mixed oxide reduction method. Sample B was prepared by reduction (at 673 K for 2 h) of the ruthenium aluminium mixed oxide particles which had been prepared in the same way with the same raw materials and the same conditions except use of air instead of hydrogen.

3) Impregnation method. Alumina particles (ALCOA F110, 32–60 mesh, surface area=190 m\(^2\)/g)
were impregnated with a RuCl₃ solution and calcined at 623 K for 16 h. The sample C was reduced at 673 K for 2 h.

2.3 Characterization

Infrared (IR) spectrum of adsorbed carbon monoxide was recorded with a JASCO FT/IR-3 Fourier-transform IR spectrometer. The construction of the vacuum IR cell used for the measurements was similar to that reported by Peri and Hannan. The sample was pressed into a thin self-supporting wafer and pretreated in the cell. After reduction with hydrogen at 673 K for 2 h, the sample was evacuated at the same temperature for 30 min and the temperature of the sample was lowered to room temperature for adsorption of carbon monoxide. The adsorption was carried out at a constant pressure of 5300 Pa for 15 min at room temperature. Carbon monoxide in the gas phase was evacuated at room temperature for 5 min before IR measurement. The spectrum taken before carbon monoxide adsorption was used as the background spectrum.

Specific surface areas were measured by the BET method with adsorption of nitrogen at 77 K. A JEOL JSM-T200 scanning electron microscope (SEM), a JEOL JEM-2000EX transmission electron microscope (TEM) and a Rigaku Denki powder X-ray diffractometer with nickel filtered Cu Kα radiation were used for characterization of the samples.

3. Results and discussion

X-ray diffraction (XRD) spectra of the composite particles were measured after coating the surface of reduced samples (673 K, 2 h) with liquid paraffin, and are shown in Fig. 1. Crystalline peaks of ruthenium metal are observed only in the sample prepared by the impregnation method. The cluster size of ruthenium metal is too small to be characterized by XRD method, in the samples A and B.

SEM observations showed that the particles of sample A were spherical. The particle size distribution was narrow with an average diameter of 0.64 μm. A cumulative surface area of 1.9 m²/g was obtained from the distribution curve. Comparison between the cumulative and BET (5.4 m²/g) surface areas suggests that the particles are porous. Temperature-programmed reduction measurement showed that the amount of hydrogen consumed below 570 K was much smaller than that of a ruthenium alumina mixed oxide. This indicates that most of the ruthenium ions were reduced in this sample. Transmission electron microscopy as well as electron diffraction measurements showed that amorphous ruthenium clusters (< 2 nm) were dispersed in an amorphous alumina particle. Amorphous ruthenium clusters in the amorphous alumina may be prepared because the fine droplets were rapidly dried and then rapidly reduced by hydrogen.

The particles of sample B were also spherical. The particle size distribution is narrow with an average diameter of 0.72 μm as shown in Fig. 2. Comparison between the cumulative (1.5 m²/g) and BET (4.1 m²/g) surface areas suggests that the particles are porous. Almost same TEM micrographs were obtained with sample B and we could not distinguish between samples A and B by the micrographs.

An IR study with a probe molecule was undertaken for surface characterization of the ruthenium atoms. In the adsorption of carbon monoxide on ruthenium-containing samples, general agreement exists on the presence of three IR bands. The low frequency (LF) band at 1990–2030 cm⁻¹ is assigned to the vibration of carbon monoxide linearly bonded on ruthenium crystallites. On the other hand, the middle (MF) and high frequency (HF) bands at 2080 and 2140 cm⁻¹ have been assigned to the vibrations

Fig. 1. XRD spectra of ruthenium-alumina composites. A: sample A, B: sample B, C: sample C

Fig. 2. Particle size distribution of sample B.
of a multicarbonyl.\textsuperscript{4,5)}

**Figure 3** shows the IR spectra of carbon monoxide adsorbed on the three samples A, B and C. XRD investigation showed that ruthenium metal was crystalline only in the sample C. Three characteristic absorption bands are observed in all samples, but their frequencies and relative intensities are different, depending upon the method of preparation. The presence of the LF band in all samples indicates that ruthenium crystallites or clusters are contained in all the samples. In sample A, the intensity of MF band is the highest at 2070 cm\(^{-1}\). Relative intensities of the three bands remained almost constant when temperature of reduction (573–773 K), temperature of adsorption (290–423 K) and adsorption period (15 min–3 h) were changed. Almost same spectrum was obtained on the sample without reduction, i.e., with only evacuation at 673 K for 2 h. In the samples B and C, on the other hand, the intensity of LF band is the highest at 2000 and 2030 cm\(^{-1}\), respectively. The spectrum C was similar to those reported for impregnated ruthenium catalysts.\textsuperscript{4)

Effect of heat treatment was studied with the sample prepared by the direct synthesis method. The sample was treated at various temperatures for 30 min in the stream of helium. XRD spectra of the treated samples are shown in **Fig. 4**. No crystalline peak was observed in the samples treated at temperatures lower than 1100 K. However, crystalline peaks of ruthenium metal, ruthenium dioxide and \(\alpha\)-alumina appeared after the sample was treated at 1273 K. This indicates that the original sample was amorphous, and that the size of the ruthenium clusters increased by sintering during the high temperature treatment.

**Figure 5** shows the effect of the heat treatment on the IR spectrum of adsorbed carbon monoxide. As
the temperature of treatment increases, or as the sample is crystallized, the spectrum changed. The treatment at 873 K increased the intensity of LF band, indicating the formation of the flat crystalline surfaces which enhance the adsorption of the linearly bonded carbon monoxide molecules. The spectrum obtained after the heat treatment at 1073 K (spectrum 3) are almost similar to that of sample B in Fig. 3. The spectrum 4, where ruthenium metal in the sample became crystalline as shown in Fig. 4, was almost same as that of the impregnated sample shown in Fig. 3. These facts indicate that the surface structures of ruthenium clusters in samples B and C can be realized by the high temperature treatment of sample A.

In the consequence of above discussion, it is concluded that ruthenium clusters are the finest in the sample prepared by direct synthesis method among the three methods studied. The dispersion of metal may be improved by direct synthesis of metal-oxide composite, because the chance of the aggregation of metal atoms is diminished in the direct synthesis. Moreover, clusters with a different chemical reactivity may be obtained by the direct synthesis because the conditions of cluster formation are different. Results of this study have shown that the carbon monoxide adsorption is an effective method for the surface characterization of highly dispersed metal-ceramics composites.

References