Silver Fine Particle Aggregate on a α -Al₂O₃ Surface Using a Sonochemical Reaction

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音響化学反応による α -アルミナ表面上への銀微粒子の凝集

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Key Words : Sonochemical Reaction, Ag Fine Particle Aggtegate, α -Al₂O₃

Introduction

Silver catalyst is a typical example of an industrial application using silver. Silver in particular is the only effective catalyst for manufacturing reactions using ethylene oxidation. Silver is usually fortified with oxides that have a high melting point and large specific surface area such as alumina, because the sintering of silver is done at a comparatively low temperature.

Silver has also been used as a substrate for surface-enhanced Raman spectroscopy (SERS). The ruggedness of the aggregate surface of the silver particle used for SERS measurement is usually prepared from 10 nm to several hundred nm, corresponding to wide plasmon absorption^{1),2)}.

A procedure to prepare fine particles of silver using ultrasound has been reported³⁾. When an AgClO₄ or AgNO₃ aqueous solution is irradiated with ultrasonic wave, fine Ag particles form according to the following reactions :

Cavitation has been reported when a water medium is irradiated with relatively strong ultrasonic wave, the radical decomposition of water molecules occurs and an H $\cdot$ and OH $\cdot$ radical (reaction(1))³⁾. In this paper, the adsorption of fine silver particles on α -alumina produced by irradiating an AgNO₃ $\cdot$ propanol aqueous solution with ultrasound, α -alumina

coexistence was examined using SEM, XRD and UV-VIS reflection spectra.

Experiments

First, the AgNO₃ was added to a propanol aqueous solution at a concentration of $20.0 \times 10^{-3} \text{ moldm}^{-3}$ and was adjusted to a concentration of $10.0 \times 10^{-3} \text{ moldm}^{-3}$. Alumina was then added to the AgNO₃ $\cdot$ 1-propanol aqueous solution at a concentration of $10.0 \times 10^{-3} \text{ moldm}^{-3}$. The reagents used were a special grade of AgNO₃ (WAKO : <99.8%), 1-propanol (WAKO : <99.5%) and alumina (WAKO <99.0%). Commercial reagents were not purified further were used as is. The water used as a solvent was commercial pure water (WAKO). Ultrasonic irradiation was done using a commercial 60-W ultrasonic cleaner of the bathtub type (Branson : Bransonic model 1210 J) at a frequency of 47 kHz. Ultrasonic irradiation was continuously used with the sample solution for 12 hr. The temperature of the sample solution was kept at $20.0 \pm 0.1^\circ\text{C}$ through the circulation of cooling water. Drying was done at a reduced pressure for the silver-alumina adsorption complex. The Aggregated structure of fine silver particles on the alumina surface was observed using SEM (JEOL : JXA-8600). The crystallinity of silver aggregate formed on the alumina surface was examined from XRD measurement (Rigaku : RAD-II VC, CuK α). Plasma oscillation of the aggregated fine silver particles on the alumina surface was evaluated from the measurement of the ultraviolet-visible reflection spectrum (JEOL : JMN-LA 300).

Results and Discussion

Macroscopic confirmed that the color of the solution

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Fig. 1 SEM photograph of the alumina surface before (A) and after (B) irradiation of ultrasound for an $\text{AgNO}_3 \cdot 1$ -propanol aqueous solution in which alumina coexists.

Fig. 2 XRD pattern of alumina before ultrasound irradiation (A) and alumina with a fine silver particle aggregate that formed on the surface after ultrasound irradiation (B).

changed to purple when the sample solution consisting of a mixture of $\text{AgNO}_3 \cdot 1$ -propanol $\cdot$ alumina was adjusted to the concentrations cited and then irradiated with ultrasound. **Figure. 1** is an SEM photograph of the surface of the alumina in the sample solution before and after ultrasonic irradiation; the image was taken at a magnification of $10000\times$. The alumina before ultrasonic irradiation (**Fig. 1** (A)) was a plate crystal of μm size. Fine particle aggregate of a submicron size was observed on the alumina crystal surface after ultrasonic irradiation using SEM images (**Fig. 1** (B)).

Figure. 2 shows the measurement results for the XRD pattern when using the same samples as for the SEM observation shown in **Fig. 1** (A) and (B). The XRD pattern in **Fig. 2** (A) matched the α -type of alumina as was noted from the literature⁴⁾. The patterns were assigned miller indexes corresponding to the crystal plane shown in **Fig. 2** (A). **Figure. 2** (B) is the XRD pattern of the fine particle composite sample

formed on the α -alumina surface using ultrasonic irradiation for 12 h. Circles in **Fig. 2** (B) represent peaks that agreed with the XRD patterns of Ag as noted in the literature⁵⁾. Observation of the clear diffraction peak demonstrated that the silver aggregate formed on the alumina surface had crystallinity. The XRD strength for the silver adsorption sample decreased about 40% in comparison to the alumina sample before ultrasonic irradiation. As seen in the XRD pattern in **Fig. 2** (B), the existence of silver oxide (Ag_2O) on the alumina surface was not confirmed. The coexistence of the reaction below is believed to be one reason why silver oxide was not formed, namely;

Hydrogen peroxide is formed by the bimolecular collision of hydroxyl radicals generated by reaction (1) from the literature⁶⁾. In addition, the mechanism of the reaction that forms the 1-propanol radical believed to be the pulling of a hydrogen atom from 1-

Fig. 3 UV-VIS reflection spectrum of alumina before ultrasonic irradiation (A) and alumina with fine silver particle aggregate formed on the surface after ultrasound irradiation (B).

The inserted figure depicts how the reflectivity of the spectrum increased after ultrasound irradiation.

propanol by the hydroxyl radical, as shown in reaction (5);

Though ultrasonic irradiation was performed under the same conditions for a silver nitrate aqueous solution without 1-propanol added, the quantity of silver particle aggregate formed in relation to the alumina surface decreased by about 1/4 from the XRD strength of Ag adsorbed on the alumina surface after 12 hr of ultrasonic irradiation.

Figure 3 depicts the measurement of reflection spectra in the ultraviolet and visible wavelength regions for alumina and the sample of Ag adsorbed on an alumina surface. For alumina prior to ultrasonic irradiation, the reflection spectrum did not display a large wavelength dependence. The reflectivity was about 90%. On the other hand, though, the reflection spectrum did not display large wavelength dependence for the sample of Ag adsorption on the alumina surface, though the reflectivity decreased significantly by about 20%. The reason for not the lack of wavelength-dependence for the reflection spectrum of the sample used for Ag adsorption on an alumina surface seems to correlate with the grain size distribution of silver particles formed. Results indicated that the grain size of silver aggregate on the alumina surface in Fig. 1 (B) is distributed from 10 nm to 10 μm . This almost corresponds to the wavelength distribution of UV-VIS light. The spectrum in Fig. 3 (B) seems to reflect the scattering characteristics of silver particle aggregate formed on the alumina surface. The inserted figure in Fig. 3 (B) shows the spectrum that increased the reflectivity of the reflection spectrum for the sample

with Ag adsorption on an alumina surface. The reflection spectrum of the sample for Ag adsorption on an alumina surface had slight wavelength characteristics, and there was absorption generated for plasma oscillation from the visible wavelength region in the vicinity of 400 nm.

Conclusion

Results confirmed for aggregation in terms of the wide distribution of the grain size of fine silver particles formed on an α -alumina surface when ultrasonic irradiation was performed for an $\text{AgNO}_3 \cdot 1$ -propanol aqueous solution in which the alumina co-exists. Light scattering appears to be more dominant than light reflection produced by the excitation of plasma oscillation, which is induced by optical illumination on the surface. This result is attributed to the grain size of silver aggregate formed on the alumina surface, which is almost equal to the distribution noted with a continuous wavelength distribution of ultraviolet-visible light.

(Received June 20, 2000 ; Accepted September 18, 2000)

References

- 1) A. Hartstein, J. R. Kirtley and J. C. Tsang; *Phy. Rev. Lett.* 45, 201 (1980).
- 2) K. Aramaki; *J. Sur. Fin. Soc. Jpn.*, 49, 64 (1998).
- 3) Y. Nagata, Y. Watanabe, S. Fujita, T. Dohmaru and S. Taniguchi; *J. Chem. Soc., Chem. Commun.*, 1620 (1992).
- 4) Powder Diffraction File, Card NO. 46-1212. International Centre for Diffraction Data, Newtown Square PA, 1996.
- 5) Powder Diffraction File, Card NO. 4-0783. International Centre for Diffraction Data, Newton Square PA, 1996.
- 6) K. Makino, M. Mossoba and P. Riesz; *J. Phy. Chem.*, 87, 1369 (1983).