State-controlled Rh nanoparticles synthesized via microwave-assisted alcohol reduction and their catalysis of CO oxidation

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Abstract: Size-controlled Rh nanoparticles stabilized by polyvinylpyrrolidone (PVP) were quickly synthesized via alcohol reduction. Microwave-assisted synthesis in closed vessels allowed alcohols with low-to-high boiling points to be used as reductants under the same preparation conditions. Pure ethanol has not been used previously because its boiling point is lower than the temperature required for Rh^{3+} reduction. Alcohols with strong reduction ability were found to lead to smaller Rh nanoparticles. The turn over frequency (TOF) for CO oxidation increased as the Rh particle size decreased. This is because the electronic state of Rh surface was modified by PVP to more electron-enriched state.

Keywords: State-controlled Rh nanoparticles, Microwave-assisted alcohol reduction, CO oxidation

1. Introduction

Recently catalytic applications of metal nanoparticles have been investigated because nanoparticles have unique properties differing from bulk induced by quantum size effects and high surface-area-to-volume ratios. In catalytic chemistry, size-controlled synthesis of metal nanoparticles is needed to tune their catalytic activity for each catalytic reaction. In previous works, size control of metal nanoparticles has been achieved by the alcohol reduction method with sophisticated and rigid control of several factors. High-boiling-point alcohols such as polyols are often used to reduce metal cations because the boiling points of the polyols are higher than the temperatures required to reduce the metal cations. In contrast, it is difficult to use monovalent alcohol including a small number of carbons, e.g. ethanol, because the temperatures required to reduce metal cations such as Rh^{3+} is higher than the boiling point of such alcohols. Therefore, the influence of the reduction ability of low- and high-boiling-point alcohols on the particle size of metal nanoparticles has not been investigated under the same reduction temperature. In addition, heating the alcohols with a conventional electric heater is slow and leads to inhomogeneous temperatures in the beaker; thus, it takes a long time to prepare nanoparticles, and nanometals with a wide particle-size distribution are obtained.

To solve these problems, we used microwave heating apparatus equipping a closed vessel achieving rapid and homogeneous heating and solvothermal conditions, which made it possible for each alcohol to be used at same temperature. The experimental design assisted by microwave heating allowed us to understand the relationship between the reduction ability of alcohol and Rh particle size, and easily synthesize size-controlled Rh nanoparticles with narrow size distribution within 20 min. We also studied the particle size and surface electronic state dependence of the CO oxidation ability of the Rh nanoparticles, because Rh is known to be an excellent catalyst for the oxidation of CO in car exhaust gas.(1)

2. Experimental

Rh nanoparticles with different sizes were prepared by microwave-assisted alcohol reduction. Initially, $RhCl_3 \cdot 3H_2O$ as the metal precursor and PVP as the stabilizer were dissolved in either ethanol, ethylene glycol, diethylene glycol, 2-ethoxyethanol, triethylene glycol, or 2-(2-ethoxyethoxy)ethanol as the reductant. These solutions were heated to 165 °C within 90 s via microwave irradiation and maintained at that temperature for 15 min. The colloidal solutions were precipitated and finally dried. Rh-PVP/γ-Al_2O_3 for CO oxidation reaction were prepared via wet impregnation. The Rh loading was set to 1 wt%.

Catalytic activity test for CO oxidation was carried out under oxidizing atmosphere ($CO/O_2/N_2$: 0.5/0.5/49 mL/min) without reduction pretreatment.

3. Results and discussion

Figure 1 shows HAADF-STEM images of Rh nanoparticles. Particle sizes, estimated by averaging the sizes of 100 particles, were (A) 3.3 ± 0.5 nm, (B) 5.7 ± 1.3 nm, (C) 6.7 ± 0.8 nm, (D) 8.9 ± 1.1 nm, (E) 9.5 ± 1.4 nm, and (F) 10.9 ± 2.1 nm. Alcohols with relatively strong reduction ability evaluated by cyclic voltammetry led to small Rh nanoparticles. We consider that this is because the nucleation of nanoparticles occurred at relatively lower temperatures, and then, nucleated nanoparticles were immediately covered with PVP when the alcohols having stronger reduction ability were used. This result suggested size-controlled synthesis of Rh nanoparticles was enabled by changing only the type of alcohol.

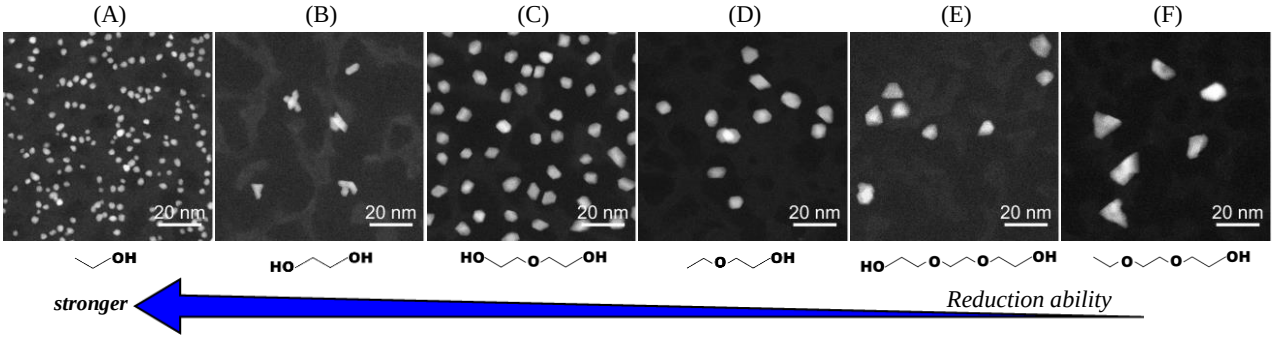

Figure 1. HAADF-STEM images for of Rh nanoparticles reduced by (A) ethanol, (B) ethylene glycol, (C) diethylene glycol, (D) 2-ethoxyethanol, (E) triethylene glycol, and (F) 2-(2-ethoxyethoxy)ethanol.

Figure 2 shows the influence of particle size on the extent of CO oxidation over Rh-PVP/γ-Al_2O_3. Catalytic activity increased as particle size decreased. On the other hand, the TOF was not steady among the size-controlled Rh catalysts, implicating that some factors in addition to particle size affected the catalytic activity (Figure 3). We also observed the XP spectra of the Rh 3d orbital. The binding energy of the largest Rh nanoparticles was identical to that of Rh bulk and shifted to a lower energy with decreasing Rh particle size (Figure 3). This indicates charge transfer from PVP to Rh occurred. The smaller Rh particle size is, the larger interface between Rh and PVP get, which facilitates charge transfer, and thus, more electron-enriched Rh surface is formed. It has been reported that a reactive oxygen layer is easily formed on small Rh nanoparticles and the catalyst then shows high TOF for CO oxidation.[(2)] In this study, oxygen activation is promoted on electron-enriched and small Rh nanoparticles, which results in formation of reactive oxide layer and enhances the ability to oxidize CO.

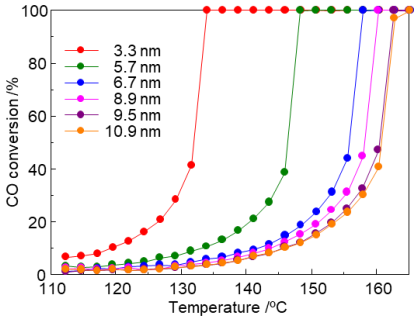

Figure 2. Size dependence of CO oxidation activity of Rh catalysts

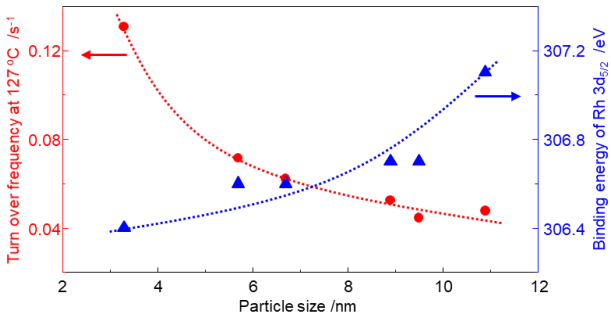

Figure 3. Size dependence of TOF at 127 °C and binding energy in XP spectra of Rh $3d_{5/2}$

4. Conclusions

Size-controlled Rh nanoparticles were simply and quickly synthesized by changing only the kind of alcohol in alcohol reduction method. Rh particle size depended on reduction ability of alcohol. CO oxidation was efficiently catalyzed over electron-enriched Rh nanoparticles, which have a high metal surface area.

References

1. Y. Nishida, et al., Chem. Lett. 46 (2017) 1254
2. M. E. Grass, et al., Angew. Chem., Int. Ed. 47 (2008) 8893