

Catalytic Activity of Ultra-fine Gold Particles Deposited on Pt/MoO_x/C for Electro-oxidation of Methanol

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Direct methanol fuel cells (DMFCs) have been expected for use as portable power sources since the cell can produce electric energy without reformers, resulting in the downsizing (of size and weight). Although numerous researches have been done for development of electrode catalysts in DMFCs to enhance their performance, there are still severe problems, such as CO poisoning etc, to be solved for a practical use.

Our group has been focusing on the ultra-fine gold particles as a catalyst for suppressing CO poisoning. Ultra-fine gold particles less than about 10 nm are known to give a great catalytic activity for CO oxidation in the gas phase.¹⁾ It should be also noted that catalytic activities appear only when the ultra-fine gold particles are deposited on some oxides. Recently, Ioroi et al. reported high electro-catalytic activities of Pt/MoO_x/C for CO oxidation. Therefore, molybdenum oxide is one of the promising oxides which activate the catalytic activities of ultra-fine gold particles.²⁾ Here we report electrochemical methanol oxidation on Pt/MoO_x/C containing ultra-fine gold particles.

The electrode catalysts Pt/MoO_x/C were prepared by the conventional impregnation method, using Denka-black ONB-250 (Denkikagaku Kogyo, Inc.) as the carbon support and (NH₄)₆Mo₇O₂₄·4H₂O (Nacalai Tesque, Inc.) and [Pt(NH₃)₄](NO₃)₂ (Strem Chemical, Inc.) as MoO_x and Pt precursors, respectively. Supporting carbon was dispersed ultrasonically in de-ionized water. And molybdenum solution was added into the carbon suspension, and the solution was stirred vigorously and evaporated to remove solvent water. After drying, obtained powder was calcined at two different temperatures of 400°C and 600°C. Platinum was also added in the similar way as mentioned above. Ultra-fine gold particles were deposited on Pt/MoO_x/C by the gas-phase grafting method³⁾, in which (CH₃)₂Au(C₅H₇O₂) was used as Au precursor. The prepared catalysts were characterized by XRD, atomic absorption spectrometry, and XPS. Figure 1 shows XRD patterns of resultant catalysts, Au/Pt/MoO_x/C. Very broad peak at around 38° in 2θ corresponds to Au, whose particle sizes are evaluated to be less than 4 nm. As is clear from Fig. 1, the crystallinity of MoO_x was greatly increased with increasing the calcination temperatures.

The electro-catalytic activities for methanol oxidation were studied by cyclic voltammetry and steady-state polarization measurements in 1 mol/dm³ (M) HClO₄ containing 1 M CH₃OH. The electrochemical measurements were carried out by using a conventional three-electrode cell at 30°C. Figure 2 shows steady-state polarization curves. In the region above 450 mV, four prepared catalysts showed almost the same oxidation current densities, but in the region below 450 mV, the activity for methanol oxidation was in the order of Au/Pt/MoO_x/C > Pt/MoO_x/C. Improvement of activities for methanol electro-oxidation should be ascribed to the

addition of ultra-fine gold particles, and the effect of ultra-fine gold particles was explicit in the particular potential region less than 450 mV. As the calcination temperature increased, the oxidation current density for methanol increased. Therefore, crystallinity of molybdenum oxide also played an important role on the catalytic activities of ultra-fine gold particles.

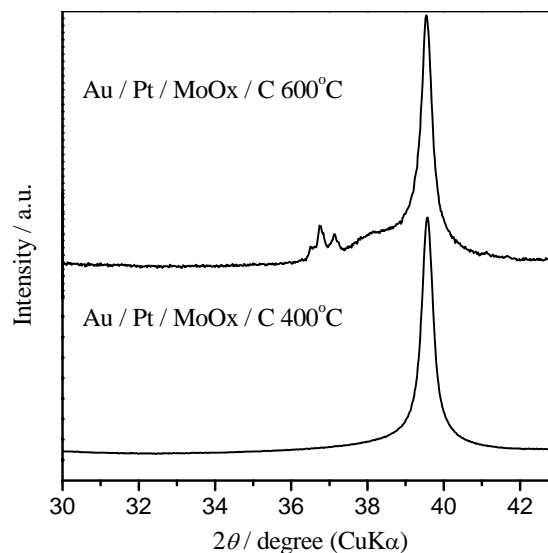


Fig. 1. XRD patterns of Au/Pt/MoO_x/C calcined at different temperatures: (a) 600°C, (b) 400°C.

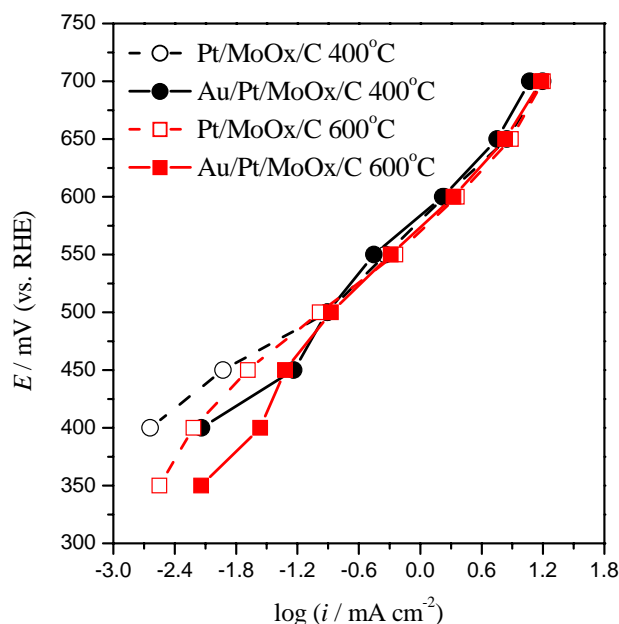


Fig. 2. Steady-state polarization curves for methanol oxidation on Pt/MoO_x/C and Au/Pt/MoO_x/C in 1 M HClO₄ + 1 M CH₃OH at 30°C.

References

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Acknowledgement

This work was supported by Research and Development of Polymer Electrolyte Fuel Cell of New Energy and Industrial Technology Development Organization (NEDO).