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Substructure and catalysis of PtRu/C bimetallic nanoparticle catalyst

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Introduction

PtRu alloy is one of the most promising materials for an anode catalyst of direct methanol fuel cell , because of its high CO tolerance. Watanabe et al. explained this CO tolerance with "bi-functional mechanism" in 1975 [1]. Generally downsizing of catalysis particle leads to a higher specific surface then to reductions in weight and cost of fuel cells, but no report was found regarding application of this mechanism to nanoparticles of PtRu alloy. For developing much more advanced catalyst, it is necessary to check whether the "bi-functional mechanism" would be valid for the nanoparticles system. In this work, we synthesized PtRu alloy nanoparticles loaded on a carbon support and investigated a relationship between catalytic activity and atomic structure of them.

Experimental

Five samples of PtRu alloy nanoparticles loaded on a carbon support (PtRu/C) catalysts were synthesized by a polyol reduction method with various compositions of initially loaded materials. $Pt(acac)_2$, $Ru(acac)_3$ and commercial nano-sized carbon black powder were add into the ethylene glycol bath. Then the solution was refluxed at 473 K for 4 hours with a mechanical stirring under a nitrogen atmosphere. After evaporating ethylene glycol, PtRu/C catalyst was obtained by washing with ion-exchanged water and ethanol, and drying. Pt-L_{III} (11549 eV) and Ru-K (22120 eV) edges XAFS spectrum of PtRu/C were obtained at the BL-7C beam line of KEK-PF and at the BL-19B2 beam line of the SPring-8, respectively. Si(111) crystals were used to monochromate X-ray. The X-ray energy was calibrated by setting the first inflection point obtained from a Pt foil and a Ru powder to 11919 eV and 22120 eV, respectively. Unwanted higher harmonic waves were eliminated by detuning (KEK-PF) and a Rh mirror (SPring-8). All the measurements were performed in air at room temperature with the transmission mode. The PtRu/C catalysts were mixed with an appropriate dose of boron nitride powder and shaped into 7-mm diameter pellets. The intensities of incident and transmitted X-rays were measured with ion chambers. Methanol oxidation catalytic activities of synthesized PtRu/C catalysts were estimated by linear sweep voltammetry (LSV).

Results and Discussions

EXAFS spectrum of PtRu/C catalysts were analyzed with "IFEFFIT" and "FEFF7" code assuming the single scattering path of Pt-Pt, Pt-Ru, Ru-Pt and Ru-Ru bonds. Optimized values of structural parameters were R, N, σ^2, and ΔE_0. According to the "bi-functional mechanism", existence of Pt-Ru atomic pair on the surface of the catalyst material is an important factor for high activity catalyst. Therefore, we tried to extract information on the inhomogeneity from coordination numbers and defined "paring factor" as, $P_{Pt} = N_{Pt-Ru} / (N_{Pt-Pt} + N_{Pt-Ru})$, and $P_{Ru} = N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru})$. It has a meaning of the probability that Pt-Ru bonds around Pt and Ru atoms. The relationships between these "paring factor" and catalytic activity which evaluated by LSV measurements are shown in Figure. There is a clear correlation between P_{Ru} and catalytic activity, while there is not such correlation with P_{Pt}. This result is explainable by considering that PtRu/C has the Pt-rich core / Ru-rich shell substructure which is reasonable from the point of view of chemical redox reactions. These facts and all the other experimental results well support the hypothesis of formation of nanoparticles with Pt-rich core and Ru-rich surface on which catalytic activity is enhanced by Ru-Pt pairs according to the "bi-functional mechanism". Thus we demonstrated the validity of the "bi-functional mechanism" even for the nanoparticle system.
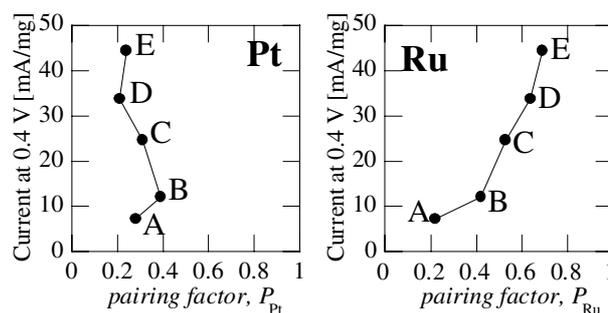

Fig. Relation ships between "pairing factor" and catalytic activity. Left: P_{Pt} and Right: P_{Ru}.

References

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