Study on Element–Electronic Structure–Catalytic Property Relationship in Multi-Element Alloy Nanoparticles Catalysts Based on XANES Spectra

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Multi-element alloy nanoparticles (MEA NPs) are now attracting much attention as catalysts due to their distinctive properties, including excellent activities or durabilities^{1,2,3}. Although MEA NPs catalysts with various properties have been developed by taking advantage of their huge compositional space, the strategy to control the properties of the complicated system has not been established⁴. We assumed that the investigation into the electronic structure of the catalysts would be the key to associating the combination of elements with the catalytic properties. Here, we targeted a series of alloy catalysts composed of the elements with different electronic natures, base metals (BMs) and platinum-group metals (PGMs). Their electronic structures were probed employing XANES, and the correlations with the catalytic properties in CO₂ hydrogenation were examined.

The NPs of PGM quinary alloy (Ru, Rh, Pd, Ir, and Pt) and a series of senary alloys with additional BMs (Fe, Co, Ni, Ga, In, and Sn) were synthesized by wetchemical method in the exactly same procedure. The catalysts were prepared by loading the NPs on γ -Al₂O₃. The catalytic tests were performed using a fixed-bed flow reactor under 0.75 MPa and 100-450 °C. As a result, PGM quinary alloy NPs showed CH₄ dominant selectivity, while all the BM–PGM senary alloy NPs showed CO dominant selectivity.

The XANES spectra of Ru, Rh, Pd L_3 edges were measured at SR Center BL10 and those of Ir, Pt L_3 edges and Ru, Rh, Pd K edges were measured at SPring-8 BL14B2. All the BM–PGM senary NPs had smaller whiteline (WL) intensity or smaller edge energy (E_0) than PGM quinary NPs, indicating that electron transfer take place from BM to PGM in the senary NPs following electronegativity. Although the analyses of Ru, Rh, Pd L_3 were challenging due to the proximity of the edge energies and the resulting spectral overlap, the reliability was supported by strong correlations of WL intensities in Ru, Rh, Pd L_3 edges with E_0 in Ru, Rh, Pd K edges (**Fig. 1a**). Furthermore, the correlations among the XANES spectral features and CO selectivity were found to be significant (**Fig. 1b**). It indicates that the valence states of PGM play a key role in determining the catalytic properties of the alloy catalysts.

Further investigation on microscopic properties of catalysts like CO adsorption energy would give deeper insight on the catalytic mechanism.

References

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Fig. 1. (a) Correlation between E_0 in Rh K edge and WL intensity in Rh L_3 edge. (b) Correlation between WL intensity in Rh L_3 edge and CO selectivity at 450 °C. Similar trends were found in other PGMs than Rh.