

Analysis of local structures of Pt-based alloy nanoparticles coated with silica layers upon formation of nanoscale carbon

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Introduction

It is known that unique catalytic activity could be emerged by alloying of the metal particles on the supported catalysts. The supported metal catalysts are conventionally prepared by impregnation methods. However, the metal particles are easily aggregated to form large particles, because they are supported on the outer surface of the carriers. Thus, it is difficult to form homogenous alloys on the supported catalysts.

We have studied the preparation of silica-coated metal catalysts using microemulsion.¹ By this method, metal particles such as Ni, Co, and Pt are uniformly covered with silica layers. The metal particles in the catalysts show a high sustainability to sintering, because each particle is covered with silica layers. Thus, it is expected that compositionally-homogeneous alloys nanoparticles would be formed in the silica layers by this method.

In the present study, we prepared Pt-Ni alloys covered with silica and they were used as the catalysts for ethylene decomposition to form nanoscale carbons. Relation between the local structure of Pt-based alloys and catalytic activity was investigated.

Experimental

Silica-coated Pt-Ni alloys (denoted as coated Pt-Ni) were prepared in a water-in-oil-type microemulsion.¹

Ethylene decomposition to form nanoscale carbons was performed at 973 K with a conventional gas-flow system with a fixed catalyst bed. Heat treatment at 973 K was performed before ethylene decomposition in order to promote the alloying between Pt and Ni.

X-ray absorption spectra for the samples were measured at the Photon Factory for High Energy Accelerator Research Organization. Pt L_{III}-edge EXAFS was measured at the beam line BL-9C equipped with Si(111) in a transmission mode at room temperature.

Results and Discussion

We prepared silica-coated Pt-Ni nanoparticles using microemulsion. Small particles with diameters of a few nanometers were observed in the silica. Loading amounts of metal were evaluated by XRF spectra to be 2.0 wt% of Pt and 0.2 wt% of Ni.

The effects of heat treatment at 973 K of coated Pt-Ni were studied. The formation of nanoscaled carbons on the catalyst with heat treatment was not obtained. In contrast,

coated Pt-Ni without heat treatment formed carbon nanofibers with the diameter of ca. 10 nm.

Figure 1 shows Fourier transforms of Pt L_{III}-edge k^3 -weighted EXAFS spectra (RSFs; radial structural functions) for coated Pt-Ni alloys as well as for Pt foil. In a RSF for Pt foil, a strong peak due to Pt-Pt bonds is observed at around 2.8 Å. In contrast, two peaks were observed in the R range from 1.5 to 3.0 Å in the RSFs for coated Pt-Ni, suggesting the formation of alloys between Pt and Ni. The peaks in the R range of 1.5 to 3.0 Å for coated Pt-Ni were analyzed by the curve-fitting methods. The peaks for coated Pt-Ni were fitted by Pt-Pt and Pt-Ni bonds. The interatomic distances for these bonds in the samples were very similar to those of the corresponding alloys in the previous reports.² Thus, metal species in coated Pt-Ni were present as alloys. In addition, it was found that the coordination number of Pt-Ni bond increased with heat treatment at 973 K. We consider that inadequately alloyed part exists in the coated Pt-Ni without heat treatment and this decompose ethylene to form carbon nanofibers.

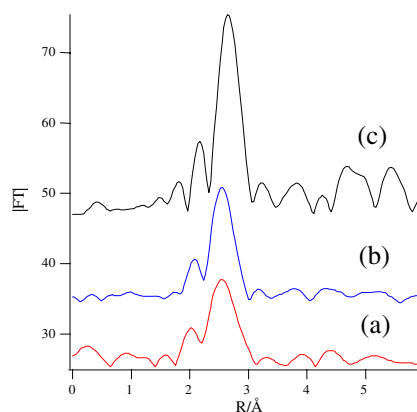


Figure 1. Fourier transforms of Pt L_{III}-edge k^3 -weighted EXAFS for coated Pt-Ni without heat treatment (a), with heat treatment (b) and Pt foil (c).

References

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