

Analysis of Local Structure of Pt Nanoparticles Covered with Organosilica Layer

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Introduction

We have studied the preparation of silica-coated metal catalysts^{1,2}. Metal particles such as Ni, Co, and Pt are uniformly covered with silica layer by this method. In the present study, carbon-supported Pt catalysts covered with silica layer using organosilanes as the silica source were prepared and used for the dehydrogenation of cyclohexane. We found that the catalysts covered with organosilica layer containing phenyl or methyl groups showed higher conversion than that covered with a silica layer without any functional group. In order to investigate the effect of the coverage with organosilica layer containing functional groups, the local structure of Pt L_{III}-edge EXAFS spectra was analyzed.

Experimental

The coverage of carbon black (CB) supported Pt metal particles with organosilica layer was performed using hydrolysis of some organosilanes, such as tetraethoxysilane (TEOS), phenyltriethoxysilane (PhTES), methyltriethoxysilane (MTES)². Hereafter, the obtained sample is denoted as SiO₂(organosilane)/Pt/CB.

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-7C equipped with Si(111) in a transmission mode at room temperature.

Results and Discussion

Highly dispersed Pt metal particles with diameters of 1 to 3 nm were observed in all samples by TEM measurement. The amount of Pt in all samples was about 1.5–2 wt %, and that of SiO₂ in SiO₂(TEOS)/Pt/CB, SiO₂(PhTES)/Pt/CB, and SiO₂(MTES)/Pt/CB was 55.1, 31.4, and 35.0 wt %, respectively.

Figure 1 shows Fourier transforms of Pt L_{III}-edge k^3 -weighted EXAFS spectra (RSFs; radial structural functions) for SiO₂(TEOS)/Pt/CB, SiO₂(PhTES)/Pt/CB and SiO₂(MTES)/Pt/CB as well as for Pt foil. In the RSF for all samples, a strong peak was observed at around 2.8 Å. This peak was assignable to Pt-Pt bonds in Pt metal. The intensity of the peak due to Pt-Pt bonds for SiO₂(PhTES)/Pt/CB and SiO₂(MTES)/Pt/CB was lower

than SiO₂(TEOS)/Pt/CB. It is generally accepted that the intensity of the peak in the RSFs for any metal corresponds to the crystallite size of the metals. These results suggest that an average crystallite size of Pt metal in SiO₂(PhTES)/Pt/CB and SiO₂(MTES)/Pt/CB was smaller than that of SiO₂(TEOS)/Pt/CB. In order to make the structure of Pt species clearer, the curve-fitting analyses for EXAFS spectra were also performed. All the EXAFS spectra could be fitted with a shell of Pt-Pt bond. The coordination number and interatomic distance of Pt-Pt bond for SiO₂(PhTES)/Pt/CB and SiO₂(MTES)/Pt/CB was tend to smaller than that for SiO₂(TEOS)/Pt/CB. These results imply that the size of Pt particles of Pt/CB covered with organosilica layer containing phenyl or methyl groups became smaller than that covered with a silica layer without any functional group.

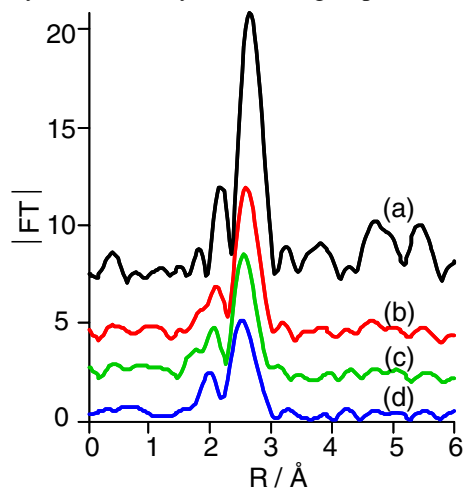


Figure 1. Fourier transforms of Pt L_{III}-edge k^3 -weighted EXAFS for (a) Pt foil, (b) SiO₂(TEOS)/Pt/CB, (c) SiO₂(PhTES)/Pt/CB, (d) SiO₂(MTES)/Pt/CB. The intensity of the peak for Pt foil was halved.

References

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