

XAFS Analysis of Pt Nanoparticles Covered with Microporous Silica Layers Prepared Using Different Organosilanes

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Introduction

The development of supported metal catalysts with high resistance toward sintering at high temperature is required. We have prepared Pt catalysts covered with microporous silica layers using organosilanes such as methyltriethoxysilane (MTES) or phenyltriethoxysilane (PhTES) [1]. Micropores were formed in the silica layers by decomposition of the functional groups by thermal treatment. As a result, these catalysts showed higher conversion in the dehydrogenation of cyclohexane, compared with Pt catalysts covered with silica layers using tetraethoxysilane (TEOS). Further research on the sintering resistance of Pt metal particles covered with microporous silica layers is needed because the sintering resistance might decrease with the increasing porosity of the silica layer. In this study, XANES and EXAFS measurements were performed to investigate the local structure of Pt covered with microporous silica layers with thermal treatments.

Experimental

The coverage of carbon black (CB) supported Pt metal particles with microporous silica layers was performed by hydrolysis of some organosilanes, such as TEOS, PhTES, and MTES. Hereafter, the obtained sample is denoted SiO₂(organosilane)/Pt/CB. The catalysts were treated at 773 K or 973 K for 3 h in an atmosphere of H₂, to clarify the durability of sintering of Pt metal particles. For comparison, Pt/CB was prepared by a conventional impregnation method. X-ray absorption spectra were measured at the Photon Factory for High Energy Accelerator Research Organization. Pt L_{III}-edge XANES/EXAFS measurements were performed at the beam line BL-7C equipped with Si(111) in a transmission mode at room temperature.

Results and Discussion

After thermal treatment at 973 K, the average diameter of Pt metal particles estimated by TEM images in all of the silica-coated Pt catalysts was about 2.3 nm, which was smaller than that of Pt/CB after thermal treatment (3.4 nm). Figure 1 shows Fourier transforms of *k*³-weighted Pt L_{III}-edge EXAFS spectra for the obtained samples. A strong peak is present in the R range from 2.2 to 3.0 Å in the RSFs for all catalysts. The peaks in the RSFs for all catalysts are located at around 2.5 Å. The structural parameters estimated by the curve-fitting analyses are listed in Table 1. The EXAFS spectra for all

of the SiO₂/Pt/CB samples can be fitted by a Pt-Pt shell. The estimated coordination numbers of the Pt-Pt bond were 11.4 in Pt/CB, 8.7 in SiO₂(TEOS)/Pt/CB, 8.6 in SiO₂(MTES)/Pt/CB, and 9.0 in SiO₂(PhTES)/Pt/CB. The increase in the coordination number of Pt-Pt bond for Pt/CB suggests that aggregation of the Pt particles occurred during thermal treatment at 973 K. Thus we can conclude that the coverage of Pt/CB with microporous silica layers inhibits the aggregation of metal particles during thermal treatment of the catalysts at high temperatures.

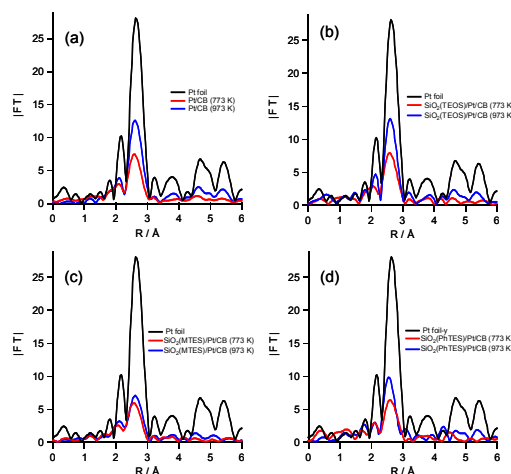


Fig. 1. Fourier transforms of *k*³-weighted EXAFS spectra of Pt/CB (a), SiO₂(TEOS)/Pt/CB (b), SiO₂(MTES)/Pt/CB (c) and SiO₂(PhTES)/Pt/CB (d).

Table 1. Structural parameters of Pt species in Pt catalysts estimated by curve-fitting analyses of EXAFS spectra.

Catalyst (973K)	shell	CN ^a	R (Å) ^b	DW (Å) ^c
Pt/CB	Pt-Pt	11.4	2.75	0.081
SiO ₂ (TEOS)/Pt/CB	Pt-Pt	8.7	2.75	0.074
SiO ₂ (MTES)/Pt/CB	Pt-Pt	8.6	2.74	0.089
SiO ₂ (PhTES)/Pt/CB	Pt-Pt	9.0	2.72	0.085

^a Coordination number. ^b Interatomic distance. ^c Debye Waller factor.

References

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