XAFS Study on Precursor Dependent Structures of Rh / Alumina Catalysts

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Introduction

Choice of a catalyst precursor sometimes affects the activity and selectivity of the catalyst due to its local structure is apart from the thermodynamically favored one. We have studied on precursor dependent structure of Rh/Al₂O₃ catalysts by STM measurements and found that homogeneous Rh clusters, which contain two Rh atoms each, could be randomly dispersed on an Al₂O₃ thin film (0.5 nm) on NiAl(110) by thermal decomposition of the [Rh(II)₂(OAc)₂]₂ precursor in vacuum [1]. When RhCl₃ is used for the precursor instead, larger metallic Rh particles were formed. In previous X-ray absorption fine structure (XAFS) measurements, it was confirmed that consistent results could be obtained when the Al₂O₃ support with high surface area was used as a substrate and similar preparation procedure was adopted [2]. The predominant contribution of Rh-O bonds accompanied by a smaller Rh-Rh peak was observed by thermal decomposition of the [Rh(II)₂(OAc)₂]₂ precursor at 650 K. In this study, polarization-dependent total-reflection fluorescence (PTRF) XAFS was adopted for the [Rh(II)₂(OAc)₂]/α-Al₂O₃(0001) system to elucidate the detailed local structure of the homogeneous Rh clusters.

Experimental

A polished α-Al₂O₃(0001) substrate (Shinkosha) was heated at 1070 K under N₂ gas flow for 1 h prior to use. Ethanol solution of the [Rh(II)₂(OAc)₂]₂ precursor (Alfa Aesar) was deposited on the Al₂O₃(0001) as small volume droplets (0.5 µL each) of one thousand to achieve the homogeneity of the concentration. Then the sample was heated under N₂ gas flow at 650 K to decompose the precursor to obtain the Rh/Al₂O₃ catalyst (sc 650 K). As a reference sample, the [Rh(II)₂(OAc)₂]₂ precursor was deposited on α-Al₂O₃ powder (Sumitomo Chemical) by incipient wetness impregnation method (0.1 wt%) under N₂ atmosphere in a glove box and heated under N₂ gas flow at 650 K (pw 650 K).

Rh K-edge XAFS spectra of the samples were measured at NW10A. Data analysis was performed by using REX2000 ver. 2.5 (Rigaku Co.)

Results and discussion

The oxidation state analysis by X-ray photoelectron spectroscopy (XPS) prior to XAFS measurements showed that the Rh/α-Al₂O₃(0001) prepared by thermal decomposition of the [Rh(II)₂(OAc)₂]₂ precursor showed a Rh 3d₅/₂ peak at 309.8 eV. The value was the same as that measured for the Rh/α-Al₂O₃, powder catalyst [1]. Judging from the peak energy, the Rh species is highly oxidized. It was also confirmed from XANES spectra of these samples. They gave an identical peak shape and it was rather similar to Rh₂O₃ [2].

An XAFS oscillation was extracted from PTRF-XAFS signal of the sc 650 K sample at s-polarized x-ray irradiation as shown in Fig. 1(a). By comparing with the XAFS oscillation of the pw 650 K sample in Fig. 1(b), one can find the similarity of these two samples. Almost the same oscillation was obtained when γ-Al₂O₃ powder was used for the substrate for Rh/γ-Al₂O₃ from the [Rh(II)₂(OAc)₂]₂ precursor [2]. Thus the local structure of the Rh species is similar for three substrates. Corresponding Fourier transforms in Fig. 1 also suggest the similarity of the two structures. Curve fitting analyses are in progress.

We have not succeeded in obtaining PTRF-XAFS spectra of the sc 650 K sample with p-polarized x-ray at sufficient S/N ratio, which is inevitable to discuss the detailed local structure of the homogeneous Rh clusters.

References

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