

## XAFS Study on Precursor Dependent Structures of Rh / Alumina Catalysts

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and Ken-ichi FUKUI \*<sup>1</sup><sup>1</sup>Dept. Materials Engineering Science, Osaka University, Osaka 560-8531, Japan<sup>2</sup>International Christian University, Tokyo 181-8585, Japan**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/Al<sub>2</sub>O<sub>3</sub> catalysts by STM measurements and found that homogeneous Rh clusters, which contain two Rh atoms each, could be randomly dispersed on an Al<sub>2</sub>O<sub>3</sub> thin film (0.5 nm) on NiAl(110) by thermal decomposition of the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor in vacuum [1]. When RhCl<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor at 650 K. In this study, polarization-dependent total-reflection fluorescence (PTRF) XAFS was adopted for the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub>(0001) system to elucidate the detailed local structure of the homogeneous Rh clusters.

**Experimental**

A polished α-Al<sub>2</sub>O<sub>3</sub>(0001) substrate (Shinkosha) was heated at 1070 K under N<sub>2</sub> gas flow for 1 h prior to use. Ethanol solution of the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor (Alfa Aesar) was deposited on the Al<sub>2</sub>O<sub>3</sub>(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 N<sub>2</sub> gas flow at 650 K to decompose the precursor to obtain the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (sc 650 K).

As a reference sample, the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor was deposited on α-Al<sub>2</sub>O<sub>3</sub> powder (Sumitomo chemical) by incipient wetness impregnation method (0.1 wt%) under N<sub>2</sub> atmosphere in a glove box and heated under N<sub>2</sub> 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.)

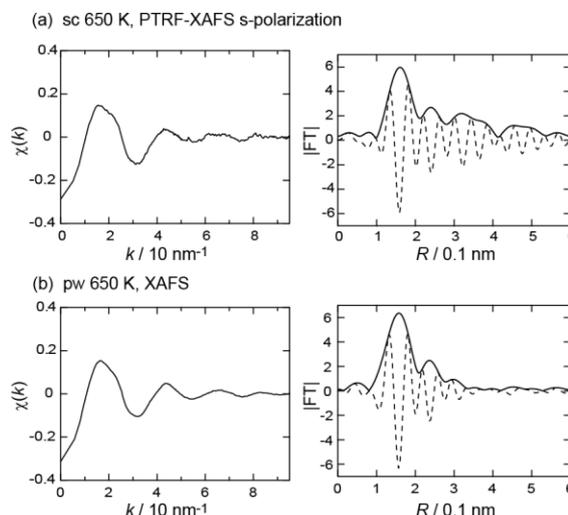
**Results and discussion**

The oxidation state analysis by X-ray photoelectron spectroscopy (XPS) prior to XAFS measurements showed that the Rh/α-Al<sub>2</sub>O<sub>3</sub>(0001) prepared by thermal decomposition of the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor showed a Rh 3d<sub>5/2</sub> peak at 309.8 eV. The value was the same as that measured for the Rh/α-Al<sub>2</sub>O<sub>3</sub> powder catalyst and the

Rh/γ-Al<sub>2</sub>O<sub>3</sub> 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 Rh<sub>2</sub>O<sub>3</sub> [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-Al<sub>2</sub>O<sub>3</sub> powder was used for the substrate for Rh/γ-Al<sub>2</sub>O<sub>3</sub> from the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> 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.



**Fig. 1** XAFS oscillations and corresponding Fourier transforms (0.3-0.95 nm<sup>-1</sup>) of (a) Rh/α-Al<sub>2</sub>O<sub>3</sub>(0001) (sc 650 K) and (b) Rh/α-Al<sub>2</sub>O<sub>3</sub> powder (pw 650 K) prepared from thermal decomposition of the [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor. (a) was obtained by PTRF-XAFS configuration with s-polarization.

**References**

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[2] Z. Chen, W.-J. Chun, K. Fukui, *PF Activity Report* **27** (2010) 54, *PF Activity Report* **26** (2009) 68.

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