

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

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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 high-resolution STM measurements and found that homogeneous Rh clusters 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 [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor in vacuum. When RhCl<sub>3</sub> is used for the precursor instead, larger Rh particles were formed. In previous X-ray absorption fine structure (XAFS) measurements [1], 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. In the case of RhCl<sub>3</sub> precursor, single peak of metallic Rh-Rh bonds appeared after heat treatment over 500 K and its coordination number increased at higher temperatures, suggesting the agglomeration of Rh particles. However, predominant contribution of Rh-O bonds accompanied by a smaller Rh-Rh peak was observed by decomposition of [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursor and the structure was stable up to 800 K. In this study, the other precursor, Rh<sup>III</sup>(OAc)<sub>3</sub>, was used for XAFS measurements to elucidate how the decomposition process affects the final Rh/Al<sub>2</sub>O<sub>3</sub> structure and how the number of Rh in the precursor differentiates the stability of the catalyst.

**Experimental**

Catalysts were prepared by the incipient wetness impregnation method in a N<sub>2</sub> glove box. Two Rh precursors, [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> (Alfa Aesar) and Rh<sup>III</sup>(OAc)<sub>3</sub> (Soekawa Chemical), were used to be deposited on Al<sub>2</sub>O<sub>3</sub> support (JRC-ALO-6; reference catalyst from the Catalysis Society of Japan) that was evacuated at 1070 K for 1 h prior to use. Ethanol solution of the rhodium precursors were added for the Al<sub>2</sub>O<sub>3</sub> support (0.2 wt%) and stirred for 5 h followed by removal of the solvent by evacuation. The samples were heated in vacuum to 650 K, 800 K, respectively and XAFS spectra were measured after each heat treatment.

Rh K-edge XAFS spectra of the samples were measured at NW10A with Si(311) double crystal monochromator in a transmission mode. Data analysis was performed by using REX2000 ver. 2.5 (Rigaku Co.)

**Results and discussion**

XANES spectra of Rh(OAc)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> on the course of heat treatment show that their local structure are rather similar to Rh<sub>2</sub>O<sub>3</sub> (Fig. 1a). More detail structure can be obtained by EXAFS in Fig. 1b, where Rh-O bonds are

dominant even after complete decomposition of Rh(OAc)<sub>3</sub> at 650 K. It is notable that no Rh-Rh peak appeared, which suggests that monomeric Rh species were formed on the Al<sub>2</sub>O<sub>3</sub> surface. It is consistent with the previous result of [Rh(OAc)<sub>2</sub>]<sub>2</sub> which contained two Rh cores in the heat treated catalyst (also listed in Table 1). Thus, preferential formation of Rh-O bond with Al<sub>2</sub>O<sub>3</sub> during thermal decomposition of Rh-acetates roughly preserved the number of the Rh core in the precursors.

By heating the monomeric species at 800 K, Rh-Rh bond started to appear (Fig. 1b and Table 1), suggesting the beginning of agglomeration. Less stability for the monomeric Rh species seems to be reasonable. But even for the monomeric species was much more stable than the Rh species prepared from RhCl<sub>3</sub>, as noted above [1]. Modeling of the local structure based on XAFS results to elucidate the origin of the stability is under progress.

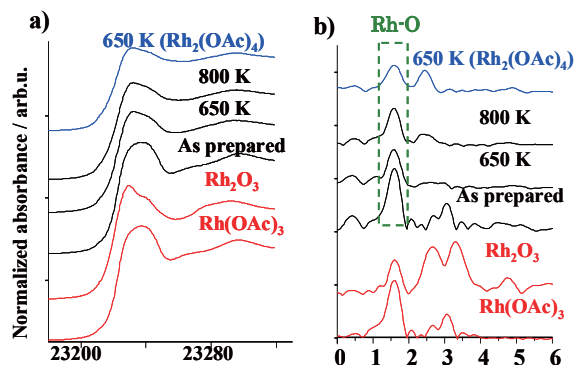


Fig. 1 (a) XANES spectra and (b) Fourier-transforms of EXAFS oscillations for Rh(OAc)<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> on the course of heat treatment (black line). Two reference spectra (red line) and one for [Rh(OAc)<sub>2</sub>]<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> after 650 K (blue line) are also indicated.

Table 1 Curve fitting results of Rh(OAc)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (M) and [Rh(OAc)<sub>2</sub>]<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (D) catalysts.

Sample	Bond	CN	R (Å)
M-as prepared	Rh-O	3.16 ± 0.43	2.04 ± 0.01
M-650 K	Rh-O	2.43 ± 0.34	2.05 ± 0.01
M-800 K	Rh-O	2.15 ± 0.30	2.05 ± 0.01
	Rh-Rh	3.15 ± 1.83	2.88 ± 0.03
D-650 K	Rh-O	4.98 ± 0.91	2.04 ± 0.02
	Rh-Rh	2.88 ± 0.92	2.90 ± 0.02

**References**

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

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