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XAFS Analyses on Formation of Homogeneous Rh Clusters on Alumina Surface

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Introduction

It is well known that choice of a catalyst precursor sometimes affects the activity and selectivity of the catalyst partly due to their local structure apart from the thermodynamically favored one. Recently, we found by high-resolution STM studies that homogeneous Rh clusters can be dispersed on the Al_2O_3 thin film on NiAl(110) by slow thermal decomposition of the $[Rh^{II}(OAc)_2]_2$ precursors in vacuum. By statistical analyses of the particle densities, height, and diameter as a function of heat treatment temperatures, we have concluded that the cluster typically includes two Rh atoms, hence reflects the precursor composition. Besides they are stable against aggregation up to 800 K. In this study, XAFS measurements were carried out to determine the local structure of the clusters and elucidate the precursor dependencies on the final structures.

Experimental

Catalysts were prepared by the incipient wetness impregnation method in a N_2 glove box. Two Rh precursors, $[Rh^{II}(OAc)_2]_2$ (Alfa Aesar) and $RhCl_3$ (Wako), were used to be deposited on Al_2O_3 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_2O_3 support (0.2 wt%) and stirred for 5 h followed by removal of the solvent by evacuation. The samples were heated in vacuum to 500 K, 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

Figure 1 shows XANES spectra observed on the course of catalyst preparation from (a) Rh acetate (b) and $RhCl_3$ on alumina, respectively. In the case of Rh acetate in (a), heat treatment by 500 K change the spectrum shape similar to that of the Rh_2O_3 reference material. In contrast, spectrum became close to that of Rh foil by 500 K annealing for (b).

There results were also confirmed by radial distribution functions shown in Fig. 2. For Rh acetate precursor in (a), predominant Rh-O factor is accompanied by weaker contribution of Rh-Rh at longer distance. Preliminary curve-fitting results indicated that small size structure with local structure slightly distorted from Rh_2O_3 was formed by 500 K and maintained even after 800 K annealing. In the case of $RhCl_3$, however, single peak of metallic Rh-Rh bond can reproduce each spectrum after heat treatment over 500 K and its coordination number increased at higher temperatures. It indicates aggregation of Rh metal particles.

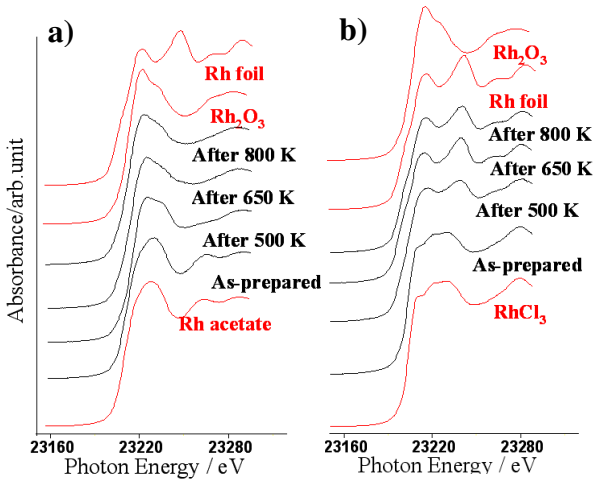

Fig. 1 XANES spectra of (a) Rh acetate and (b) $RhCl_3$ on Al_2O_3 on the course of heat treatment. Three reference spectra are also indicated.

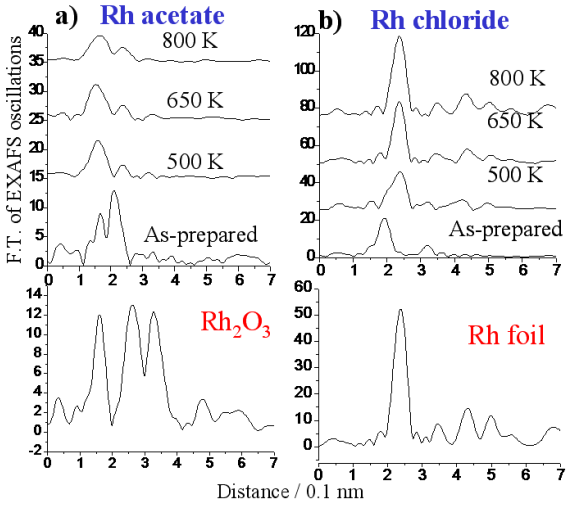

Fig. 2 Fourier-transforms of EXAFS oscillations from Fig.1 for a) Rh acetate and b) $RhCl_3$ on alumina, respectively.

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