February, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 647—648 (1986)* 647

EXAFS Studies of the Behavior of $Rh_6(CO)_{16}$ Supported on γ-Al_2O_3 Surface

Kiyotaka ASAKURA, Yasuhiro IWASAWA,* and Haruo KURODA
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received August 13, 1985)

Synopsis. The structural change of $Rh_6(CO)_{16}$ supported on γ-Al_2O_3 surface during a decarbonylation–recarbonylation cycle was studied by means of EXAFS (extended X-ray absorption fine structure) spectroscopy. $Rh_6(CO)_{16}$ cluster framework was found to be decomposed into $Rh(CO)_2(OAl\lessgtr)_2$ after the reaction with a mixture of O_2 and H_2O, and reversely regenerated by the subsequent treatment with a mixture of CO and H_2O.

Metal carbonyl clusters supported on inorganic oxides have been demonstrated to provide a new way of preparation of noble solid catalysts as well as new chemistry in the research boundary between homogeneous and heterogeneous catalytic systems. Smith et al. and Watters et al. suggested that $Rh_6(CO)_{16}$ physisorbed on Al_2O_3 surface was transformed to twin carbonyl Rh species by the treatment with a mixture of O_2 and H_2O, and reversely, the twin carbonyl Rh species was recarbonylated again to the original $Rh_6(CO)_{16}$ cluster by the subsequent treatment with a mixture of CO and H_2O from the results of IR spectroscopy.[1–3] Since the carbonyl stretching modes of Rh species give no direct information on the feature of Rh–Rh bonding, the details of the structural change of the metal framework of $Rh_6(CO)_{16}$ supported on Al_2O_3 surface still remaind to be solved.

In the present paper we report the EXAFS and XANES studies on a $Rh_6(CO)_{16}/\gamma$-Al_2O_3 system to obtain the information on structural changes of the Rh_6 framework.

Experimental

Supporting $Rh_6(CO)_{16}$ onto γ-Al_2O_3 was carried out by an impregnation method using a hexane or chloroform solution of $Rh_6(CO)_{16}$ under high purity Ar (99.9995%) atmosphere, followed by evacuation to remove the solvent. γ-Al_2O_3 was pretreated at 773 K for 2 h in a dry air in situ before use as a support. Hereinafter, the Al_2O_3 supported $Rh_6(CO)_{16}$ thus obtained is denoted as Sample 1. The sample was treated with a mixture of O_2 (26.6 kPa) and H_2O(2 kPa) at room temperature for 30 h in a closed-circulating system to which the cells for EXAFS measurements were connected. The treated sample is denoted as Sample 2. Sample 2 was further treated with a mixture of CO(26.6 kPa) and H_2O(2 kPa) at 323 k for 15 h, Sample 3 being thus obtained. After each treatment, the samples were transferred to EXAFS cells without contacting air. EXAFS measurements were conducted by use of synchrotron radiation at Photon Factory in National Laboratory for High Energy Physics (KEK-PF).[4] The analysis of EXAFS spectra was performed by a curve fitting technique employing theoretically derived phase shift and amplitude function.[5–7]

Results and Discussion

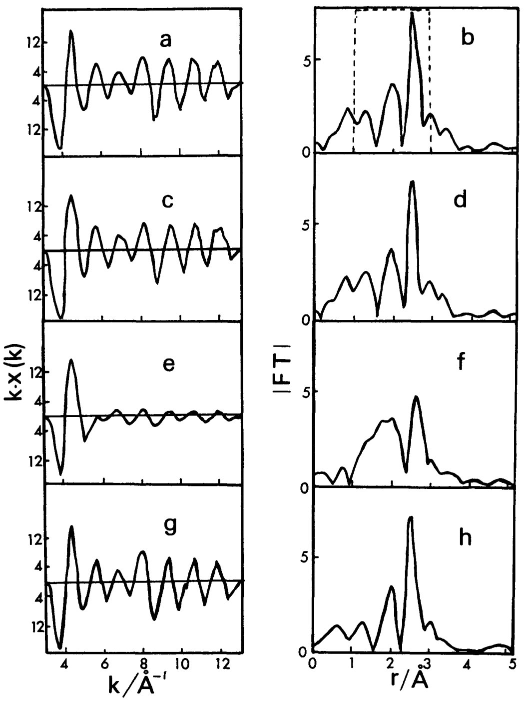

Fig. 1. *k*-Weighted EXAFS oscillations and Fourier transforms.
(a), (c), (e), and (g) are the *k*-weighted EXAFS oscillations of $Rh_6(CO)_{16}$ powder, Sample 1, Sample 2, and Sample 3, respectively. (b), (d), (f), and (h) are the Fourier transforms of $Rh_6(CO)_{16}$ powder, Sample 1, Sample 2, and Sample 3, respectively. The broken line in the Fig. 1b is the Fourier filtering window.

Figure 1 shows the EXAFS oscillations and Fourier transforms of the Rh K-edge EXAFS of $Rh_6(CO)_{16}$ powder, Samples 1, and 3, respectively. The Fourier transform of $Rh_6(CO)_{16}$ showed a strong peak at 2.75 Å referred to the Rh–Rh bond in Fig. 1b. The contribution of back-scattering by Rh atoms to the Rh K-edge EXAFS oscillation was observed over a wide range of the wave number of ejected photoelectron(*k*) as shown in Fig. 1a. Thus the information obtained from the EXAFS analysis largely reflects the structure of Rh metal framework. The main peak in Fig. 1b was back-Fourier transformed in the range of 1—3 Å as shown in the Figure and four-shell curve fitting analyses were carried out considering Rh–C(terminal carbonyl group), Rh–C(triply bridged carbonyl group), Rh–O and Rh–Rh and the results were obtained to be given in Table 1. The Rh–Rh bond length (2.76 Å) was in good agreement with the crystallographic data of $Rh_6(CO)_{16}$[8] (Rh–Rh=2.78 Å).

The EXAFS oscillation (Fig. 1c) and the Fourier transform (Fig. 1d) of Sample 1 were similar to those of $Rh_6(CO)_{16}$ cluster itself. The bond length and coordination number of each coordination shell around a Rh atom were found by the curve-fitting analysis to be about the same as those of $Rh_6(CO)_{16}$ as shown in Table 1. Thus, $Rh_6(CO)_{16}$ is concluded to be

Table 1. The Curve Fitting Results

Sample	Rh-C(term)[a]		Rh-C(bridge)[b]		Rh-O[c]		Rh-Rh[c]	
	N	r/Å	N	r/Å	N	r/Å	N	r/Å
$Rh_6(CO)_{16}$	(2)	1.93	(2)	2.27	(4)	2.99	(4)	2.76
Sample 1	2.2	1.93	2.2	2.26	4.0	2.97	4.1	2.75
Sample 2[d]							2.1	2.75
Sample 2[e]	2.1	1.94	2.3	2.20	4.2	2.98	2.0	2.74
Sample 3	2.0	1.94	2.0	2.25	3.9	2.96	3.8	2.74

a), b) C(term) and C(bridge) mean the carbon atoms of terminal and μ_3-bridged carbonyl ligands, respectively. c) Rh-O means the interaction between Rh and O in carbonyl ligand. d) 1-term curve fitting analysis of Rh-Rh. e) 4-term curve fitting analysis of Rh-C(term)+Rh-C(bridge)+Rh-O+Rh-Rh

supported on γ-Al_2O_3 retaining its cluster framework.

The EXAFS oscillation and Fourier transform of Sample 2 shown in Figs. 1e and 1f were much different from those of Sample 1. The decrease in the intensity of the main peak in the Fourier transform indicates the partial breaking of Rh-Rh bond of the cluster. Smith et al.[2] suggested by IR studies that $Rh_6(CO)_{16}$ supported on Al_2O_3 is decomposed to mononuclear $Rh^I(CO)_2$ species by O_2 treatments(more easily in the presence of moisture). The present EXAFS analysis also indicates the Rh-Rh bond breaking. However, in contrast to the almost complete decomposition of the Rh_6 framework by the IR studies,[2] the Rh-Rh bond was still observed at a distance of 2.75 Å similar to that found in $Rh_6(CO)_{16}$. The EXAFS data suggested that part of $Rh_6(CO)_{16}$ remained almost unchanged after O_2+H_2O treatment. The discrepancy between the IR observation[2] and the present EXAFS analysis is not clear at the present, but the generally known surface heterogeneity of Al_2O_3 employed may give an effect to the behaviors of Rh clusters.

The EXAFS oscillation and the Fourier transform of Sample 3 in Figs. 1g and 1h were identical to those of $Rh_6(CO)_{16}$ as well as Sample 1. The EXAFS analysis in Table 1 clearly reveals that the $Rh_6(CO)_{16}$ framework was completely regenerated on the γ-Al_2O_3 surface by the CO+H_2O treatment for 15 h.

The XANES spectra of Rh K-edge of Samples 1 and 3 given in Fig. 2b and Fig. 2d, respectively were similar to that of $Rh_6(CO)_{16}$ as shown in Fig. 2a, which is compatible with the EXAFS data. The relative intensity of peak A to peak B in the XANES region of Sample 2 changed as shown in Fig. 2c. In the EXAFS studies of a $Ru_3(CO)_{12}/Al_2O_3$ system, peak A near the Ru K-edge becomes stronger than peak B when the Ru_3 cluster was converted to a mononuclear $Ru(CO)_2(OAl\lessdot)_2$ species forming the chemical bonds between Ru atoms and surface oxygens.[9] The XANES spectra suggest the formation of the γ-Al_2O_3-attached species $Rh(CO)_2(OAl\lessdot)_2$ as previously proposed.

In summary, $Rh_6(CO)_{16}$ was physisorbed on the γ-Al_2O_3 surface without any structural change of the Rh_6 framework. $Rh_6(CO)_{16}$ was mostly decomposed into the mononuclear species $Rh(CO)_2(OAl\lessdot)_2$ by a mixture of O_2+H_2O treatment, but some of the cluster remained in the form of $Rh_6(CO)_{16}$. After the subsequent treatment of the $Rh(CO)_2(OAl\lessdot)_2$ with a mixture of CO+H_2O, $Rh_6(CO)_{16}$ was found to be completely regenerated on the basis of the EXAFS and XANES spectra.

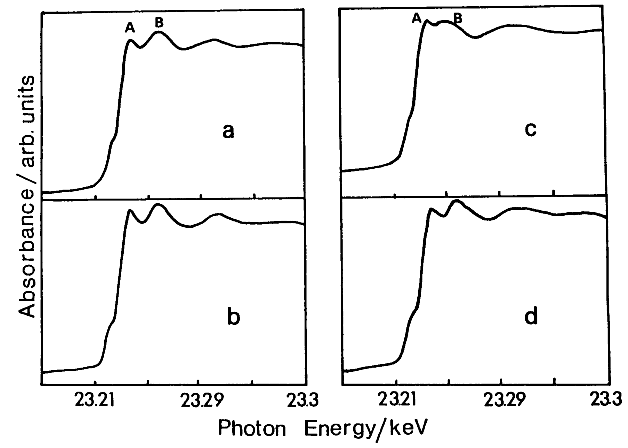

Fig. 2. XANES spectra of unsupported $Rh_6(CO)_{16}$ cluster (a), Sample 1 (b), Sample 2 (c), and Sample 3 (d).

Reference

1) G. C. Smith, T. P. Chojnacki, S. R. Dasgupta, K. Iwatate, and K. L. Watters, *Inorg. Chem.*, **14**, 1419 (1975).

2) A. K. Smith, F. Hugues, A. Theolier, J. M. Basset, R. Ugo, G. M. Zanderighi, J. L. Bilhou, V. B. Bougnol, and W. F. Groydon, *Inorg, Chem.*, **28**, 3104 (1979).

3) K. L. Watters, R. F. Howe, T. P. Chojnacki, C. M. Fu, R. L. Schneider, and N. B. Wong, *J. Catal.*, **66**, 424 (1980).

4) H. Oyanagi, T. Matsushita, M. Ito, and H. Kuroda, *KEK Report* 8330, (1984).

5) B. K. Teo and P. A. Lee, *J. Am. Chem. Soc.*, **101**, 2815 (1979).

6) B. K. Teo, *J. Am. Chem. Soc.*, **104**, 3992 (1981).

7) N. Kosugi and H. Kuroda, Program EXAFS 1, Research Center for Spectrochemistry, the University of Tokyo (1985).

8) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem.Soc.*, **85**, 1202 (1963).

9) K. Asakura, Y. Iwasawa, and H. Kuroda, *Chem. Lett.*, **1985** 551.