Structures of the Catalysts derived from Rh–Co Bimetallic Carbonyls supported on γ-Al_2O_3: Study of Rh-*K* EXAFS

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It is revealed from the analysis of Rh-*K* EXAFS data that, in the catalysts derived from $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ supported on γ-Al_2O_3, metal atoms are present as bimetallic clusters similar to the ones which originally exist in the carbonyl molecules, whereas relatively large Rh–Co alloy particles are formed in the case of the catalysts prepared by the co-impregnation of $RhCl_3$ and $CoCl_2$.

Activities and selectivities of supported metal catalysts are strongly dependent on the state of metal dispersion and on the surface composition. A good method for the preparation of highly-dispersed metal clusters with uniform composition employs metal carbonyls as the precursors.[1] One of the present authors has previously studied the catalysts derived from bimetallic Rh–Co carbonyls, and shown that they exhibit catalytic activities much higher than the Rh–Co catalysts which are prepared conventionally by impregnating the support with a solution containing $RhCl_3$ and $CoCl_2$ and that their catalytic activities and selectivities, such as those in alkene hydroformylation, vary depending on the Rh : Co ratio in the original carbonyl.[2]

The present communication reports the structural information obtained on the catalysts derived from Rh–Co bimetallic carbonyls, by the analysis of the extended *X*-ray absorption fine structure (EXAFS) of their Rh-*K* spectra.

The catalysts were prepared by the method described elsewhere;[2] the starting carbonyls were synthesized after Martinengo *et al.*,[3] and identified by i.r. spectroscopy. The total content of the supported metals was about 4 wt.% in all cases. All *X*-ray absorption measurements[4] were carried out at room temperature on samples sealed with pure He and/or N_2 in the specially designed sample cells. EXAFS spectra were also measured on the catalysts which were prepared by impregnation of the support with an aqueous solution containing $RhCl_3$ and $CoCl_2$ (1 : 1 or 1 : 3 mole ratio).

Examples of the Fourier transforms of $k^3\chi(k)$, which were calculated by use of the EXAFS data over the region of k 4—12 Å^{-1}, are shown in Figures 1 and 2. Using the

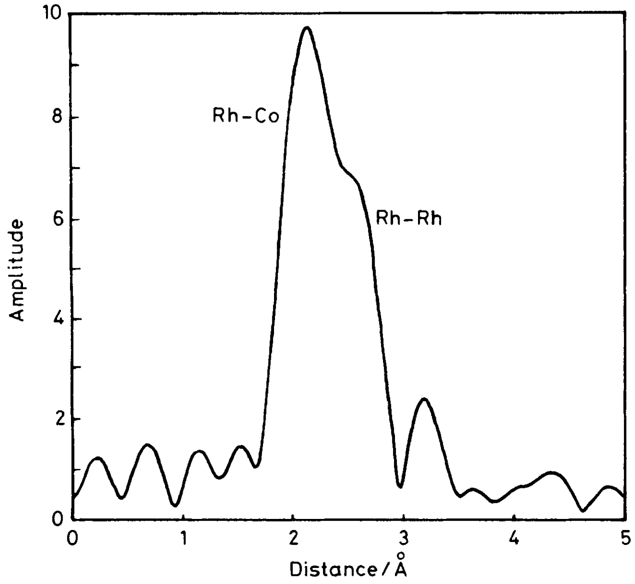

Figure 1. Fourier transform of $k^3\chi(k)$ of $Rh_2Co_2(CO)_{12}/Al_2O_3$, reduced with H_2 at 400 °C [sample (6) in Table 1].

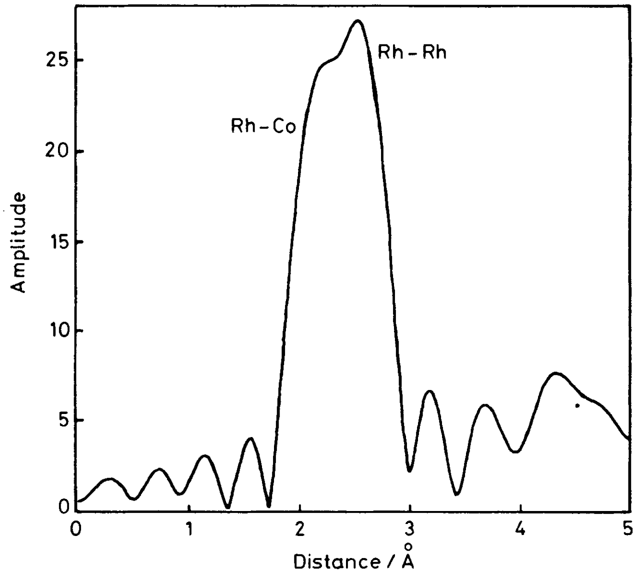

Figure 2. Fourier transform of $k^3\chi(k)$ of Rh–Co (1 : 1)/Al_2O_3, reduced with H_2 at 400 °C [sample (8) in Table 1].

Table 1. Results of the curve-fitting analyses.

	Rh–Rh		Rh–Co	
Sample[a]	N[b]	R[c]/Å	N[b]	R[c]/Å
(1) $Rh_4(CO)_{12}$, crystalline powder[d]	(3)	2.73	—	—
(2) $RhCo_3(CO)_{12}$, crystalline powder[d]	—	—	(3)	2.62
(3) $Rh_2Co_2(CO)_{12}$, crystalline powder	1.3	2.77	1.9	2.61
(4) $Rh_2Co_2(CO)_{12}/Al_2O_3$	0.8	2.81	2.0	2.60
(5) $Rh_2Co_2(CO)_{12}/Al_2O_3$, heated at 200 °C	—	—	2.2	2.64
(6) $Rh_2Co_2(CO)_{12}/Al_2O_3$, red. with H_2	0.7	2.69	2.0	2.55
(7) $RhCo_3(CO)_{12}/Al_2O_3$, red. with H_2	—	—	2.7	2.60
(8) Rh–Co (1 : 1)/Al_2O_3,[e] red. with H_2	8.7	2.70	3.3	2.57
(9) Rh–Co (1 : 3)/Al_2O_3,[e] red. with H_2	7.6	2.70	3.5	2.58

[a] Refer to the text for the descriptions of the samples. [b] Co-ordination number. [c] Interatomic distance. [d] Standard compounds to determine the empirical parameters. [e] Prepared by the impregnation of the support with a solution containing $RhCl_3$ and $CoCl_2$ (mole ratio given in parentheses). (Rh metal where $N = 12$, $R = 2.69$ Å, was used as a standard for Rh–Rh.)

reverse-Fourier transformation for the region of the peaks corresponding to Rh–Co and Rh–Rh bonds, we carried out the curve-fitting analysis by use of the empirical parameters derived from the analysis of the EXAFS data of $Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$. The region of k 6—12 Å^{-1} was used in the curve-fitting procedure and the method of the curve-fitting analysis used here was essentially the same as that described by Teo *et al.*[5] Using the observed EXAFS data of Rh–Co bimetallic carbonyls, we carefully examined the effect of the selection of the k region in the Fourier transformation and curve-fitting analysis and found that the contributions from Rh–C and Rh–O interactions could be sufficiently reduced by using the k regions mentioned above. The crystallographic data for $Rh_4(CO)_{12}$ is known,[6] and the Rh–Rh distance was used to derive the empirical parameters. However, the crystal structure analysis for $RhCo_3(CO)_{12}$ has not yet been performed. Thus the Rh–Co distance in this compound and the empirical parameters concerned with Rh–Co were determined from the analysis of the Rh-K and Co-K EXAFS data employing the procedure reported by Meitzner *et al.*[7] The results of the curve-fitting analyses are given in Table 1.

In sample (4), where dehydrated γ-Al_2O_3 was simply impregnated with $Rh_2Co_2(CO)_{12}$, the bond lengths and co-ordination numbers obtained are almost the same as those obtained for the powder of the original carbonyl, except for a slight increase in the Rh–Rh bond length. This seems to indicate that the Rh–Co cluster in the original carbonyl molecule is retained in the species supported on γ-Al_2O_3, although a deformation of the molecular structure might have taken place as revealed by the i.r. spectrum: considerable shifts of the CO bands to lower wave numbers, possibly due to the strong interaction of the bridging CO with the Al^{3+} sites of the support, are observed. The EXAFS data after the heat-treatment *in vacuo* at 200 °C to remove the CO groups [sample (5) in Table 1] show that Rh–Rh bonds are broken, but Rh–Co bonds are retained with a slight increase of the bond length. When the carbonyl-impregnated specimen was first exposed to the air and subsequently reduced with hydrogen at 400 °C [sample (6)], the EXAFS data gave the co-ordination numbers 0.7 for Rh–Rh and 2.0 for Rh–Co. These values are nearly the same as those for the original carbonyl, indicating that the Rh–Co bimetallic cluster skeleton of the carbonyl is retained in this catalyst. Note that the Rh–Co distance is appreciably shorter than the distance in the original carbonyl molecule.

In the case of sample (7) which is obtained by a similar treatment after the impregnation of $RhCo_3(CO)_{12}$, the EXAFS data show that there exist Rh–Co interactions with co-ordination number of about 3, but no Rh–Rh bonds. This result again indicates that the original $RhCo_3$ cluster is retained after the treatment.

In contrast to the results for the carbonyl-impregnated cases, the Rh–Rh and Rh–Co co-ordination numbers are markedly higher in the catalysts prepared by the co-impregnation of $RhCl_3$ and $CoCl_2$; the sum of the Rh–Rh and Rh–Co co-ordination numbers was found to be 12, which is the value expected for a bulk metal. This fact implies that the metal atoms form relatively large alloy particles. It should be noted also that the Rh–Rh co-ordination number is 8—9 and the Rh–Co co-ordination number is 3—4, irrespective of the $RhCl_3/CoCl_2$ mole ratio in the impregnating solution. Thus the bulk of the metal particles in these catalysts seems to have a rather fixed Rh-rich composition, possibly by segregating the excess of Co on the surfaces of the particles.

In conclusion, the results of the present EXAFS study have revealed that the supported catalysts derived from Rh–Co bimetallic carbonyls keep the Rh–Co cluster skeletons which originally exist in the carbonyl molecules, whereas relatively large metal particles with a Rh-rich bulk composition are formed when the catalysts are prepared from a solution containing Rh and Co salts. The highly and uniformly dispersed structures of the carbonyl-derived catalysts might be responsible for their high catalytic activities and selectivities for reactions such as the hydroformylation of alkenes and CO–H_2 conversion into methanol and ethanol.

The X-ray absorption spectra were measured using the EXAFS facilities installed at the Beam Line 10B in the Photon Factory at the National Laboratory for High-Energy Physics (KEK-PF).[4]

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