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An XPS Study of $Rh_6(CO)_{16}$–Al_2O_3

Transition metal cluster carbonyl complexes supported on high-surface-area oxides are widely studied as potential models for supported metal catalysts (*1*). The rhodium complex $Rh_6(CO)_{16}$ supported on Al_2O_3 has been shown to undergo reversible decarbonylation and carbonylation reactions at room temperature when treated successively with O_2 and CO (*2, 3*). An important question in the chemistry of supported $Rh_6(CO)_{16}$ (or any other complex) is whether or not the original transition metal cluster remains intact following adsorption of the complex onto the support and subsequent treatment. We have suggested, from volumetric adsorption and infrared spectroscopic data (*3*) that the Rh_6 cluster on Al_2O_3 remains intact during carbonylation and decarbonylation reactions at room temperature, but is destroyed on heating at 250°C. Smith *et al.* (*4*), on the other hand, have concluded, also from infrared spectroscopic data, that adsorption and oxidation of $Rh_6(CO)_{16}$ at room temperature causes destruction of the cluster. A final answer to this question cannot be given from the information so far available.

This Note describes the results of a study of $Rh_6(CO)_{16}$ on Al_2O_3 using X-ray photoelectron spectroscopy (XPS), undertaken with the objective of learning more about the nature of the adsorbed rhodium species. The $Rh_6(CO)_{16}$–Al_2O_3 samples (1 and 0.6% Rh by weight) were prepared by the solution impregnation technique described earlier (*2, 3*), using a fully hydroxylated Al_2O_3 support. Spectra were obtained from samples pressed onto Au foil or Ag mesh with the AEI ES200B spectrometer described in (*5*), using Al$K\alpha$ radiation. Binding energies were referenced to the Au $4f_{7/2}$ line at 84.0 eV from Au which was evaporated onto selected samples. Sample charging was corrected for by adjusting the core binding energies of Al_2O_3 to coincide with the Au calibrated values. The binding energies quoted are considered to be accurate to within ±0.2 eV. All sample treatments were carried out *in situ* in the spectrometer's preparation chamber.

Table 1 summarizes the Rh $3d_{5/2}$ binding energies for various rhodium-containing samples. The Rh $3d_{5/2}$ binding energy of the parent complex $Rh_6(CO)_{16}$ is significantly higher than that of Rh metal. Similar shifts relative to the metal have been reported for the series of platinum cluster carbonyl complexes $[Pt_3(CO)_6]_n^{-2}$, and attributed to a combination of two factors: withdrawal of electrons from the Pt by CO ligands, and a diminished extraatomic relaxation relative to the bulk metal (*6*).

The XPS spectra of the Al_2O_3 supported Rh samples were found to undergo significant changes upon X irradiation for several hours. The Rh $3d$ lines broadened asymmetrically toward lower binding energies, whereas the Al_2O_3 lines were unchanged. Similar changes have been observed for Rh-exchanged zeolites (*5*) and other compounds (see, for example, (*7*)). The nature of the X-ray-induced sample decomposition is not understood. The X-ray beam induces formation of many different excited states, and there is a wide energy spectrum of secondary electrons present as well, all of which may contribute to the observed effects. The binding energies reported in Table 1 are initial values, obtained as rapidly as possible (within 15 min) from samples freshly exposed to the X-ray beam. Because of the irreversible

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TABLE 1

Rh $3d_{5/2}$ Binding Energies and Half-Widths

Sample	Treatment	Rh $3d_{5/2}$ (eV)	FWHM (eV)	Ref.
$Rh_6(CO)_{16}$	Unsupported	308.8	2.2	
$Rh_6(CO)_{16}/Al_2O_3$	Decarbonylated	310.1	3.3	
Decarbonylated	+ Dry CO	310.1	3.3	
Decarbonylated	+ Wet CO	309.2	3.2	
Decarbonylated	Evac. 150°C	308.9	4.1	
Decarbonylated	Red. in H_2, 150°C	308.7	3.4	
Decarbonylated	Evac. 200–500°C	308.1	3.1	
Decarbonylated	Red. in H_2, 330°C	307.9	3.6	
Rh/C (5%)	Evac. 400°C	307.3	2.2	
Rh metal		307.1		(*5*)
$RhCl_3$, $3H_2O$		310.2	1.9	(*5*)
$Rh^{3+}X$ zeolite		310.1	2.2	(*5*)
$Rh^{3+}Y$ zeolite		310.8		(*8*)
Rh^{3+} compounds		308.8–311.3 (310.3)[a]		(*9*)
Rh^{+1} compounds		307.6–309.6 (308.8)[a]		(*9*)

[a] Mean B.E. for 48 and 16 compounds, respectively.

decomposition it was not possible to carry out successive treatments with the same sample.

The fully decarbonylated $Rh_6(CO)_{16}$–Al_2O_3 samples had been exposed to air for several weeks, which is known to cause complete removal of CO ligands (*2, 3*). These samples gave a Rh $3d_{5/2}$ binding energy 1.3 eV higher than that of $Rh_6(CO)_{16}$. Treatment of a decarbonylated sample with 1 atm of water-saturated CO at 25°C for 70 h shifted the binding energy back close to that of the parent complex, althouth the linewidths of the supported samples were significantly larger than that of unsupported $Rh_6(CO)_{16}$. According to our volumetric and infrared measurements, such treatment results in at least 60% of the Rh forming $Rh_6(CO)_{16}$ ads (*3*). The XPS data thus confirm that the decarbonylation of $Rh_6(CO)_{16}$ on Al_2O_3 can be largely reversed by treatment with wet CO. The binding energy of adsorbed $Rh_6(CO)_{16}$ is not significantly removed from that of the unsupported complex, indicating the absence of a strong support interaction.

Treatment of a decarbonylated sample with dry CO caused no change in the Rh $3d_{5/2}$ binding energy. In this case, the infrared and volumetric experiments indicate formation of an intermediate dicarbonyl species (*3*). Attempts to obtain the CO/Rh ratio from the C 1*s*, O 1*s*, and Rh $3d_{5/2}$ lines were not successful, due to masking of the carbonyl core lines by those of carbon contaminants and oxide ions of the support.

Binding energies close to those of $Rh_6(CO)_{16}$ were also obtained when decarbonylated samples were outgassed *in vacuo* at 150°C or reduced in H_2 at 150°C. Evacuation or reduction above this temperature gave significantly lower binding energies. A binding energy characteristic of bulk Rh metal was not obtained, however, even after evacuation at 500°C, or reduction in H_2 at 330°C for 20 h.

The nature of the various Rh species cannot be unambiguously deduced from the XPS data alone. Comparison of the binding energies of the decarbonylated and partially carbonylated samples with those of known Rh compounds or Rh-exchanged zeolites may suggest that the formal oxidation state in both species is 3+. Such a comparison does not take account of possible differences in binding energy (caused by relaxation effects and initial-state chemical shifts) between bulk compounds, isolated Rh species (as in the zeolite), and Rh in cluster form. The carbonyl stretching frequencies of the intermediate dicarbonyl species formed by adding dry CO to decarbonylated samples (2090, 2020 cm^{-1}), do not fall in the range expected for $Rh^{3+}(CO)_2$ (*8*), and no Rh^{2+} could be detected by EPR spectroscopy (*3*). Smith *et al.* (*4*) have suggested that the intermediate species is $Rh^+(CO)_2$ formed by fragmentation of the Rh_6 cluster. However, the binding energy of the intermediate species (and the fully decarbonylated cluster) lies above the range for Rh^+ compounds (see Table 1). We believe that the XPS spectra may best be explained in terms of a retention of the Rh_6 cluster throughout the room-temperature carbonylation and decarbonylation cycles. The scheme proposed from our infrared and volumetric measurements was (*3*)

$$Rh_6(CO)_{16} \underset{+CO}{\overset{+O_2}{\rightleftharpoons}} Rh_6(CO)_{12}O_{12} \underset{+CO}{\overset{-CO}{\rightleftharpoons}} Rh_6O_{12}.$$

The binding energy shift of about 1 eV between the fully carbonylated cluster and the intermediate and fully oxidized forms, and the carbonyl stretching frequencies of the intermediate species, suggest that each Rh is oxidized relative to $Rh_6(CO)_{16}$, and the oxidized clusters may perhaps be described as $(Rh^+)_6(O_2^-)_6$.

In terms of the above scheme, evacuation at 150°C or reduction in H_2 at 150°C evidently removes the adsorbed oxygen, giving a binding energy characteristic of $(Rh^\circ)_6$. Evacuation (or reduction) above 200°C is known to destroy the ability of $Rh_6(CO)_{16}$–Al_2O_3 to undergo reversible carbonylation–decarbonylation cycles (*3*), due to destruction of the cluster. The XPS spectra of high-temperature-treated samples suggest that under these conditions highly dispersed Rh metal is formed. It is well known that very small metal particles give core lines shifted toward higher binding energy relative to the bulk (*10, 11*), and we were unable to detect metal crystallites larger than 10 Å in diameter by means of transmission electron microscopy on heat-treated samples (*3*).

The chemistry of $Rh_6(CO)_{16}$ on a fully hydroxylated Al_2O_3 support may be compared with that described by Knözinger *et al.* (*12, 13*) for $Rh_6(CO)_{16}$ on various ligand modified SiO_2 supports. On the modified SiO_2 supports, extensive ligand substitution is believed to lead to fragmentation of the cluster, forming mononuclear $L_nRh^+(CO)_2$ and L_mRh^+CO species, where L are surface-attached ligands. The Rh $3d_{5/2}$ binding energies for these species are reported to lie in the range 307.0 to 307.6 eV (*13*). The binding energies in (*13*) were referenced to Si $2p$ and C $1s$ values about 0.9 eV lower than those used here. After correcting to C $1s = 285.0$ eV (e.g., (*14*)) and Si $2p = 103.9$ eV, the binding energies reported by Knözinger become 307.9–308.5 eV. These fall within the range of Rh^+ compounds, and are significantly lower than the values obtained for $Rh_6(CO)_{16}$ on Al_2O_3.

The XPS results thus appear to rule out fragmentation of $Rh_6(CO)_{16}$ into mononuclear Rh^+ species on Al_2O_3. The alternative interpretation of the XPS spectra, fragmentation into mononuclear Rh^{3+} species on decarbonylation, is not consistent with the infrared spectra and the ease of reversibility of the decarbonylation reaction.

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