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XPS Photoelectron Study of Rhodium Complexes Attached to Chemically Modified Silicas

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We have recently reported on the preparation and catalytic activity for alkene hydrogenation of Rh complexes which were attached to chemically modified silica supports [1–3]. In one attempt (method A) [1], $RhCl_3$ was reacted with pendent $-(CH_2)_3$-PPh_2 ligands on the SiO_2 support and then activated by various reduction treatments before their use as hydrogenation catalysts in solution. Another preparative procedure (method B) [2, 3] consisted in the attachment from solution of $Rh_6(CO)_{12}$ onto silica surfaces bearing pendent $-(CH_2)_3PPh_2$, $-(CH_2)_3$-NHC_6H_{11} or $-(CH_2)_3NH(CH_2)_2NH_2$ ligands. Infrared spectroscopy proved the formation of *mononuclear* complexes of the type $L_nRh(CO)_2$, where L designates a surface ligand and n remained unknown. These catalysts were active alkene hydrogenation catalysts [4]. The Rh content of all these systems was between approximately 0.3 and 1.5% wt.

On the basis of CO uptake measurements and turnover numbers for alkene hydrogenation [1] and of infrared spectroscopic data [2], it was suggested that the oxidation state of the metal in these catalysts should probably be the Rh^{+1} state, although no unequivocal experimental valence state determination was yet available. We have therefore studied these Rh catalysts by X-ray photoelectron spectroscopy (XPS).

The XPS spectra were recorded on an AEI Scientific Apparatus spectrometer type ES 100. The accuracy of the binding energies was 0.2 eV. A binding energy of 103 eV of the Si 2p level [5] was used as an internal standard. The C1s binding energy was then 284 eV in all samples. Because of the low metal loadings, spectra were usually obtained by data acquisition.

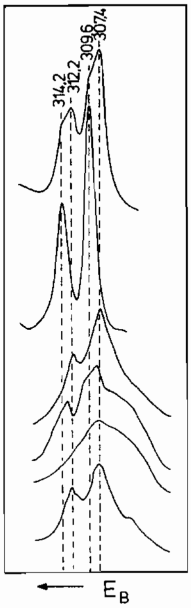

Fig. 1. Photoelectron spectra of attached rhodium complexes (binding energies E_B in eV): (1) $(PPh_3)_3Rh^{+1}Cl$; (2) $(PPh_3)_3Rh^{+3}Cl_3$; (3) $(PPh_3)_3Rh^{+1}Cl$ adsorbed on SiO_2; (4) $RhCl_3$ attached to phosphine modified silica; (5) same as (4) after reduction in H_2 (50 atm) at 50 °C; (6) same as (4) after reduction by hydrazine.

Figure 1 shows the Rh $3d_{3/2}$ and Rh $3d_{5/2}$ peaks of catalysts prepared according to method A. Spectra of $(PPh_3)_3Rh^{+3}Cl_3$ and $(PPh_3)_3Rh^{+1}Cl$ are also shown for comparison; the latter compound was not pure and contained some Rh^{+3}. The positions of the $3d_{3/2}$ and $3d_{5/2}$ peaks of the reference compounds are observed at 312.2 and 307.4 eV for Rh^{+1} and at 314.2 and 309.6 eV for Rh^{+3}, respectively. The spectra of the catalysts are more complex and the width at half maximum is larger than in the reference compounds. The peak positions of $(PPh_3)_3Rh^{+1}Cl$ adsorbed on SiO_2 (spectrum 3) are identical with those of the corresponding Rh^{+1} reference although the peak half width is larger. The attachment of $RhCl_3$ onto the phosphine modified SiO_2 immediately leads to a partial reduction of Rh^{+3} (spectrum 4). The $3d_{3/2}$ and $3d_{5/2}$ peaks in this sample are asymmetric, their maxima falling between the typical positions of Rh^{+1} and Rh^{+3}, and a broad shoulder is developed at approximately 304 eV. A broad peak was found at 305.6 eV for a conventional supported Rh/SiO_2 catalyst (not shown in Fig. 1). The attachment of $RhCl_3$ onto the phosphine modified silica obviously leads to an ill-defined system in which Rh species occur in different oxidation states, *i.e.* the +3, +1 and zero valent state. Further reduction in H_2 (50 atm) at 50 °C produces a very broad photoemission band (spectrum 5) with maximum near 307 eV and a broad shoulder at approximately 304 eV. This reduction procedure removed Rh^{+3} quantitatively and produced mainly metallic Rh although some Rh^{+1} might still be present. Surprisingly, the binding energies of the metallic Rh appear at lower values than of conventional supported Rh metal and the band width at half maximum is extremely large. Similar phenomena have recently been reported for Fe $2p_{3/2}$ peaks of reduced NH_3 synthesis catalysts [6] and for Cu $2p_{3/2}$ peaks of reduced $CuAl_2O_4$ catalysts [7]. The low binding energy and large band width of these systems have been explained by the paracrystallinity of the small metal particles. An analogous interpretation should also hold for the reduced Rh catalysts.

Reduction of the originally pale pink attached $RhCl_3$ with hydrazine in aqueous solution gave a yellow-brown complex, the XPS spectrum of which is shown in Fig. 1, no. 6. Though band shape and some structure indicate that the system is not completely uniform, the binding energies of the Rh 3d levels very closely resemble those of the Rh^{+1} reference complex. It is therefore suggested that the reduction by hydrazine of the attached $RhCl_3$ complexes yields the most uniform oxidation state +1 among the reduction procedures tested. This catalyst, however, had a very low hydrogenation activity as compared to the activity of the H_2 reduced catalyst [1], which suggests that the activity of the latter catalyst was mainly due to the formation of Rh metal.

TABLE I. Binding Energies E_b (eV) of Rh $3d_{5/2}$ Levels.

Pendent Ligand	E_b
$-(CH_2)_3PPh_2$	307.2
$-(CH_2)_3NHC_6H_{11}$	307.0
$-(CH_2)_3NH(CH_2)_2NH_2$	307.6
$-(CH_2)_3NH(CH_2)_2NH_2$ (used for hydrogenation of alkenes)	307.6

The Rh $3d_{5/2}$ binding energies of the catalysts which were obtained by the attachment of $Rh_6(CO)_{16}$ according to method B are summarized in Table I. In all cases the binding energies of the Rh $3d_{5/2}$ level 307.0 to 307.6 eV are very close to the value of Rh^{+1} complexes. The catalysts obtained by method B must therefore be described as $L_nRh^{+1}(CO)_2$ complexes in agreement with previously reported infrared data. Table I also contains the Rh $3d_{5/2}$ binding energy of a complex with L = $-(CH_2)_3NH(CH_2)_2NH_2$, which had been used for gas phase alkene hydrogenation [4] for several weeks. The binding energy is identical with that of the original fresh catalyst, indicating that the Rh^{+1} state of the catalyst was maintained during its use for gas phase hydrogenation at 100 °C and up to 3×10^4 Nm^{-2} H_2 pressure.

In conclusion, the attachment of $RhCl_3$ onto a phosphine-modified silica support and subsequent reduction usually yields non-uniform catalyst systems, in which various oxidation states coexist, Rh metal being the dominant active component for alkene hydrogenation. Only reduction with hydrazine gave a fairly uniform catalyst with Rh in the +1 oxidation state, which, however, was only poorly active. The attachment of the polynuclear $Rh_6(CO)_{16}$, according to method B, on the other hand, gave uniform complexes of the general form $L_nRh^{+1}(CO)_2$, which are active catalysts for gas phase hydrogenations.

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