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Preparation of a rhodium catalyst from rhodium trichloride on a flat, conducting alumina support studied with static secondary ion mass spectrometry and monochromatic X-ray photoelectron spectroscopy

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A rhodium catalyst has been prepared by electrostatic adsorption of $RhCl_3$-derived species in aqueous solution on a model support, consisting of a 4–5 nm thick layer of aluminum oxide on an aluminum foil. The conversion of the rhodium precursor species into metallic rhodium has been studied by monochromatic XPS and static SIMS. Freshly prepared catalysts contain adsorbed Rh-complexes with only one chloro ligand; this is explained by a mechanism in which chloro ligands of the initially adsorbed complex, of the form $[RhCl_n(OH)_{4-n}(H_2O)_2]^-$, are displaced by surface OH groups. Analysis of molecular secondary cluster ions of the type $RhCl^-$ shows that the Rh–Cl species decompose at reduction temperatures below 200°C, whereas reduction temperatures well in excess of 200°C are needed to remove chlorine from the alumina support.

Keywords: Rh/alumina; model catalysts; catalyst preparation; surface characterization; XPS; SIMS

1. Introduction

The use of thin film oxides of alumina or silica on a conducting substrate as model supports offers excellent possibilities for studying catalyst preparation by surface science techniques, if one applies catalytically active components by the same wet chemical methods that are used in the fabrication of technical catalysts [1–3]. Previous papers from our group describe how impregnation and anchoring of catalyst precursors by exchange and condensation reactions [1,3] or by electrostatic adsorption [2] onto these model supports is carried out. The inherently low concentrations of the active phase (on the order of 10^{14}–10^{16}

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atoms per cm^2) can readily be determined by Rutherford backscattering spectrometry (RBS) [2,3].

Here we study the preparation of Rh catalysts from a $RhCl_3$ precursor on an Al_2O_3/Al model support. In aqueous solutions, $RhCl_3 \cdot xH_2O$ forms neutral as well as charged complexes, of the type $[RhCl_n(H_2O)_m(OH)_{6-n-m}]^{(3-n-m)-}$. At low pH, negatively charged complexes may adsorb on the positively charged alumina surface. Chlorine is known to be retained in significant amounts by alumina supports [4,5] and is expected to affect the catalytic properties of rhodium surfaces [6]. In this letter we use static secondary ion mass spectrometry (SIMS) and monochromatic X-ray photoelectron spectroscopy (XPS) to characterize the state of the catalyst in various stages of the preparation, and we investigate in particular whether chlorine residues from the catalyst precursor are in contact with rhodium in the reduced catalyst.

2. Experimental

The alumina model support was a 99.999% pure aluminum foil (Aldrich Chemical Company, Inc.) with a native oxide layer. Rhodium was applied by immersing a piece of the Al foil (approximately $10 \times 15 \times 0.5$ mm) in a solution of 35 mg $RhCl_3 \cdot xH_2O$ (Johnson Matthey) in 700 ml water (i.e. 2×10^{-4} M). The solution had a pH of 4, which is well below the isoelectric point of aluminum oxide (pH = 7–8). After 1 h, the sample was taken from the solution and subsequently rinsed with water in order to remove unadsorbed metal complexes, thus preventing undesirable deposition of rhodium. Drying was done in air at 60 and at 110°C for several hours. Samples were reduced in a quartz reactor in 1 bar of flowing H_2. In order to avoid exposure of the catalysts to air, the reactor was unloaded in a glove box under dry nitrogen and brought to the XPS and SIMS spectrometers with a transport vessel.

Reference samples of the $RhCl_3 \cdot xH_2O$ catalyst precursor were prepared by dissolving the salt in acetone (under dry nitrogen to avoid contact with the air) and by letting a few drops of this solution dry on a tantalum foil.

XPS spectra were measured with a VG Scientific Escalab 200 system, equipped with a monochromated Al Kα source and a hemispherical analyzer with a five channel detector. Samples were mounted on stainless steel sample stubs by using tantalum masks. Spectra were recorded with a pass energy of 10 eV. Charging was uniform and nowhere more than 1 eV, and was corrected for by using the C 1s peak of carbon impurities at 284.6 eV as a reference. Considering the pass energy, and uncertainties due to peak fitting and charge corrections, we estimate the accuracy of the given binding energies to be 0.1 eV, unless otherwise stated.

SIMS spectra were measured with a Leybold SSM 200 quadrupole mass spectrometer, using a 5 keV Ar^+ beam with a current density of 0.5 $\mu A/cm^2$.

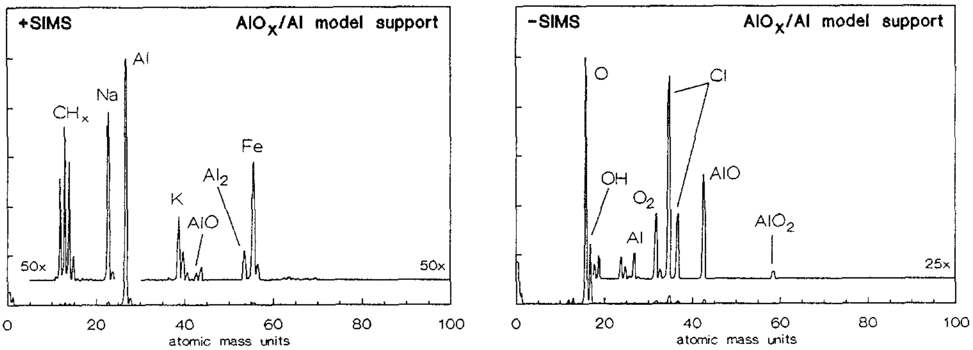

Fig. 1. Positive (left) and negative (right) static SIMS spectra of an approximately 4 nm thick layer of aluminum oxide on an aluminum foil, used as model support for preparing a rhodium model catalyst.

The typical time to record a spectrum was 100 s, estimated to result in the removal of about 25% of a monolayer. The samples were mounted on the sample rod by using tantalum masks. Charge compensation was not necessary on these samples.

RBS spectra were measured with an incident beam of 3.92 MeV He^+, produced with the AVF-cyclotron at Eindhoven University of Technology. For details we refer to ref. [2].

3. Results

First we will describe SIMS and XPS spectra of the thin film alumina model support and the $RhCl_3 \cdot xH_2O$ catalyst precursor, then we discuss the state of the freshly adsorbed rhodium species on the support and the changes that occur upon reduction and exposure of the catalyst to air.

3.1. THE ALUMINA MODEL SUPPORT

The support consists of a native aluminum oxide layer on a high purity aluminum foil. The positive and negative SIMS spectra (fig. 1) of the model support show high intensities for the peaks of Al^+ (27 amu), O^- (16 amu) and OH^- (17 amu) as well as peaks of the molecular fragment ions AlO^+ (43 amu), $AlOH^+$ (44 amu), Al_2^+ (54 amu), AlO^- (43 amu), and AlO_2^- (59 amu). The only significant contamination is due to iron (56 amu) and hydrocarbons, as indicated by the peaks of CH_x^+ (12–15 amu) and $C_2H_x^-$ (24–26 amu). The signals from Na^+, K^+, and Cl^- are practically always present in SIMS spectra, even when these elements are present in trace amounts, due to their low ionization potential (Na, K) or their high electro-negativity (Cl).

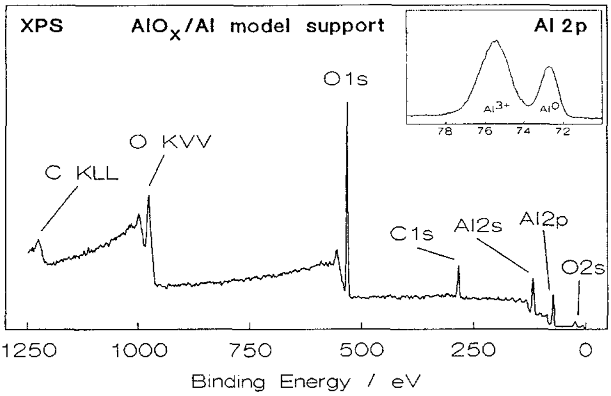

Fig. 2. XPS wide scan of the Al_2O_3/Al model support at low resolution (pass energy 100 eV). The inset shows the Al 2p region taken at high resolution (pass energy 10 eV). The Al^{3+}/Al^0 intensity ratio corresponds to an oxide thickness of approximately 4 nm.

The XPS wide spectrum of the AlO_x/Al model support (fig. 2) confirms the presence of carbon in the surface region, but contains no other peaks than the expected ones of Al (2p and 2s), O (1s, 2s, and Auger KVV) and C (1s, Auger KVV). The series of small peaks at the high binding energy side of the Al 2p

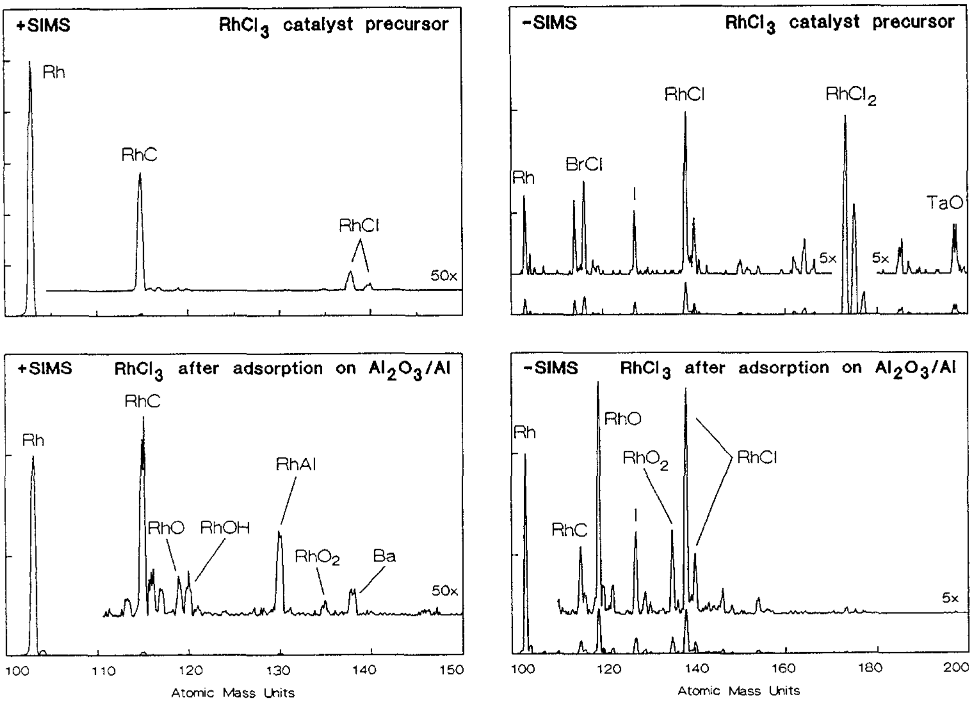

Fig. 3. Positive (left) and negative (right) static SIMS spectra of the $RhCl_3 \cdot xH_2O$ catalyst precursor deposited on tantalum (top) and of a model catalyst prepared by adsorbing rhodium complexes derived from $RhCl_3 \cdot xH_2O$ in water on the Al_2O_3/Al model support (bottom).

and 2s peaks are due to plasmon losses in the aluminum metal substrate. Note that an Fe 2p signal between 705 and 715 eV corresponding to the iron contamination detected by SIMS cannot be discerned, indicating that the iron concentration is probably well below 1%.

The inset of fig. 2 shows the Al 2p signal which consists of a component from Al bulk metal at 72.4 eV (measured after removing the oxide to ensure direct electrical contact with the spectrometer) and one from the oxide at 74.5 eV (corrected for an approximately 1 eV charge shift by using the C 1s signal). The latter value is in agreement with the presence of Al^{3+} ions [7]. The O 1s peak (not shown) has a binding energy of 531.6 eV, consistent with the values between 531.3 and 531.8 eV quoted for γ-Al_2O_3 [7] but substantially lower than the O 1s binding energies between 532.8 and 533.2 eV of aluminum hydroxide [7]. However, the large FWHM value of the O 1s peak, 2.5 eV in comparison with 1.9 eV for the Al^{3+} 2p signal, does not rule out that hydroxyl groups are present.

The Al^{3+}/Al^0 intensity ratio of 2.8 corresponds to an oxide layer of approximately 4.3 nm, if we take an inelastic mean free path of 2.79 nm for Al_2O_3 and 2.56 nm for Al [8]. In this calculation we assume that the layer is flat and has uniform thickness and composition. We note, however, that the assumption of a flat surface is a particularly critical one. Surface roughness may cause the actual average layer thickness to deviate as much as 1 nm from the calculated value [9].

3.2. THE $RhCl_3 \cdot xH_2O$ CATALYST PRECURSOR

Negative SIMS spectra of the $RhCl_3 \cdot xH_2O$ catalyst precursor on a tantalum foil (fig. 3, top) contain intense peaks due to $RhCl^-$ and $RhCl_2^-$ ions. The contact between Rh and Cl can also be demonstrated with positive SIMS, and is reflected by the $RhCl^+$ peaks at 138 and 140 amu. The sensitivity of positive SIMS towards Cl-containing Rh peaks is, however, limited, which can be understood from the high electronegativity of Cl. We conclude that negative SIMS appears well suited for investigating contact between Rh and Cl.

Fig. 4a shows the monochromatic XPS spectrum of the Rh 3d region of the $RhCl_3 \cdot xH_2O$ reference sample. The Rh 3d doublet represents a single rhodium state with a Rh $3d_{5/2}$ binding energy of 310.0 eV, in good agreement with the values in the range of 309.7–310.3 eV reported in the literature [7,10–12]. The Cl 2p spectrum (fig. 5a) can only be interpreted if we assume that it consists of at least two doublets, corresponding to Cl $2p_{3/2}$ binding energies of 198.3 and 199.2 eV, respectively. In agreement with a review by Srivastava [13], we assign the Cl 2p doublet with the lower binding energy to terminal Cl species, and the one with the higher binding energy to bridging Cl species. It should be noted that the presence of two Cl doublets cannot be explained by charging, regarding the small peak width of the Rh 3d doublet.

The Cl 2p / Rh 3d intensity ratio for the $RhCl_3 \cdot xH_2O$ reference compound

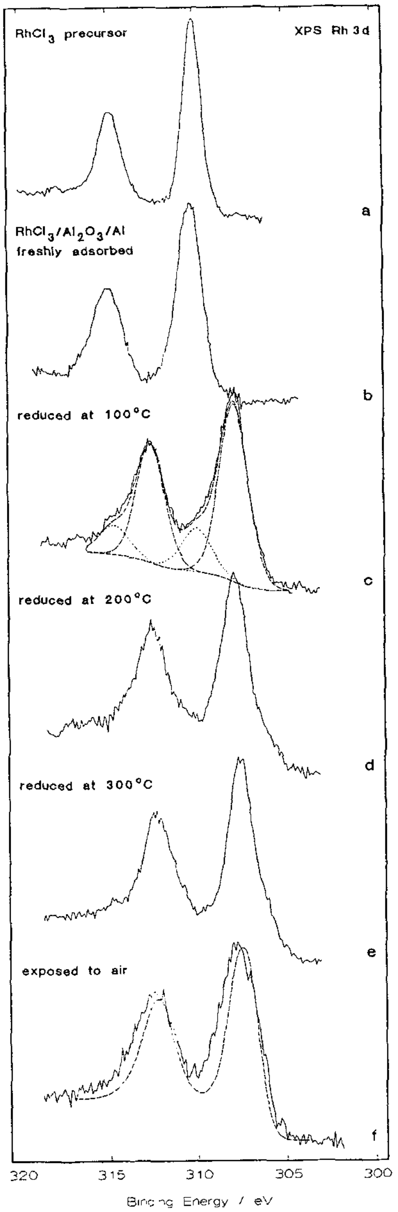

Fig. 4. Rh 3d XPS spectra of (a) the $RhCl_3 \cdot xH_2O$ catalyst precursor deposited on tantalum and of the $RhCl_3/Al_2O_3/Al$ model catalyst, (b) after adsorption and drying, after reduction at (c) 100°C, (d) 200°C, (e) 300°C and (f) after subsequent exposure to air at room temperature. The dashed line represents the Rh $3d_{5/2}$ spectrum of the reduced catalyst and is included to illustrate the effect of exposing the catalyst to air.

is 0.6 ± 0.1. Using Scofield cross sections [14], this corresponds to an atomic Cl/Rh ratio of approximately 3.5 ± 0.5, in reasonable agreement with the expected stoichiometry.

3.3. THE FRESHLY PREPARED CATALYST BEFORE REDUCTION

The standard procedure for making a $Rh/Al_2O_3/Al$ catalyst, as described in section 2, reproducibly yielded catalysts with a Rh loading between 0.6 and 1.3×10^{15} Rh atoms per cm^2, as determined with RBS.

Fig. 4b shows the Rh 3d XPS spectrum of the freshly prepared catalyst. Rhodium is present in a single state with a $3d_{5/2}$ binding energy of 310.2 eV, which is within experimental error equal to that of Rh in the $RhCl_3 \cdot xH_2O$ precursor. The linewidth has increased somewhat, from 1.3 eV in the spectrum of the precursor to 1.7 eV in that of the catalyst. We attribute this to a small charging effect in the latter, where the Rh species are adsorbed on an approximately 4 nm thick layer of aluminum oxide.

The Cl 2p spectrum of the catalyst (fig. 5b) differs from that of the precursor in that only one Cl 2p doublet is present. Its binding energy of 198.4 eV is characteristic of terminal Cl ions. The Cl 2p/Rh 3d intensity ratio is 0.3 ± 0.05,

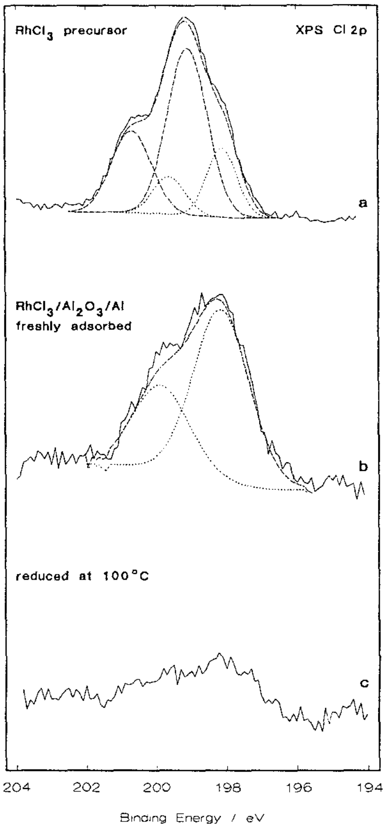

Fig. 5. Cl 2p XPS spectra of (a) the $RhCl_3 \cdot xH_2O$ catalyst precursor deposited on tantalum and of the $RhCl_3/Al_2O_3/Al$ model catalyst, (b) after adsorption and drying, and (c) after reduction at 100°C. Spectrum (a) has been fitted with contributions from bridged (dashed line) and terminal Cl species (dotted line), the catalysts contain only terminal Cl species.

a factor of two lower than in the spectrum of the $RhCl_3$ precursor. Thus the atomic Cl/Rh ratio corresponds to about 1.4, which is not meant to imply that all Cl ions are connected to Rh ions.

The O 1s/Al^{3+} 2p intensity ratio increased from 8 ± 1 for the untreated model support to 10 ± 1 in the XPS spectrum of the fresh catalyst. Also the ratio Al^{3+} 2p/Al^0 2p increased, from 2.8 ± 0.5 to 6.1 ± 0.5, indicating the growth of the oxidic film on the model support. Considering this growth and mean free path effects, we conclude that the additional oxygen can not only be due to the support, but may be explained by the presence of O atoms in the adsorbed rhodium complexes, as well as by the presence of hydroxyl groups or water adsorbed on the support.

The SIMS spectra of the freshly prepared, unreduced model catalyst are shown at the bottom of fig. 3. The positive SIMS spectrum between 100 and 150 amu is dominated by the Rh^+ peak at 103 amu, but clear signals of RhC^+, RhO^+, $RhOH^+$, RhO_2^+, and $RhAl^+$ are present as well. The $RhCl^+$ pair is partially masked by the Ba^+ peak, a contamination of the water that we used. The negative SIMS spectrum between 100 and 200 amu contains an intense pair of $RhCl^-$ peaks but the intensity of $RhCl_2^-$ peaks is almost zero, indicating that the Rh : Cl stoichiometry must be much lower than 1 : 3. In addition, significant contributions from RhO and RhOH combinations have appeared, suggesting that Cl ligands of Rh in the precursor have been replaced by O- or OH-containing ligands in the aqueous solution. Part of these clusters may also result from the contact of Rh with the oxidic support, like the $RhAl^+$ cluster in positive SIMS.

Finally, as described before, an essential step in the preparation of the model catalysts is that they are carefully rinsed with doubly distilled water in order to avoid the deposition of unadsorbed Rh species on the support. If this step is left out, one measures an XPS spectrum with two Rh 3d doublets, one characteristic of adsorbed Rh(III) species as in fig. 3b, and another characteristic of Rh^{3+} ions, but with a charge shift of about 4 eV. We attribute the latter to large particles formed from loosely deposited Rh complexes, which agglomerate upon drying at 110°C.

3.4. REDUCTION OF THE CATALYSTS

The model catalyst was reduced in 1 bar of flowing hydrogen at 100, 200, and 300°C. Figs. 4c–4e give the corresponding Rh 3d XPS spectra. Reduction of the catalyst at 200 and 300°C gives rise to Rh spectra which can be fitted with a single state, corresponding to a Rh $3d_{5/2}$ binding energy of 307.4 eV, which is in good agreement with values observed for reduced rhodium in alumina-supported catalysts [15], but 0.4 eV higher than the binding energy of bulk rhodium metal [7]. The spectrum of the catalyst after reduction at 100°C contains at least two Rh contributions, one of reduced rhodium at 307.6 eV and one characteristic of rhodium in the unreduced catalyst with a binding energy of 309.8 eV, which accounts for about 25% of the spectrum.

A Cl 2p signal could be detected in the spectrum of a catalyst after reduction at 100°C (fig. 5), but was absent in the spectra of catalysts reduced at a higher temperature. The binding energy of this Cl 2p is within experimental error equal to that obtained with the unreduced catalyst. The Cl 2p/Rh 3d intensity ratio for the catalyst reduced at 100°C is 0.13 ± 0.05, compared to 0.30 ± 0.05 before reduction.

Negative SIMS was used to investigate whether the chlorine ions detected in XPS were still in contact with rhodium. Static SIMS spectra of the reduced catalysts are given in fig. 6. The $RhCl^-$ signal at 138 and 140 amu is observed in the spectrum of the catalyst after reduction at 100°C, but has disappeared after reduction at 200°C, indicating that Rh–Cl species are absent. SIMS spectra in the range of 15–65 amu, however, show that Cl is still present on the system, the ClO^- peak (at 51 and 53 amu) may be taken as evidence that this chlorine is in contact with the alumina support. The Cl^- intensity has decreased with a factor of about 10 after reduction at 300°C, indicating that Cl is only present in trace amounts. Significant signals from RhO^- and RhO_2^- are observed even after reduction at 300°C. We suggest that these clusters originate from locations where the rhodium particles are in contact with the oxidic support, like the $RhAl^+$ clusters in positive SIMS. Note the presence of RhC^- and $RhCH_x^-$ peaks, which reflect the presence of adsorbed carbon or hydrocarbons in the spectrum of the unreduced catalyst. The $RhCH^-$ intensity decreases after reduction at 100°C and disappears after reduction at 300°C, although a small signal due to RhC^- remains.

3.5. OXIDATION OF REDUCED RHODIUM IN AIR

The effect of exposing the reduced $Rh/Al_2O_3/Al$ model catalyst to air is shown in fig. 4f: the Rh 3d XPS spectrum broadens significantly towards higher binding energy in comparison with the spectrum of the reduced catalyst. A fit based on two Rh contributions, one equal to the spectrum of reduced rhodium and one with unconstrained parameters, indicates that about 30–35% of the spectrum is due to a Rh 3d doublet with a binding energy of 308.7 eV, in good agreement with the binding energy of 308.4 eV reported for Rh_2O_3 [16] and with the value of 308.5 eV we measured from a rhodium oxide prepared by calcining $RhCl_3 \cdot xH_2O$ powder in air at 600°C for several hours.

3.6. PREPARATIONS AT DIFFERENT pH VALUES

The pH of the $RhCl_3$ solution from which rhodium species are applied onto the support is an important parameter. The results discussed so far concern the standard preparation at $pH = 4$. This value appears to be an optimum for

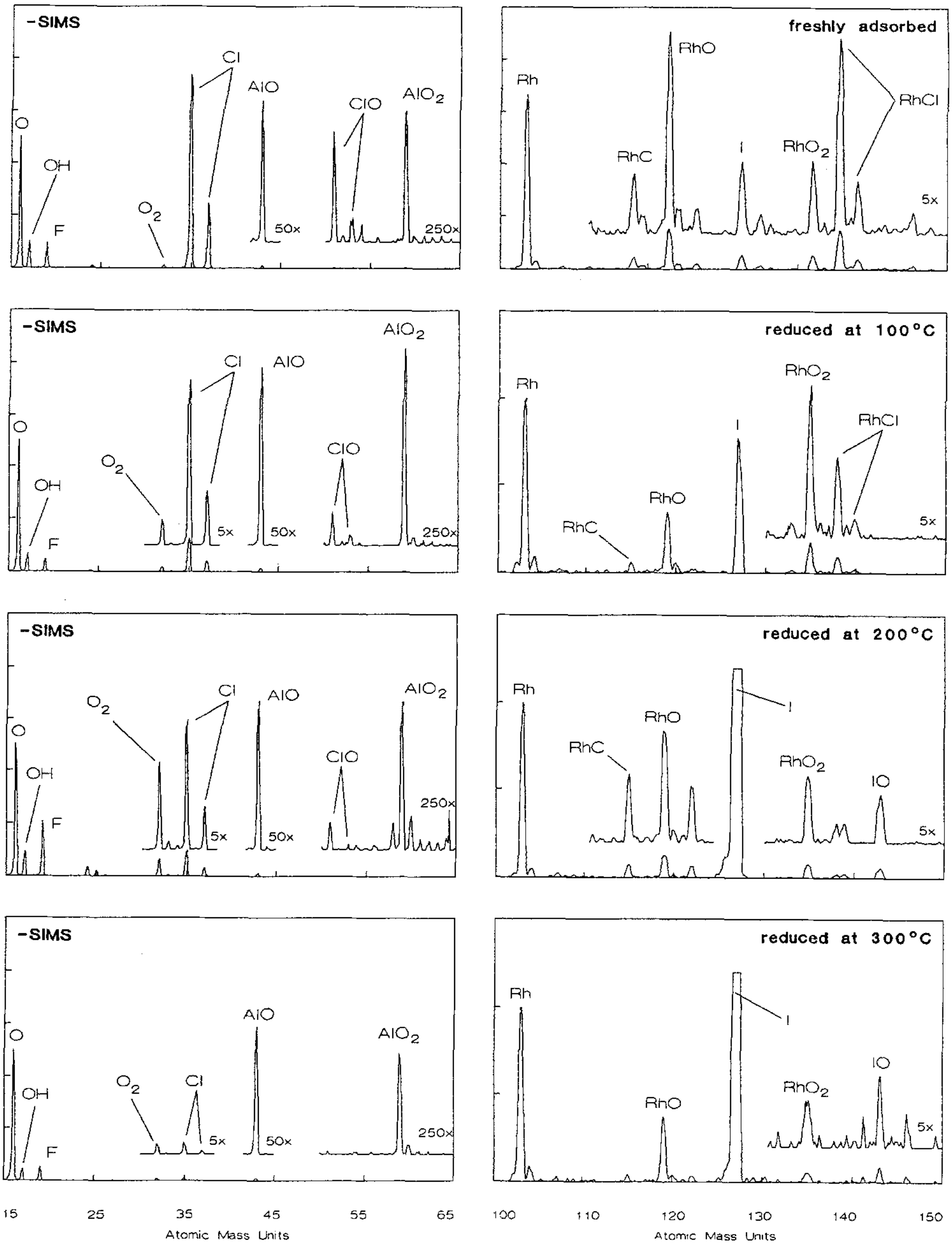

Fig. 6. Negative static SIMS spectra in the mass ranges of 15–65 (left) and 100–150 amu (right) of the $RhCl_3/Al_2O_3/Al$ model catalyst, freshly prepared (top) and after reduction at various temperatures. Note the disappearance of the $RhCl^-$ signal after reduction at 200°C, whereas significant signals from Cl^- and ClO^- are still observed.

preparing Rh/Al_2O_3 catalysts by electrostatic adsorption. A sample prepared by adsorption from a rhodium chloride solution of pH = 6, followed by rinsing with water, showed no detectable signals of Rh and Cl in XPS, indicating that no chemical bonding between Rh complexes and the support occurred. Adsorption from a solution with $pH = 3$, achieved by adding HCl, gave only weak intensities of Rh and Cl in the XPS spectrum, whereas hardly any Rh and Cl could be detected with XPS if the pH of the impregnating solution was lowered to 2 and 1. Interestingly, the Al^{3+}/Al^0 intensity ratio measured with XPS also decreased for supports exposed to solutions of low pH, indicating that alumina dissolves at low pH.

In contrast to the low surface concentrations of Rh detected by XPS in catalysts prepared at a pH of 3 and lower, RBS indicates that large amounts of rhodium are present, however, inside the model support at depths upto 1000 nm below the surface. We interpret this as follows. Aluminum oxide dissolves in solutions with a pH of 3 and lower and so does aluminum metal whenever it becomes exposed. Channels into the bulk of the substrate develop along grain boundaries, and are filled up by the Rh solution. When the sample is taken out of the impregnating solution, rinsed, and dried, Rh complexes may remain trapped inside the pores, which according to RBS extend to several hundreds of nanometers below the surface. This phenomenon is an artefact of working with a thin oxide layer on top of an aluminum bulk. The process, however, is initiated by the dissolution of aluminum oxide in acid solutions with a $pH \leqslant 3$ and therefore plays a role in the preparation of catalysts on alumina powder supports as well.

4. Discussion

The substitution of porous, non-conducting oxidic catalyst supports by a flat, conducting oxide film is a successful method to obtain better resolved XPS spectra and truly static SIMS spectra. Such model supports have already been used by other authors. Different preparation methods of these so-called model catalysts were applied, e.g. evaporation of the active phase [17–19] or decomposition of a gaseous precursor complex [20,21]. Although such methods may be well-defined, they do not mimic the preparation methods of technical catalysts very well. Making model systems via the wet-chemical adsorption method is more relevant with regard to catalyst preparation, and is expected to result in systems that are closer to technical rhodium catalysts.

The preparation of supported Rh catalysts from aqueous solutions of $RhCl_3 \cdot xH_2O$ has been described by several authors [22,23]. The presence of $[RhCl_n(OH)_m(H_2O)_{6-n-m}]^{3-n-m}$ complexes in such solutions appears well established [24–26]. Our results form strong evidence that after adsorption and drying the majority of Rh species on the support contains one Cl ligand. The following observations support this conclusion:

First, XPS spectra of the freshly prepared catalyst indicate that the atomic ratio Cl/Rh has decreased from 3.5 ± 0.5 in the $RhCl_3 \cdot xH_2O$ precursor to

1.4 ± 0.2 in the catalyst. This value includes both Cl bound to Rh and Cl attached to the alumina support. Second, Rh is present in a single state with a binding energy of 310.2 eV, characteristic of Rh^{3+} ions. Third, the SIMS spectrum of the fresh catalyst shows $RhCl^-$ as the only secondary cluster containing both Rh and Cl, whereas $RhCl_2^-$ is not observed. Because the SIMS spectrum of the $RhCl_3 \cdot xH_2O$ precursor confirms that $RhCl_2^-$ is a very stable and easily detectable secondary ion, we consider the absence of this species in the spectra of the model catalyst as a strong indication that Rh complexes with two Cl ligands are not present. This strongly suggests that the majority of Rh complexes on the support contains at most one Cl ligand.

According to literature [22–24,27], two routes to a Rh complex of the expected type with a single Cl ligand can be envisaged. The first is the direct adsorption of a $[RhCl(OH)_3(H_2O)_2]^-$ anion complex on positive sites of the support:

$$\text{Al-OH}_2^+ + [\text{RhCl(OH)}_3(\text{H}_2\text{O})_2]^- \rightarrow \text{Al-OH}_2^+\text{---}[\text{RhCl(OH)}_3(\text{H}_2\text{O})_2]^- . \quad (1)$$

In view of the pH value of 4, the concentration of Rh-complexes with three OH ligands will be low, making the second possibility, proposed by Fenoglio et al. for TiO_2 supported Rh [23], more probable: An anion complex with several Cl ligands adsorbs in a similar way as in (1), followed by a ligand exchange reaction, in which the more weakly bound Cl ligand is exchanged by a surface OH group:

$$\begin{aligned} &\text{Al-OH}_2^+\text{---}[\text{RhCl}_n(\text{OH})_{4-n}(\text{H}_2\text{O})_2]^- + \text{Al-OH} \\ &\quad \rightarrow \text{Al-OH}_2^+\text{---RhCl}_{n-1}(\text{OH})_{4-n}(\text{H}_2\text{O})_2\text{---}^-\text{O-Al} + \text{H}^+ + \text{Cl}^- . \qquad (2) \end{aligned}$$

As OH^- is more strongly bound to Rh than Cl^-, another likely reaction, which may occur simultaneously with (2), is the exchange of Cl for an OH^- group of the surface:

$$\begin{aligned} &\text{Al-OH}_2^+\text{---}[\text{RhCl}_n(\text{OH})_{4-n}(\text{H}_2\text{O})_2]^- + \text{Al-OH} \\ &\quad \rightarrow \text{Al-OH}_2^+\text{---}[\text{RhCl}_{n-1}(\text{OH})_{5-n}(\text{H}_2\text{O})_2]^- + \text{Al}^+ + \text{Cl}^- . \qquad (3) \end{aligned}$$

These Cl displacement reactions may occur several times, leaving a Rh-complex with only one Cl ligand. If the mechanism represented by (2) and (3) is correct, the question arises why the adsorbed complex retains one Cl^- ligand at all. We wonder if this may be taken as evidence that the remaining Cl^- is at the position on Rh^{3+} pointing away from the support surface, where it cannot participate in the surface-mediated reactions (2) and (3). We stress that the purpose of this mechanistic discussion is only to indicate how the formation of an adsorbed Rh-complex with a single Cl^- ligand is conceivable in terms of well documented reactions. The conclusive point is that the species appears to be present, not how it is formed.

Another phenomenon during the adsorption process is the so-called acid-attack [23,24]. At low pH, alumina dissolves in the solution. The dissolved species can readsorb on the support, possibly after reaction with Rh complexes [28]. Already adsorbed Rh complexes may be covered by redeposited alumina. This process occurs at pH values well below 4, and can be neglected under the standard conditions (pH = 4) that we used.

As determined with RBS, the adsorption mechanism leads to a projected Rh density of about 10^{15} atoms/cm^2. This would correspond to a 30 wt% Rh powder catalyst supported on γ-alumina with a specific surface of 200 m^2/g, which is a rather high loading. However, in this calculation we assumed an atomically flat surface of the model support. Atomic force microscopy topography measurements of the model support show roughness, so that in fact the Rh surface concentration is lower.

Activation of the catalyst by reduction in 1 bar of H_2 proceeds via two steps. First, the Rh reduces to its metallic state. Rh–Cl bonds are broken, as can be seen in the SIMS spectra, and the Rh $3d_{5/2}$ binding energy decreases from 310.2 eV in the fresh catalyst to 307.4 eV after reduction. This first step is only partially complete after reduction at 100°C, and complete after the same treatment at 200°C. The second step involves the removal of residual chlorine from the support, reduction at 300°C is sufficient to decrease the Cl^- and ClO^- intensities to typical background levels. Porous alumina-supported catalysts retain considerably more chlorine [4,5], also after reduction at 300°C. We think that diffusion limitations and readsorption, which are present in porous but absent in flat supports, may explain the difference in behavior with respect to Cl retention.

For structure sensitive reactions, such as between CO and H_2, and CO and NO, the Rh metal particle size strongly affects the catalytic activity and selectivity. An indication of the particle size is given by the Rh $3d_{5/2}$ binding energy. As described by Mason [29], the binding energy of small metallic particles is somewhat higher than their bulk value. This shift is nowadays mainly attributed to an initial state effect: the small particles have not yet attained the normal bulk band structure. Increasing shifts of the Rh $3d_{5/2}$ binding energy towards higher values with decreasing Rh particle size were also reported by Huizinga et al. [15], although they ascribed these shifts to a final state (core–hole screening) effect. The Rh $3d_{5/2}$ binding energy values reported in this work, 307.4 eV after reduction at 200 or 300°C, are 0.4 eV higher than the bulk value of 307.0 eV, which indicates that the Rh particle diameter is on the order of 1–2 nm. This value is consistent with earlier reported angle-dependent XPS data [2], which yielded an effective Rh particle size of 1.5 nm and a coverage of 10% of the support. Moreover, the sensitivity of the Rh particles towards air, as shown in fig. 3f, is another indication that the particles have a diameter on the order of a few nm at most.

5. Conclusions

Rhodium model catalysts have been prepared by adsorbing Rh-complexes from an aqueous solution of $RhCl_3 \cdot xH_2O$ on a model support, consisting of an approximately 4 nm thick Al_2O_3 film on an Al foil.

The freshly prepared, dried catalyst contains on the order of 10^{15} Rh atoms per cm^2 of the support, which may be lower if surface roughness is accounted for, and has a Cl content corresponding to 1.4 Cl per Rh, which includes Cl adsorbed on the support. SIMS spectra strongly suggest that the Cl-containing Rh-complexes have only one Cl^- ligand. The use of impregnating solutions with $pH \leqslant 3$ leads to dissolution of the Al_2O_3 support and eventually of the Al bulk as well.

Activation of the $Rh/Al_2O_3/Al$ model catalyst in 1 bar of H_2 entails two processes: the actual reduction of Rh^{3+} to Rh^0 which is complete at 200°C, and the removal of Cl^- from the support, which is complete at 300°C. Rh–Cl contact, sensitively detected with static SIMS, exists in the partially reduced catalyst treated in H_2 at 100°C, but is absent after reduction at 200°C. The Rh $3d_{5/2}$ binding energy of 307.4 eV (0.4 eV higher than for bulk Rh) and the oxidation of about 30% of the Rh upon exposing the catalyst to air indicate that the size of the reduced Rh particles is on the order of 1–2 nm.

The use of thin oxide films on a flat, conducting substrate, instead of porous, insulating oxides, as model supports minimizes charging phenomena and enables one to apply surface spectroscopies to their full potential. Monochromatic XPS and static SIMS appear suited to study in molecular detail the preparation of catalysts by the common wet chemical methods on these model supports.

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