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Influence of pH on the Preparation of Monometallic Rhodium and Platinum, and Bimetallic Rhodium–Platinum Catalysts supported on γ-Alumina

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ABSTRACT

[195]PtNMR and Raman experiments indicated that H_2PtCl_6 adsorbed monomolecularly on the surface of alumina up to a loading of 1μmol m^{-2} during pore volume impregnation. Above this limit crystalline H_2PtCl_6 was formed during the subsequent drying procedure. Adsorption experiments showed that $RhCl_3$ exhibited the same behaviour, with an even larger monomolecular coverage. The coverage of both metal complexes was dependent on the pH during adsorption and decreased with decreasing pH, due to a shift in the bonding equilibrium between the metal complexes in solution and the complexes adsorbed on the support surface. Because of the acidic properties of $RhCl_3$ and H_2PtCl_6, the amounts of rhodium and platinum adsorbed during co-adsorption were smaller than during adsorption of the separate metal complexes. The reduction of $RhCl_3 + H_2PtCl_6$ supported on Al_2O_3 was governed by mobile rhodium atoms and small bimetallic clusters. Large metal salt crystals smothered the reduction process.

INTRODUCTION

The introduction of a metal precursor onto the internal surface area of the support, the very first step in the preparation of a supported metal catalyst, is of vital importance. This first step dictates the lower limit of the size of the eventual metal particles and, in addition, it may be the prelude for the formation of bimetallic particles. Here we describe a study of the factors which are of importance in the preparation of $RhCl_3$ and H_2PtCl_6 catalyst precursors supported on γ-Al_2O_3 by the pore volume impregnation method and the adsorption method. For the H_2PtCl_6 samples, we used [195]Pt NMR and laser Raman spectroscopy to follow the growth of H_2PtCl_6 crystallites during the pore volume impregnation method. From these experiments it became evident that

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crystals of H_2PtCl_6 started to form above a loading of 1 μmol H_2PtCl_6 per m^2 of Al_2O_3 surface area. This confirmed the suggestion in the literature that H_2PtCl_6 can adsorb as single entities on the Al_2O_3 support at low loadings [1, 2]. Furthermore, we studied the adsorption of H_2PtCl_6 and $RhCl_3$ on γ-Al_2O_3 and the temperature programmed reduction (TPR) profiles of $RhCl_3$, H_2PtCl_6 and ($RhCl_3 + H_2PtCl_6$) supported on Al_2O_3 in order to follow the formation of bimetallic particles. It is shown that the pH had a large influence on the loading of monomolecularly adsorbed metal complexes which can be attained during adsorption. Consequently, since many transition metal salts are acidic in nature, during co-adsorption there is a strong mutual influence of the different metal salts on the individual amounts adsorbed.

EXPERIMENTAL

NMR and laser Raman experiments

In all experiments we used γ-Al_2O_3 from Ketjen (000 − 1.5E) with a particle diameter of about 0.2 mm, a surface area of 180 m^2 g^{-1}, and a pore volume of 0.65 ml g^{-1}. H_2PtCl_6/Al_2O_3 samples, prepared according to the pore volume impregnation method, were dried at room temperature for 24 h and at 393 K for another 24 h. The NMR experiments on these samples were carried out on a Bruker CXP300 spectrometer under Magic Angle Spinning conditions in a Beams-Andrew rotor. For each spectrum, 4096 Bloch decays were accumulated at room temperature and Fourier transformed to give the resulting spectrum.

For the Raman experiments, the dried samples were pressed into circular tablets which were mounted in a holder and rotated at an angle of 45° with respect to the laser beam, in order to avoid damage to the sample by heating and possibly burning. A dye laser ($\lambda = 514$ nm and $p = 90$ mW) was used and the spectra were recorded at room temperature.

Adsorption experiments

For the adsorption experiments, two solutions containing $RhCl_3$ (15.5 and 31.2 mM) and two solutions containing H_2PtCl_6 (9.76 and 17.5 mM) were prepared. Various amounts of Al_2O_3, ranging from 0.1 to 1.4 g, were added to a fixed amount of these solutions (20 ml for the solutions of lower concentration and 10 ml for the solutions of higher concentration). After allowing the metal salts to adsorb on the support for four days, the equilibrium concentrations of $RhCl_3$ and H_2PtCl_6 in the solutions were measured. From these concentrations, the amount of metal salt adsorbed on the support was calculated. The concentrations of $RhCl_3$ and H_2PtCl_6 were measured according to the following procedure. A volume of 5 ml of a concentrated HCl solution and 5 ml of a 1 M $SnCl_2$ solution were added to 5 ml of the metal salt solution. This mixture

was heated on a water bath to the boiling point. Highly coloured $[Rh_2Cl_4(SnCl_3)_4]^{4-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$ complexes were formed, and their extinction coefficients were measured at $\lambda = 471$ nm for the rhodium complex and at $\lambda = 401$ nm for the platinum complex. For the rhodium complex, the extinction coefficient is linearly dependent on the concentration only between 4 and 20 mM and for the platinum complex between 3 and 12 mM. Therefore, in some cases the 5 ml of salt solution mentioned above had to be diluted with distilled water in order to ensure that the concentration of the final solution was in the desired range. For both complexes, the extinction coefficient was calibrated.

In order to establish the influence of acidity on the adsorption process, the adsorption procedure was also carried out using the lower concentrated solutions, while continuously adjusting the pH value of the solution at 1.9 ± 0.2 with 0.1 M HCl. To study the effect of the initial pH, the pH of the solutions with low concentrations of $RhCl_3$ and H_2PtCl_6 was adjusted to values between 0.5 and 5.0 directly after preparation of the adsorption mixture, and after a week the final pH value and the amount of adsorbed metal were measured.

Finally, in order to establish whether there was any competition between $RhCl_3$ and H_2PtCl_6 during the adsorption process, 0.6 g Al_2O_3 was added to a solution of 10 ml containing 31.2 mM $RhCl_3$ and 17.5 mM H_2PtCl_6. After a week, the rhodium and platinum content of the solution and the support were measured using the procedure described above.

TPR of Rh, Pt and Rh–Pt/Al$_2$O$_3$

Six bimetallic Rh–Pt/γ-Al$_2$O$_3$ precursor catalysts were prepared using the pore volume impregnation method. For all samples the $RhCl_3$ and H_2PtCl_6 loadings were 0.100 ± 0.005 mmol g^{-1} Al$_2$O$_3$. Four of these samples were prepared using equimolar aqueous solutions of $RhCl_3 \cdot 3H_2O$ and a platinum chloride. The acidity of the solution and the chloride content were increased by using respectively $PtCl_4 \cdot 5H_2O$ and $H_2PtCl_6 \cdot 3H_2O$, dissolved in distilled water, and H_2PtCl_6 dissolved in 0.5 and 1.0 M HCl. 0.5 M HCl was equivalent to 3 HCl molecules per rhodium or platinum atom, and 1.0 M HCl to 6 HCl molecules per rhodium or platinum atom. These samples are denoted as RPA1, RPA2, RPA3 and RPA4, respectively. The other two samples were prepared using a mixture of equimolar amounts of $RhCl_3 \cdot 3H_2O$ and $H_2PtCl_6 \cdot 3H_2O$ dissolved in either methanol (sample RPA5) or ethanol (sample RPA6). For comparison, TPR profiles of the corresponding monometallic precursor catalysts, prepared from aqueous as well as methanolic solutions, were also measured.

After impregnating and careful drying, TPR experiments were carried out using a heating rate of 5 K min^{-1}. Drying of the samples impregnated with methanol and ethanol gave problems because of strong adsorption and slow desorption. Drying at elevated temperatures (up to 500 K for 10 h, even in

vacuum) was insufficient to remove the alcohol completely. The only effective procedure was to dry the sample at 393 K for a few hours and then for at least two weeks at room temperature.

RESULTS AND DISCUSSION

NMR and laser Raman experiments

In Fig. 1a the NMR spectra of four supported H_2PtCl_6 samples are shown. The chemical shift indicated that the peak observed originated from Pt in $[PtCl_6]^{2-}$ octahedra [3,4]. Apart from this, no other peaks were observed. The (arbitrary) intensities of these peaks (peak height times width at half height) are plotted in Fig. 1b as a function of H_2PtCl_6 loading. A straight line can be constructed through the points, which intersects the abscissa at a loading of 0.16 ± 0.01 mmol H_2PtCl_6 per g Al_2O_3. Obviously, H_2PtCl_6 crystals start to form only above this limit. Below this limit, the platinum salt adsorbs strongly on the support, as will be demonstrated by the adsorption experiments. We did not observe any peaks in the spectrum that could possibly be attributed to such adsorbed complexes. This might be due to the fact that small deviations in the chemical environment of platinum result in very large chemical shifts. Adsorbed platinum chloride complexes usually have exchanged one or more chloride ions for an oxygen ion or a hydroxyl group of the support [5]. The variation in the chemical environment of these strongly adsorbed complexes may be relatively large, giving rise to a large spread in chemical shifts and therefore to low, broad peaks, which are difficult to detect.

In Fig. 2a, the Raman spectra of a H_2PtCl_6 solution and of three supported H_2PtCl_6 samples are shown. In these spectra, the three Raman active vibrations of the $(PtCl_6)^{2-}$ units are clearly visible. The intensities of the corre-

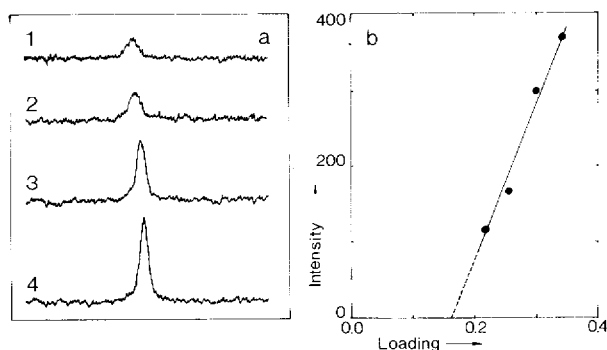Fig. 1. (a) NMR spectra of H_2PtCl_6/Al_2O_3 with loadings of (1) 0.215 mmol g^{-1}; (2) 0.256 mmol g^{-1}; (3) 0.297 mmol g$^-$; (4) 0.343 mmol g^{-1}. (b) NMR intensities as a function of H_2PtCl_6 loading.
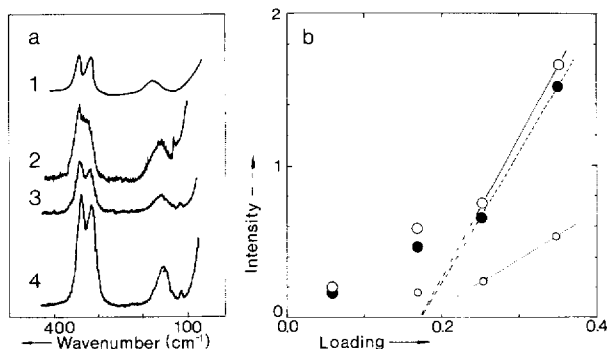
Fig. 2. (a) Raman spectra of H_2PtCl_6 and H_2PtCl_6/Al_2O_3 (spectrum 1 is on a different scale than spectra 2–4). (1) H_2PtCl_6 in aqueous solution; (2) 0.169 mmol g^{-1}; (3) 0.256 mmol g^{-1}; (4) 0.343 mmol g^{-1}. (b) Raman intensities as a function of H_2PtCl_6 loading. 340 cm^{-1}, solid line; 320 cm^{-1}, dashed line; 150 cm^{-1}, dotted line.

sponding bands (measured as peak heights) are presented in Fig. 2b. The general behaviour of the peak height as a function of loading was the same for all three bands. Above a loading of about 0.18 ± 0.02 mmolH_2PtCl_6 $g^{-1}Al_2O_3$, the peak height increased more with increasing H_2PtCl_6 loading than below that loading. This can be explained by assuming that below the limit of 0.18 mmol H_2PtCl_5 g^{-1} Al_2O_3, H_2PtCl_6 adsorbed as single entities on the support and that these adsorbed platinum complexes were not perfect $(PtCl_6)^{2-}$ octahedra, as could be concluded from a slight shift in the frequencies in the spectra. A spread in the variation of the chemical environment of the adsorbed complexes will lead to a broadening of the bands and therefore to lower peak heights. Above the limit of 0.18 mmol H_2PtCl_6 g^{-1} Al_2O_3, the frequencies of the three bands corresponded precisely with the frequencies of pure H_2PtCl_6, which indicated that H_2PtCl_6 crystals had started to from.

Both the NMR and Raman experiments indicated that up to loadings of 0.16–0.18 mmol H_2PtCl_6 $g^{-1}Al_2O_3$ platinum complexes were monomolecularly adsorbed on this support. These complexes differed from perfect $(PtCl_6)^{2-}$ octahedra and had probably exchanged one or more Cl^- ligands for oxygen ions or hydroxyl groups from the support. Above this limit, H_2PtCl_6 crystals had started to form during the drying stage of the catalyst preparation. This limit is far above the amounts of H_2PtCl_6 normally used to prepare Pt/Al_2O_3 catalysts, since it would correspond to a metal loading of 3.4 wt.-%. It should be noted, however, that these results were obtained for a γ-Al_2O_3 with a surface area of 180 m^2 g^{-1}. Therefore a better way of expressing the limit at which H_2PtCl_6 crystals are formed, is 1 μmol m^{-2}. In that way, similar values may be expected for other aluminas. Although the precursor platinum complexes are most probably monomolecularly dispersed, after reduction these catalysts are never atomically dispersed. Typical particle sizes for the Pt/Al_2O_3 catalyst

are about 8 Å and these particles contain about 10 platinum atoms [6]. Thus, the formation of these larger metal particles in the eventual catalyst must have taken place during the reduction procedure.

Adsorption experiments

In order to obtain information on the state of the complexes adsorbed on the support, we performed adsorption experiments to establish adsorption isotherms for $RhCl_3$ and H_2PtCl_6 on Al_2O_3. The results are summarized in Table 1. The maximum amount of $RhCl_3$ that was adsorbed was 0.326 ± 0.009 mmol g^{-1} for the more concentrated and 0.47 ± 0.1 mmol g^{-1} for the less concentrated $RhCl_3$ solution. For H_2PtCl_6, these amounts were 0.226 ± 0.003 and 0.24 ± 0.07 mmol g^{-1}, respectively. Because of the much lower metal concentration in the equilibrium solutions when larger amounts of Al_2O_3 were used, the uncertainty in all other metal salt loadings was much smaller ($0.002-0.004$ mmol g^{-1}). During the experiments with the solutions of low concentration the pH value of the solution in equilibrium was measured. At the maximum attainable coverage, the pH value of the solution was 3.0 for the $RhCl_3$ solution and 2.6 for the H_2PtCl_6 solution. At low metal salt coverages, the pH value was

TABLE 1

Adsorption isotherms for $RhCl_3$ and H_2PtCl_6 on Al_2O_3

Al_2O_3 (g)	[M]*	[M/S]**	pH	Al_2O_3 (g)	[M]*	[M/S]**	pH
$RhCl_3$ (10 ml, 31.2 mM)				*H_2PtCl_6 (10 ml, 17.5 mM)*			
0	31.2	0	2.0	0	17.5	0	1.5
0.6196	11.0	0.326	3.3	0.6527	2.77	0.226	2.4
1.0394	0.117	0.299		1.1057	0.038	0.158	
1.1333	0.071	0.274		1.2092	0.024	0.145	
1.2478	0.022	0.250		1.3352	0.059	0.131	
$RhCl_3$ (20 ml, 15.5 mM)				*H_2PtCl_6 (20 ml, 9.76 mM)*			
0	15.5	0	2.2	0	9.76	0	1.8
0.1031	13.1	0.47	3.0	0.1023	8.5	0.24	2.6
0.5868	2.8	0.433	3.2	0.5927	2.7	0.238	2.7
0.9362	0.30	0.324	3.4	0.9106	0.66	0.200	2.9
1.0052	0.22	0.302	3.5	1.0097	0.37	0.186	3.2
1.1067	0.144	0.276	3.6	1.0993	0.24	0.173	3.4
1.1522	0.089	0.266	3.6	1.1429	0.173	0.168	3.5
1.1905	0.084	0.258	3.6	1.2018	0.128	0.161	3.6
1.2605	0.047	0.244	3.7	1.2450	0.103	0.155	3.7
1.3917	0.018	0.222	3.7	1.2939	0.072	0.150	3.7

* [M] is the concentration (mM) of the metal salt in the solution above Al_2O_3 in equilibrium.
** [M/S] is the metal-salt loading (mmol g^{-1}) on the Al_2O_3 support.

about 3.6. Al_2O_3 served as a buffer agent and stabilized the pH value to 3.6 ± 0.1 over a wide concentration range.

Adsorption experiments in which the pH was kept constant at a value between 1.7 and 2.0 showed that at this low pH value the maximum attainable coverage was 0.056 mmol g^{-1} for $RhCl_3$ and 0.036 for H_2PtCl_6, and that it was only slightly dependent on the amount of Al_2O_3 added to 20 ml of 15.5 mM $RhCl_3$ or 9.76 mM H_2PtCl_6. This coverage is almost an order of magnitude lower than the maximum attainable coverages presented in Table 1.

The results of the adsorption experiments with different starting acidities are summarized in Table 2. From these results it is clear that acidifying the solution had a major impact on the adsorption capacity of the Al_2O_3. Note, that in the case where the starting acidity was lower than about 1.5, the Al_2O_3 did not manage to stabilize the pH value to 3.6 ± 0.1. Small amounts of Al_2O_3 were used in order to ensure that complete coverage would be obtained in all cases. Therefore, the loadings in Table 2 reflect the maximum adsorption capacity as a function of equilibrium pH value. The obvious conclusion is, that the higher the starting pH value, the more $RhCl_3$ or H_2PtCl_6 can be adsorbed on the Al_2O_3. At this point, it is easy to understand why a lower amount of metal salt was adsorbed when a more concentrated solution of these salts was brought into contact with Al_2O_3 [cf. Table 1]. The more concentrated solutions had a lower pH value and therefore less metal salt was adsorbed from these solutions. Note in Table 2 that no adsorption of H_2PtCl_6 took place at low pH, but that the pH of the solution increased. This must be due to reaction of HCl with the Al_2O_3 surface.

A similar pH-dependence for the adsorption of H_2PtCl_6 on γ-Al_2O_3 was reported by Heise and Schwarz [7]. They found a maximum in the adsorption capacity at pH 3.5–4.0. In that study, the penetration depth of the platinum complexes in γ-A_2O_3 pellets mounted above the solution and in contact with

TABLE 2

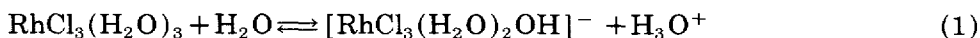Adsorption of $RhCl_3$ and H_2PtCl_6 on Al_2O_3 as a function of acidity

RhCl₃ (20 ml, 15.5 mM)					H₂PtCl₆ (20 ml, 9.76 mM)				
Al₂O₃ (g)	pH-values		[M]*	[M/S]**	Al₂O₃	pH-values		[M]*	[M/S]**
	Start	End				Start	End		
0.098	0.5	0.7	15.3	0.07	0.093	0.4	0.7	9.8	0.00
0.112	1.4	1.5	13.8	0.31	0.105	1.7	3.5	9.2	0.23
0.113	2.5	3.4	12.8	0.50	0.114	2.8	3.4	8.6	0.32
0.111	3.5	3.5	12.1	0.61	0.113	4.2	3.5	8.2	0.38
0.118	4.5	3.8	10.3	0.83	0.127	5.2	3.9	7.5	0.45

*[M] is the concentration (mM) of the metal salt in the solution above Al_2O_3 in equilibrium
**[M/S] is the metal-salt loading (mmol g^{-1}) on the Al_2O_3 support

that solution was measured. The penetration depth they reported (0.2–0.5 mm) was larger than the radius of the Al_2O_3 particles we used (0.1 mm). Thus, there is no reason to assume any depletion of the solvent in the pores during our experiments.

To explain the results of the adsorption experiments we must focus on the reactions which may take place in solution and at the Al_2O_3 surface. The following reactions are of importance for $RhCl_3$:

$$RhCl_3(H_2O)_3 + H_2O \rightleftharpoons [RhCl_3(H_2O)_2OH]^- + H_3O^+ \tag{1}$$

$$-OH + H_3O^+ \rightleftharpoons -OH_2{}^+ + H_2O \tag{2}$$

in which –OH represents a hydroxyl group on the Al_2O_3 surface. Heise and Schwarz [7] found that the point of zero charge of Al_2O_3 was at pH=8, while our own adsorption measurements showed that Al_2O_3 served as a buffer at pH=3.6, which indicates that the amounts of unprotonated and protonated hydroxyl groups were equal at that value. In acidic solutions the surface of Al_2O_3 will therefore consist of hydroxyl anions which are partially protonated. Thus, in the acidic solutions of $RhCl_3$ ($pK_a=2.5$) and H_2PtCl_6 ($pK=1.4$) adsorption of the complexes to the surface of the support may take place due to the interaction between the negatively charged complexes and the positively charged surface. However, the amount of adsorbed $RhCl_3$ was found to decrease drastically at lower pH values. On the one hand this may be due to a reversal of the equilibrium between $[RhCl_3(H_2O)_2OH]^-$ and $RhCl_3(H_2O)_3$ (cf. eqn. 1), and on the other hand it may due to the formation of H_3O^+ ions upon complexation of the rhodium complexes by hydroxyl ligands of the support:
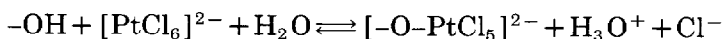

$$\tag{3}$$
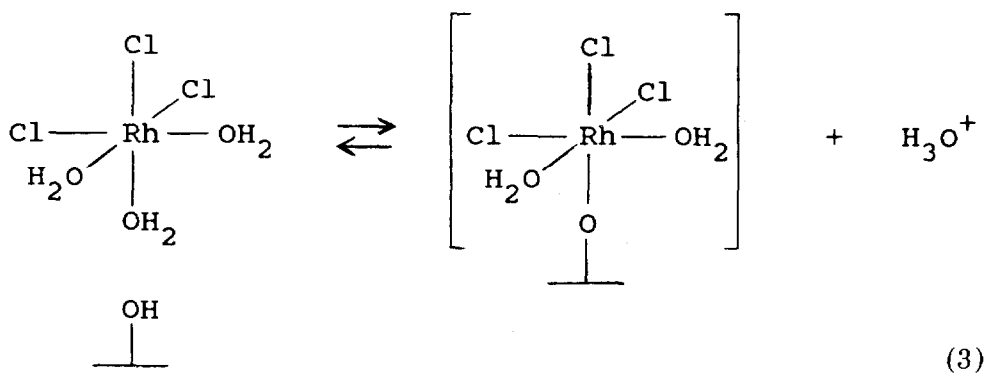
In reality, both Rh complexes (cf. eqn. 1) may react with the surface:

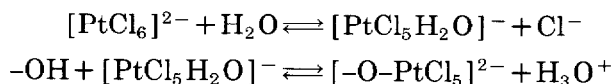$$RhCl_3(H_2O)_3 \quad + \quad H_2O \quad \rightleftharpoons \quad [RhCl_3(H_2O)_2OH]^- \quad + \quad H_3O^+$$
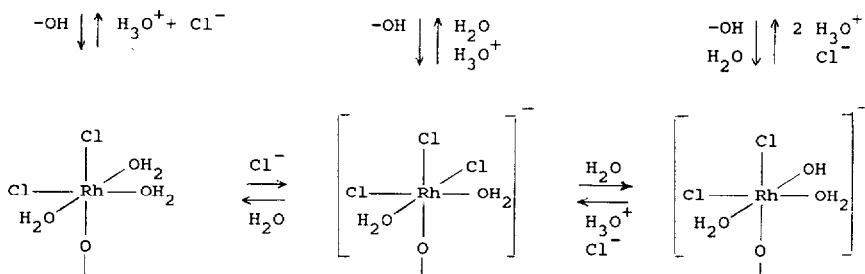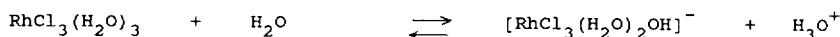
At low pH the $RhCl_3(H_2O)_3$ complex in solution is the most stable rhodium complex. Under these conditions adsorption will be low. On the other hand, at higher pH (but still in acidic solution) the adsorbed $-O-RhCl_2(H_2O)_3$ complex will be the most stable species. Hence, under these conditions adsorption of rhodium on the support will be high. In basic solution there will be no adsorption, since the $[RhCl_3(H_2O)OH]^-$ complex will be repelled by the anionic $-O^-$ surface.

From the equations given above it is clear that not only the pH (H_3O^+ concentration) influences the adsorption of the metal complex, but also the Cl^- concentration. Thus at high Cl^- concentration the $RhCl_3(H_2O)_3$ complex in solution will be stable, while at low Cl^- concentration the adsorbed complex will be stable.

Similar reactions may take place for platinum, e.g.

$$-OH + [PtCl_6]^{2-} + H_2O \rightleftharpoons [-O-PtCl_5]^{2-} + H_3O^+ + Cl^-$$

or

$$[PtCl_6]^{2-} + H_2O \rightleftharpoons [PtCl_5H_2O]^- + Cl^-$$
$$-OH + [PtCl_5H_2O]^- \rightleftharpoons [-O-PtCl_5]^{2-} + H_3O^+$$

Evidence for the exchange of Cl^- in the $[PtCl_6]^{2-}$ complex in solution by OH^- or H_2O was reported by Cox et al. [8], Van den Berg and Rijnten [9] and Botman [10].

The adsorption model proposed by Le Page [11] and Castro et al. [12], in which the $[PtCl_6]^{2-}$ complex reacts with two neighbouring surface hydroxyl groups, seems less likely:

$$2-OH + [PtCl_6]^{2-} + 2H_2O \rightleftharpoons [(-O)_2PtCl_4]^2 + 2H_3O^+ + 2Cl^-$$
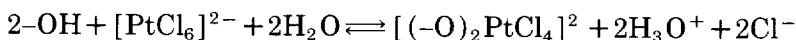
For, in this model one needs a high concentration of neighbouring $-OH$ groups,

which is unlikely at a pH around 3.6, where the Al_2O_3 surface is about half protonated.

A different model to explain the adsorption of $[PtCl_6]^{2-}$ on γ-Al_2O_3 was proposed by Heise and Schwarz [13]. They showed that the thickness of the electrical double layer on the Al_2O_3 surface could be correlated to the adsorption capacity. When the thickness of the electrical double layer decreased because of an increase in the concentration or valence of the electrolytes present, the amount of adsorbed $[PtCl_6]^{2-}$ decreased also. This explanation by Heise and Schwarz is based on a macroscopic model, while we focussed on a microscopic model. Their explanation did not take real bonding on a molecular scale into account, while our explanation with equilibria between complexes in solution and bonded to the surface does not account for long range forces in the electrical double layer. In a sense the two models are complementary. But, whereas the colloid chemistry model predicts that the metal complexes can be washed away from the support, the bonding model correctly predicts that this cannot be done simply.

The co-adsorption experiment, in which 0.6 g Al_2O_3 was added to a solution of 10 ml containing 31.2 mM $RhCl_3$ and 17.5 mM H_2PtCl_6 and having a pH value of 1.3, showed that 0.21 mmol $RhCl_3$ and 0.14 mmol H_2PtCl_6 could be simultaneously adsorbed per gram Al_2O_3. The amount of Al_2O_3 used ensured that these values were close to the maximum attainable coverages. After equilibrium was established the pH of the co-adsorption solution was equal to 2.2, lower than the lowest value measured for a monometallic solution in the presence of Al_2O_3 (cf. Table 1). Because of the lower pH during co-adsorption, the adsorption capacities for both metal complexes were lower than during adsorption of the separate complexes. In general, one may conclude that during co-adsorption of metal salts the pH will be different from that during adsorption of the separate salts and that this will lead to differences in the amounts of metal salts adsorbed. Most metal salts have pK_a values below 7 and co-adsorption of such salts on Al_2O_3 will lead to lower amounts of adsorbed salts than in the adsorption of the separate salts.

TPR of Rh, Pt and Rh–Pt/Al₂O₃

The TPR profiles of the samples RPA1 to RPA6 and the TPR profiles of $RhCl_3/Al_2O_3$, $PtCl_4/Al_2O_3$ and H_2PtCl_6/Al_2O_3 are presented in Fig. 3. Note that the metal loading was 0.10 mmol g^{-1} in al cases, which is lower than the limit (0.16–0.18 mmol g^{-1}) above which crystalline H_2PtCl_6 is present according to the NMR and Raman experiments. Although this value was obtained for H_2PtCl_6, we observed that the adsorption capacity for $RhCl_3$ was always higher than for H_2PtCl_6 and therefore we expect that the loading above which crystalline $RhCl_3$ starts to form is at least equal to or even higher than the value reported for H_2PtCl_6. Hence, we assume that in the samples in which
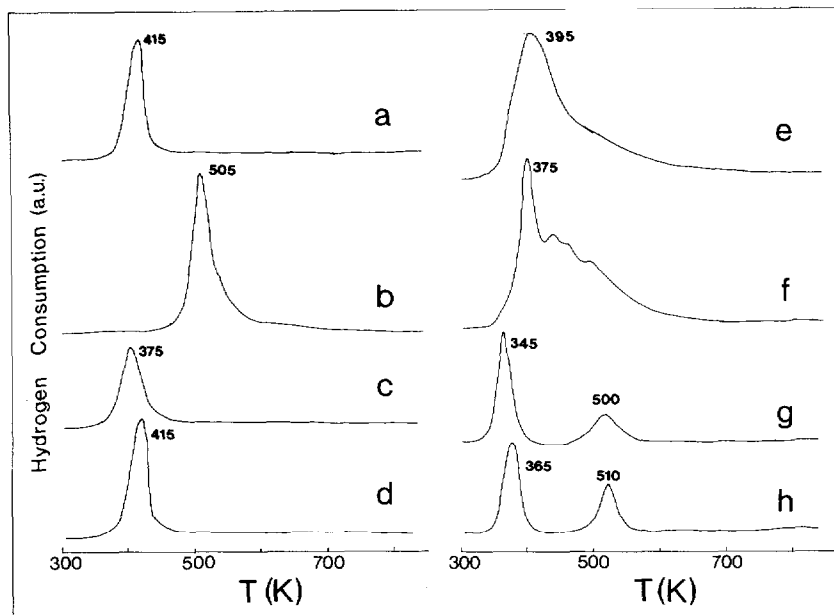
Fig. 3. TPR profiles of (a) $RhCl_3/Al_2O_3$; (b) H_2PtCl_6/Al_2O_3; (c) $(RhCl_3+PtCl_4)/Al_2O_3$, RPA1; (d) $(RhCl_3+H_2PtCl_6)/Al_2O_3$, RPA2; (e) $(RhCl_3+H_2PtCl_6)/Al_2O_3$ in 0.5 M HCl, RPA3; (f) $(RhCl_3+H_2PtCl_6)/Al_2O_3$ in 1.0 M HCl, RPA4; (g) $(RhCl_3+H_2PtCl_6)/Al_2O_3$ in methanol, RPA5; (h) $(RhCl_3+H_2PtCl_6)/Al_2O_3$ in ethanol, RPA6. Temperatures at the maximum hydrogen consumption are indicated.

$RhCl_3$, $PtCl_4$ and H_2PtCl_6 were dissolved in water (RPA1 and RPA2), the salts were adsorbed as single entities on the support. In the case where HCl was added to the solution (RPA3 and RPA4), the adsorption capacity of the support was lower and crystalline material may have been formed.

The monometallic $RhCl_3/Al_2O_3$, $PtCl_4/Al_2O_3$, and H_2PtCl_6/Al_2O_3 samples which were impregnated with aqueous solutions, had their TPR peak maximum at 415, 510 and 505 K, respectively. For the bimetallic samples which were impregnated with aqueous solutions, the reduction took place in one step at temperatures where monometallic $RhCl_3$ was reduced. For the samples impregnated with HCl solutions, the hydrogen uptake at higher temperatures increased (cf. Fig. 3e and f). On the basis of the results from the adsorption experiments, we can explain these findings as follows. Going from RPA1 to RPA4, the acidity of the solution increased. From the NMR and Raman experiments we conclude that in the samples RPA1 and RPA2 no crystalline $RhCl_3$ or crystalline H_2PtCl_6 was present. Therefore, the rhodium and platinum complexes in these samples were most probably monodispersed on the support during the adsorption stage. The H/M value determined with hydrogen chemisorption for sample RAP2 after the TPR reduction was 0.77. Using the calibration described in ref. 6, we estimate that the particles were about 15

Å in diameter and contained about 50 atoms. Obviously, the atomically dispersed rhodium and platinum complexes were reduced during the TPR and the resulting metal atoms had sintered to larger metal particles.

In order to explain why $RhCl_3$ and H_2PtCl_6 were reduced in one step, we propose the following model. During the reduction process, the adsorbed $RhCl_3$ complexes were reduced first. The resulting metallic rhodium atoms had only a weak interaction with the support and therefore these mobile rhodium metal atoms could "diffuse" over the support. In addition, they could adsorb and dissociate hydrogen. Consequently, when these mobile atoms encountered an unreduced rhodium or platinum complex during their "random walk" (or when hydrogen atoms spilled over from the rhodium atoms to the metal complexes), they may catalyse the reduction of that complex. In this way, the average particle size increases gradually due to the accumulation of additional metal atoms, until the metal particles are too large to have any significant mobility, or until all $RhCl_3$ and H_2PtCl_6 is reduced. If the random walk process of the metal atoms and the subsequent catalysed reduction of the remaining metal complexes is faster than the initial reduction of the adsorbed $RhCl_3$ complexes, only one TPR peak will be observed.

For the RPA3 and RPA4 samples, which were prepared under more acidic conditions, we suspect that not only monodispersed rhodium and platinum complexes had formed, but crystalline material as well. (The metal complexes are adsorbed onto the support during the wet stage, while the crystalline material is formed during the drying stage). These crystallites may "capture" diffusing metal atoms or small metal clusters and become reduced. But once reduced, the resulting large metallic crystallites have no significant mobility, and thus smother the reduction process. This was most pronounced for sample RPA4: after a sharp increase, due to the reduction of monodisperse $RhCl_3$ and the start of the reduction of larger crystallites, the hydrogen uptake decreased immediately. The reduction of the remaining crystallites was not catalyzed, but depended on the reducibility of the particles and thus on their (surface) composition: crystallites containing more $RhCl_3$ were reduced more easily than crystallites containing more H_2PtCl_6. This explains the tailing behaviour of the reduction profile for RPA3 and RPA4. In the TPR profile of RPA4, some hydrogen uptake was still visible in the region where pure H_2PtCl_6 was reduced, indicating that some monometallic H_2PtCl_6 crystallites were present. The main conclusion is that the reduction process was dominated by mobile metal clusters that, once formed, catalysed the reduction of the whole sample, if their mobility was not reduced drastically. When crystalline material was present, the reduction process was smothered.

The TPR profiles of the two bimetallic alcohol-impregnated samples were completely different (cf. Fig. 3g and h). There was a hydrogen uptake peak at low temperature, at the same reduction temperature as that of the alcohol-impregnated $RhCl_3$ sample, and a peak at the same reduction temperature as

that of the alcohol-impregnated H_2PtCl_6 sample. This indicates that $RhCl_3$ and H_2PtCl_6 were separately present on the support. In the Experimental part it was noted that the alcohols adsorbed strongly on the support. Therefore, it may be assumed that there were no sites left for $RhCl_3$ and H_2PtCl_6 to adsorb as single complexes. Hence, during the drying procedure, crystalline $RhCl_3$ and H_2PtCl_6 were formed. However, the hydrogen uptake of the two separate peaks did not agree with the amounts of $RhCl_3$ and H_2PtCl_6 present in the sample, although the total hydrogen uptake agreed very well. The hydrogen uptake in the low temperature peak was too high for reduction of $RhCl_3$ only. Apparently some H_2PtCl_6 had been incorporated into the $RhCl_3$ crystallites.

CONCLUSIONS

From the NMR and Raman experiments it is concluded that during the pore volume impregnation method H_2PtCl_6 most probably adsorbs monomolecularly onto the Al_2O_3 support up to a loading of about 1 μmol m^{-2}. Above this limit crystalline H_2PtCl_6 is formed. $RhCl_3$ exhibited the same behaviour, with an even larger maximum attainable monodisperse coverage. The coverage was dependent on the pH of the solution in contact with the support during adsorption and decreased with decreasing pH. As a consequence, and because of the acidic properties of $RhCl_3$ and H_2PtCl_6, the amounts of Rh and Pt adsorbed during co-adsorption were smaller than during adsorption of the separate metal salts.

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