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Reactions of ceria supported rhodium with hydrogen and nitric oxide studied with TPR / TPO and XPS techniques

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The reactions of ceria supported rhodium with H_2 and NO have been investigated by temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and X-ray photoelectron spectroscopy (XPS). In precious metal/ceria systems, both the support and the precious metal may be subject to reduction and reoxidation processes. Since partly reduced ceria is an ion-conducting material, the electrical charging of the whole sample during the XPS measurements depends on the oxidation state of the supporting ceria. Thus, the charging can be used as a sensitive indicator of the oxidation state of the support material which allows distinction between reactions of the support and of the precious metal. Rhodium oxide precursors are reduced to Rh^0 at temperatures below 200°C, but a slight reduction of the ceria support in this temperature range was also evident from the XPS spectra. At higher temperatures, the reduction of the ceria becomes more pronounced. Reoxidation of the support by NO is very fast and complete even at room temperature. Rh is oxidised to Rh_2O_3 at 200–300°C, i.e. below the normal working conditions of car exhaust catalysts.

Keywords: rhodium/ceria reduction and oxidation; TPR; TPO; XPS; charging effects in XPS

1. Introduction

Determination of oxidation states of active metals in catalysts is frequently achieved using XPS, but, in many cases, interpretation of the data is not simple and not straightforward (e.g. refs. [1,2]). Most uncertainties result from the fact that the non-conducting support material is subject to electrical charging during the XPS measurements, leading to the following effects:

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(1) A shift of the measured binding energies towards higher values is observed. This effect can, in most cases, be corrected by postcalibrating the binding energy scale of the spectra to a line with a well known binding energy value. For catalyst samples, either the C 1s peak of adventitious carbon or a prominent peak of the support material (such as Al 2s) can be used as energy references.

(2) Differential charging within the particles leads to line broadening [3]. This effect may cover features in the fine structure of the peaks of both the support material and the metal particles. Misinterpretations occur from this effect, when peaks of supported metal are directly compared with spectra of solid (conducting) metal.

(3) Different charging of the support and the metal particles. This effect cannot be accounted for and may be misinterpreted as changes in the oxidation state of the catalytically active metal.

Reducible supports such as ceria are unique in this context, since they may change from non-conducting to conducting, depending on the oxidation state. Charging effects may, therefore, be evident from one sample when different pretreatments are applied.

Both rhodium and ceria are widely used in three-way car exhaust catalysts, because the combination of the two components is most efficient for the reduction of NO [4]. There is lot of work reported on model systems dealing with the influence of precious metals (PM) and especially of rhodium on the reduction/reoxidation of ceria (e.g. refs. [4–6]). Since ceria can be partly reduced from CeO_2 to oxygen deficient ceria CeO_{2-x} it is considered to act as an oxygen storage component in the car exhaust system. In PM/CeO_2 systems, precious metal precursors are normally reduced at temperatures below 200°C. The reducibility of the ceria support is significantly enhanced by the precious metals, probably due to spillover effects [7]. This fact supports the theory that CeO_2 can act as an oxygen storage component. However, considering the thermodynamics of the CeO_{2-x}/O_2 system, it must be suspected, that any reduction of CeO_2 in car exhaust systems may be inhibited by the relatively large amounts of water and carbon dioxide which are present [8,9].

Much less investigations deal with the reoxidation of the precious metals after initial reduction, probably because they are considered noble and therefore inert after the initial reduction, or because they are normally used in very low concentrations which makes the analysis of the reoxidation more complicated. Using XPS as an analysis technique, Munuera and coworkers [10] found Rh supported on ceria to be very readily reoxidised. Indications of oxidation on samples prereduced at 700°C in hydrogen were found even at room temperature after treatment with 0.1 Torr O_2 for 30 min. Surprisingly, this group found evidence in the XPS spectra for the formation of significant amounts of Rh^{1+} at temperatures up to 200°C under 0.1 Torr of oxygen. Above this temperature, Rh^{3+} became the main oxidation state.

The present study was focused on the reactions of both the precious metal and the rare earth oxide in a ceria supported rhodium catalyst with hydrogen as a main reducing component and nitric oxide as the most noxious oxidising component of a typical car exhaust.

2. Experimental

Ceria (Aldrich, 99.9%) with a BET surface area of 10 m^2/g was used as support material. To obtain the Rh/CeO_2 with a Rh loading of 2% by mole (= 1.2% by weight), 4 g CeO_2 was mixed with a solution of 120 mg $RhCl_3 \cdot xH_2O$ (Rh-content 40%) in 75 ml H_2O. After stirring for 30 min at room temperature, the temperature was raised to 90°C to evaporate the solvent. The remaining powder was dried overnight at 150°C and calcined in air for 4 h at 600°C.

For the temperature programmed reduction and reoxidation studies, the powder samples were pressed to pellets, crushed with a razor blade, and sieved to 100–400 μm. The reactions were carried out in a flow system in which gas mixtures were passed at 40 ml/min over 100–300 mg samples fixed in a glass tube using glass wool. The tube was placed in a furnace which was programmed at a rate of 10°C/min up to 550°C. Changes in the composition of the product gas were determined using a VG SX300 quadrupole mass spectrometer.

The XPS spectra were recorded on a Kratos XSAM AXIS 800pci spectrometer equipped with a concentric hemispherical analyzer, which was run in the fixed transmission mode at pass energy 40 eV. A Mg K_α X-ray source was used at 180 W. The base pressure of the system was less than 10^{-9} Torr. The energy scale of the spectra of non-conducting samples was calibrated against the C 1s line of adventitious carbon at $E_B = 284.6$ eV. The samples were ground to fine powders and suspended in acetone. The resulting slurry was deposited on a stainless steel sample holder. After evaporation of the solvent, the powder was bound to the holder sufficiently strongly to be introduced in the vacuum system. Thermal treatments in flowing gases at ambient pressure and temperatures up to 400°C were performed in a chamber attached to the spectrometer. The treated samples were transferred into the main chamber of the instrument without contact with air.

3. Results and discussion

3.1. ANALYSIS OF THE XPS SPECTRA

The 3d spectra of Ce(III) and Ce(IV) exhibit complicated features due to shake-up and shake-down processes. These effects have been extensively investigated both theoretically and experimentally [11–13]. Fig. 1 shows typical examples of Ce 3d spectra of reduced and reoxidised Rh/CeO_2. In mixed Ce(III)/Ce(IV) systems, a splitting into four components of both the Ce $3d_{3/2}$ and Ce $3d_{5/2}$ level is observed. These features are normally labelled with u and v respectively. Strong peaks at $E_B = 886.2$ eV and $E_B = 904.7$ eV, labelled with v′ and u′, are typical for

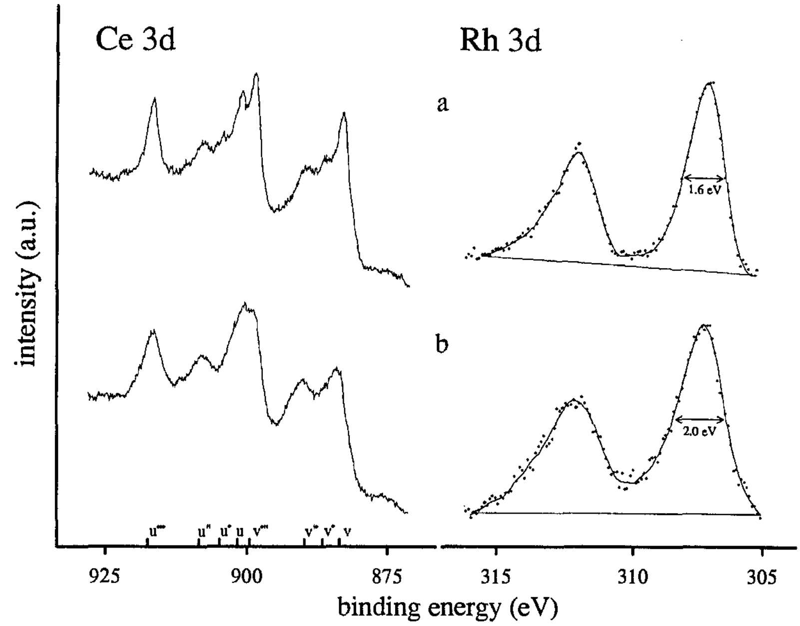

Fig. 1. Ce 3d and Rh 3d spectra of Rh/ceria (a) reduced at 400°C in 10% H_2/N_2 for 5 min and (b) reoxidised in 100 ppm NO/He at room temperature for 5 min. Under the used oxidation conditions, only the ceria support is reoxidised. The change in the Rh 3d spectra is due to the loss of conductivity of the support material in the oxidation process.

Ce(III). The main features of Ce(IV) are at $E_B = 889.2$ eV (v″), 899.1 eV (v‴), 908.2 eV (u″) and 917.3 eV (u‴), while intensity at $E_B = 883.2$ eV (v) and 901.2 eV (u) arises from both Ce(III) and Ce(IV) [13].

Our experiments showed that additional information on the cerium oxidation state could be obtained from the charging of the samples. In the spectrometer used, in which no electron flood gun was installed to compensate sample charging, charging shifts of 4–6 eV were normally observed for non-conducting powders deposited on the sample holders. For partly reduced ceria samples, the charging was reduced to about 0–0.2 eV. The effect is most probably due to the ionic conductivity of oxygen deficient ceria [14]. In addition, the peaks from partly reduced samples appear generally narrower and the multiplets better resolved (see fig. 1). This finding can reasonably be explained by lower differential charging in conducting samples [3].

The Rh signals also depend on the conductivity of the support. Fig. 1a shows the Rh 3d doublet of a reduced sample. To obtain the spectrum in fig. 1b, only the support of the sample was oxidised by dosing with NO at room temperature, as described below. The lines in fig. 1a (conducting support) are narrower and better resolved. Upon oxidation of the support, the FWHM (full width at half maximum) value of the Rh $3d_{5/2}$ line rises from 1.6 to 2.1 eV. In order to determine the distributions of different oxidation states of rhodium in further samples, the two experimental Rh 3d spectra shown in fig. 1 were used to fit the 3d signals of rhodium on conducting and non-conducting supports respectively. For this procedure, the curves (in the following named type A and type B curve respectively) were slightly smoothed (solid lines) and the linewidths and the $3d_{3/2}$–$3d_{5/2}$ splitting were fixed at the values of the experimental curves. In all samples, the Rh 3d peaks could be fitted with two doublets for Rh^{3+} and Rh^0. The binding energy difference between the two doublets was always between 1.7 and 2.1 eV, in good agreement with literature values for metallic rhodium and Rh_2O_3 [15]. No evidence was found for Rh^+ species, for which the $3d_{5/2}$ level is reported to be around 0.7 eV higher than that of Rh^0 [10].

3.2. REDUCTION OF CALCINED Rh/CeO$_2$ WITH H$_2$

Fig. 2a shows a TPR experiment of a calcined 2% Rh/CeO$_2$ sample in 2% H_2/He. The consumption of H_2 started at 40°C and goes through a first maximum

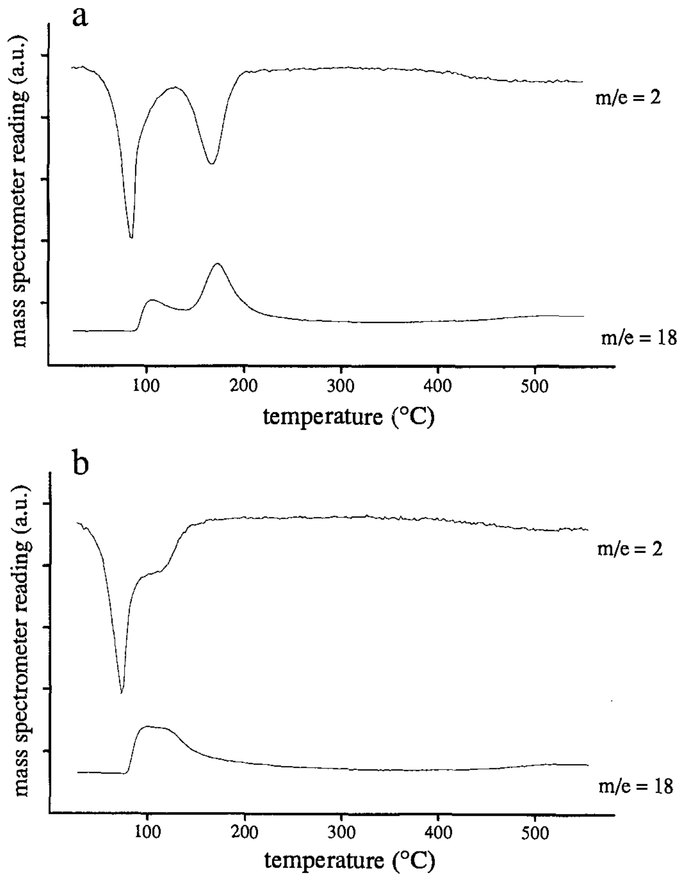

Fig. 2. TPR of 300 mg 2% Rh/CeO$_2$ in 40 ml/min 2% H_2/He. (a) Calcined, fresh sample, (b) reduced and reoxidized sample. Heating rate: 10°C/min, recorded masses: $m/e = 2$ (H_2) and $m/e = 18$ (H_2O).

at 100°C. Water started to be evolved only at this temperature because it is very well adsorbed by the calcined ceria support below this temperature. A second maximum in the reduction was reached at 200°C. Both processes are most probably due to reduction of rhodium oxide, possibly of the surface and the bulk of the particles, respectively. After the two steps, some consumption of H_2 and production of H_2O did still take place, due to ceria reduction, but no well resolved maximum was found.

Figs. 3 and 4 show XPS data of a similar reduction experiment. Unfortunately, it is often not possible to copy the exact reduction conditions of the TPR experiment in the pretreatment chamber of the XPS. In our case the samples were brought quickly to selected temperatures for 5 min instead of heating linearly up to the setpoint. In order to compensate for the shorter reaction time as well as for the lower flow rate in the XPS-reaction chamber, the hydrogen content in the reducing gas was increased to 10% H_2/N_2. The reductive treatment at 70°C did not produce any signs of reduction of the rhodium nor of the ceria support. After treatment at 100°C, the maximum intensity in the Rh 3d spectrum was shifted to lower binding energy, clearly indicating Rh reduction. Also some reduction of CeO_2 was indicated by the narrower and better resolved peaks (due to ionic conductivity) and by increased relative intensity in the Ce 3d spectra around 886 eV (peak v′). Little further change in the Ce 3d spectra was observed when the sample was treated at higher temperature. The big difference in the resolution of the O 1s spectra of the sample reduced at 70 and 150°C is again due to the increased conductivity resulting in better resolution. The shoulder on the high binding energy side

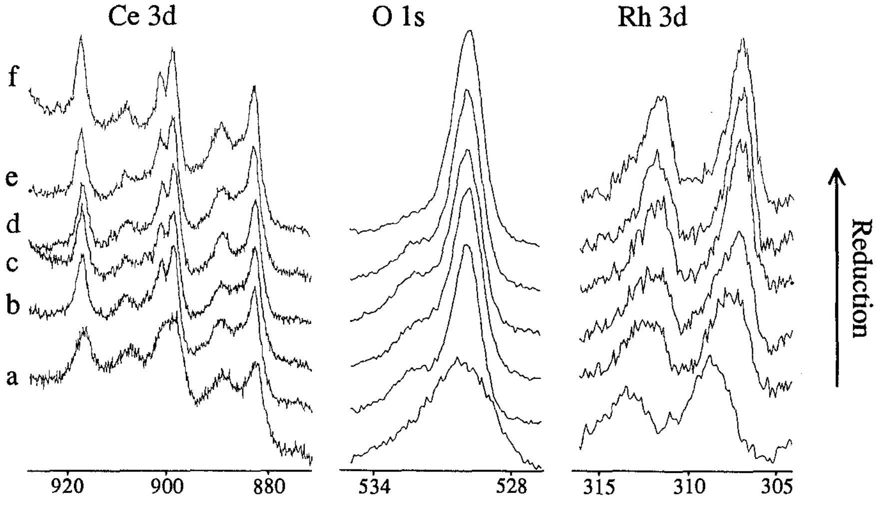

Fig. 3. Ce 3d, O 1s and Rh 3d spectra of the reduction of 2% Rh/CeO_2 in 10% H_2/N_2: after 5 min at (a) 70°C, (b) 100°C, (c) 125°C, (d) 150°C, (e) 200°C and (f) 400°C (pure H_2).

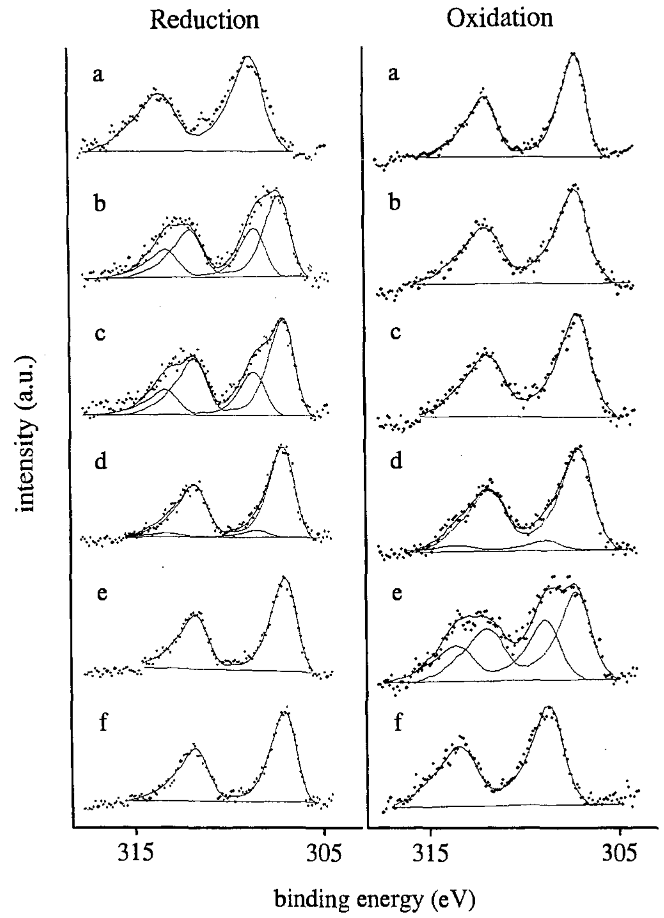

Fig. 4. Peak fitting on the Rh 3d spectra of figs. 3 and 6.

of the peaks results from surface carbonate and hydroxide species, which are readily formed on the calcined material when in contact with ambient air, and which decompose at higher temperatures, leading to a decrease in relative intensity of the corresponding peaks.

The left part of fig. 4 shows the results from curve fitting on the Rh 3d signals of the reduction sequence. In sample a, the spectrum could reasonably be fitted with one type A curve. The data must be interpreted as Rh in the trivalent oxidation state only on unreduced ceria. All the other spectra were best fitted with type B curves (reduced, conducting support). The distributions between Rh^{3+} and Rh^0 are summarized in table 1. The highest changes in distribution were observed between 70 and 100°C and between 125 and 150°C. Reduction of the precious metal was complete at 200°C. Considering the higher concentration of H_2 in the XPS pretreatment, these temperatures are in good agreement with the TPR results.

Table 1
Distribution of Rh^0 and Rh^{3+} after reduction and reoxidation of 2% Rh/CeO$_2$ at different temperatures, calculated from XPS peak fitting

Reduction in 10% H$_2$/N$_2$			Reoxidation in 100 ppm NO/He		
Temperature (°C)	%Rh^0	%Rh^{3+}	Temperature (°C)	%Rh^0	%Rh^{3+}
70	0	100	RT	100	0
100	63	37	100	100	0
125	69	31	200	91	9
150	94	6	300	59	41
200	100	0	400	0	100
400	100	0			

3.3. REOXIDATION OF Rh/CeO$_2$ WITH NO

After reduction in the TPR as described above, the sample was cooled down to room temperature in a stream of helium. Reoxidation was then performed in two parts, (1) by switching to a 1% NO/He mixture at room temperature and (2) by heating linearly up to 550°C. The two parts are shown in figs. 5a and 5b respectively. At the first contact of NO with the reduced sample, N$_2$ was evolved as the main reaction product. Later, N$_2$ and N$_2$O were produced simultaneously. As XPS measurements showed (fig. 6 and right part of fig. 4) the oxygen deficient ceria was reoxidised completely by NO even with the lower concentration of 100 ppm used in the XPS pretreatment chamber. Ce(III) features disappeared from the Ce 3d spectra, and all the lines were broadened again due to the loss of ionic conductivity. On the other hand, no reoxidation of Rh^0 took place at room temperature. The Rh 3d spectrum could be fitted with only one doublet for metallic Rh. A type B curve had to be used because of the completely oxidised non-conducting support.

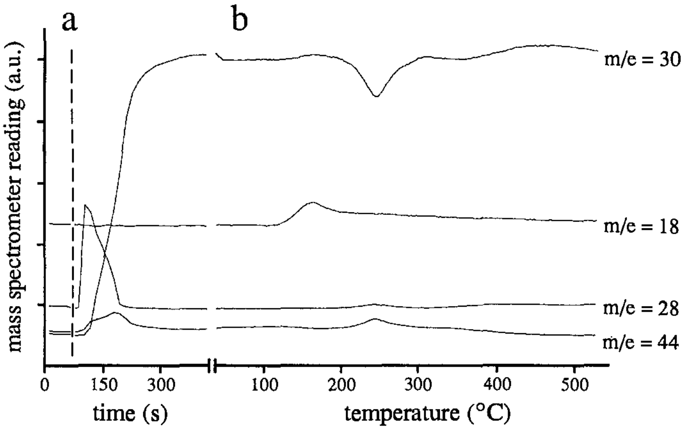

Fig. 5. Oxidation of reduced 2% Rh/CeO$_2$ in 40 ml/min 1% NO/He (a) at room temperature and (b) temperature programmed (10°C/min). Recorded masses: $m/e = 18$ (H$_2$O), $m/e = 28$ (N$_2$), $m/e = 30$ (NO) and $m/e = 44$ (N$_2$O).

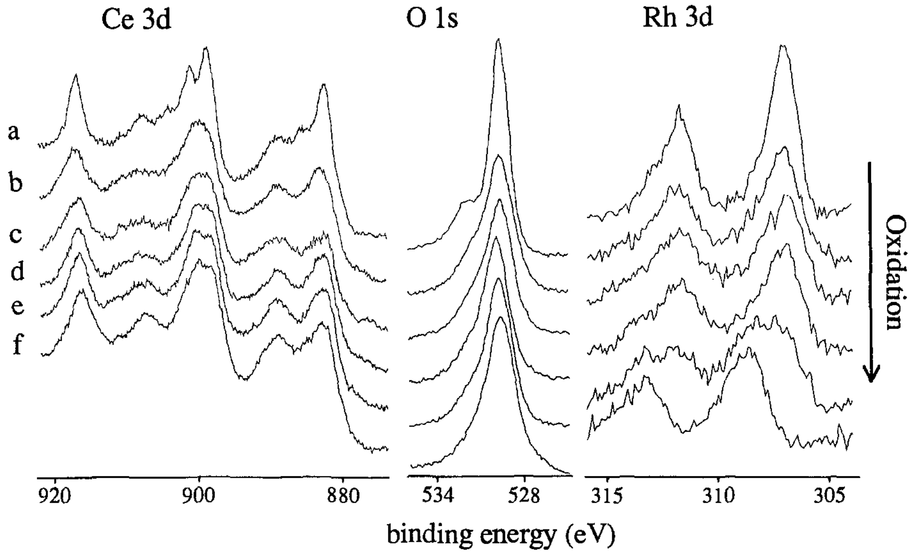

Fig. 6. Ce 3d, O 1s and Rh 3d spectra of the oxidation of reduced 2% Rh/CeO_2 in 100 ppm NO/He: (a) sample reduced in pure H_2 (400°C, 10 min); after oxidation for 5 min at (b) room temperature, (c) 100°C, (d) 200°C, (e) 300°C and (f) 400°C.

The TPO and XPS both show that the oxidation of most of the Rh took place between 200 and 300°C. In this oxidation N_2O was the more important gaseous product. The XPS data indicate that oxidation runs straight from Rh^0 to Rh^{3+}. The Rh 3d peaks could in all cases be fitted with a maximum of two doublets for Rh^0 and Rh^{3+} respectively. No better or more reasonable fit resulted when a third doublet for Rh^+ was included in the calculations. To reoxidise Rh^0 in the XPS experiment slightly higher temperatures were needed compared to the TPO, because of the lower concentration of NO used.

3.4. REDUCTION OF REOXIDIZED Rh/CeO_2 WITH H_2

As further proof of the reoxidation of rhodium, the TPO-reoxidised sample was re-reduced at the same conditions as the first reduction. The results of this experiment are shown in fig. 2b. The reaction started at even lower temperature than in the first reduction. Instead of the peak at 200°C in the first reduction, there was only a small shoulder appearing at significantly lower temperatures. This may indicate that oxidation, although it appeared complete from the XPS spectra, did not cover the core of the rhodium particles.

4. Conclusions

XPS and TPR/TPO measurements have been used as complementary techniques to characterize Rh/CeO_2 systems. In XPS, differences in line broadening due to differences in conductivity of the support material were used to distinguish reactions of the support and of the precious metal. The following behaviour of the Rh/CeO_2 system could be established:

– The reduction of Rh^{3+} in calcined systems with H_2 starts at temperatures below 100°C. It proceeds in two steps, most probably surface and bulk reduction.

– Ceria in contact with Rh is slightly reduced at surprisingly low temperatures, i.e. below 125°C.

– Oxidation of partly reduced ceria with NO is rapid and complete even at room temperature. It proceeds with evolution of N_2 and N_2O.

– NO in relatively low concentrations oxidises Rh^0 to Rh_2O_3 at temperatures between 200 and 300°C. This reaction may be facilitated by the ceria support.

– There is no evidence for intermediate Rh^+ species, neither in the reduction nor in the reoxidation process.

For car exhaust gases, where the atmosphere is cycling between reducing and oxidising, it can be concluded that, in rhodium/ceria systems, both the ceria and rhodium may be involved in reduction and oxidation reactions. Cerium is predominantly present in the Ce(IV) state while rhodium may cycle between Rh^0 and Rh^{3+}. In real catalysts, the situation may be different due to interaction of rhodium and ceria with further components of the catalysts.

Acknowledgement

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