

# Hydrogen formation in the reaction of steam with Rh/CeO<sub>2</sub> catalysts: a tool for characterising reduced centres of ceria

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## Abstract

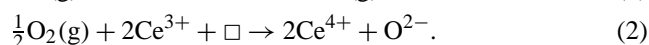
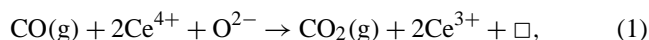
A 3.7% Rh/CeO<sub>2</sub> catalyst was prepared by wet impregnation of a low-surface-area ceria (23 m<sup>2</sup> g<sup>-1</sup>) with an aqueous solution of rhodium nitrate. This catalyst was reduced in a flow of H<sub>2</sub> at temperatures  $T_R$  ranging from 200 to 1000 °C. The number of reduced centres of ceria in Rh/CeO<sub>2</sub> catalysts was measured by in situ reoxidation of these centres at  $T_{OX}$  by pulses of water according to the following reaction: Reduced centre + H<sub>2</sub>O → Oxidised centre + H<sub>2</sub>. The amount of hydrogen,  $Q_H$ , evolved in the reaction allows us to calculate the number of reduced centres of the support since the noble metal would not be oxidised.  $Q_H$  remains relatively small for  $T_R$  not exceeding 500 °C, then increases rapidly to reach a pseudo-plateau at about 850 °C. At 900–1000 °C, the oxide composition would be close to CeO<sub>1.75</sub>. Contrasting with the effect of  $T_R$ , relatively small variations are recorded with  $T_{OX}$  for a catalyst reduced at 850 °C: a maximum value of  $Q_H$  is reached for  $T_{OX}$  close to 850 °C, but 74% of this maximum yield in H<sub>2</sub> is already obtained when the reaction with steam is carried out at 100 °C. Oxidation by steam was also carried out on a catalyst prerduced in deuterium. It was shown that the hydrogen formed comes from the decomposition of water (H<sub>2</sub>) and not from the storage of deuterium in the support during the reduction stage. In situ characterisation by XRD showed that there is a deep perturbation of the cubic structure at 850 °C, followed by a reduction of CeO<sub>2</sub> into Ce<sub>2</sub>O<sub>3</sub> (hexagonal) at higher temperatures (900–1000 °C). A treatment in water restores the cubic structure of CeO<sub>2</sub>. The support having been previously reduced at 900 °C, there is virtually no sintering of the ceria crystallites upon these high-temperature treatments in hydrogen and steam.  
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**Keywords:** H<sub>2</sub> formation; Ceria oxidation (by steam); Rh/CeO<sub>2</sub> catalysts

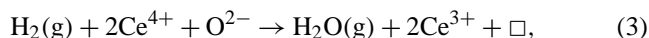
## 1. Introduction

As a support of heterogeneous catalysts, ceria has been the object of an increased number of investigations since the 1970s [1]. CeO<sub>2</sub> is a basic oxide having excellent redox properties owing to the very fast reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> associated with the formation of oxygen vacancies at the surface and in the solid. For these reasons, ceria has become an essential component of three-way catalysts, since it can store oxygen during lean phases and release it during rich ones. This is the so-called “oxygen storage capacity” (OSC), allowing metal particles to be fed in O species when O<sub>2</sub> has temporarily disappeared from the gas phase [2–5]. In most cases, alternate pulses of CO and O<sub>2</sub> were used to measure

OSC of ceria catalysts [2,5,6]



Alternate pulses of H<sub>2</sub> and O<sub>2</sub> were more rarely employed for OSC measurements [7,8],



this reaction being followed by Eq. (2), exactly as for CO. In both cases (reduction by CO or H<sub>2</sub>), O<sub>2</sub> is very often used to reoxidize the catalyst. Nevertheless, O<sub>2</sub> not only fills in the O vacancies of ceria but also reoxidises the metal particles, as clearly demonstrated by Bernal et al. by HREM in the case of Rh/CeO<sub>2</sub> [9]. Considering, however, the reverse reactions of Eqs. (1) and (3), we may infer that either CO<sub>2</sub> or H<sub>2</sub>O is a potential oxidant able to fill in O vacancies of ceria without possessing the oxidation power of O<sub>2</sub> leading to Rh<sup>0</sup> reoxidation. Water or carbon dioxide

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can thus potentially be used to determine the number of O vacancies in the support of metal catalysts reduced at high temperatures. This technique, with water, was previously developed for studying the kinetics of reduction of titania-supported Rh, Pt, and Ni catalysts [10]. Pulses of water are injected onto the in situ reduced catalyst sample and the extent of the reaction is measured by the amount of H<sub>2</sub> produced upon each pulse. A similar technique was applied to alumina-supported Rh and Pt catalysts [11]. No Al<sub>x</sub>Rh<sub>y</sub> or Al<sub>x</sub>Pt<sub>y</sub> alloy could be detected even after reduction at 1000 °C and it was proved that the formation of O vacancies was strictly localised at the metal/support interface. The same method applied to silica-supported Rh catalysts showed that the reactivity of silica was completely different from that of alumina: O vacancies are intermediates in the formation of rhodium silicides (mainly Rh<sub>2</sub>Si), which could be detected in catalysts reduced at high temperatures ( $T > 600$  °C) [12]. Steam decomposes rhodium silicides into silica and hydrogen but leaves rhodium in the zerovalent state.

The interaction of H<sub>2</sub> with CeO<sub>2</sub> or Rh/CeO<sub>2</sub> catalysts has been studied in detail and will be further discussed in this paper. Briefly, it seems that the main role of H<sub>2</sub> is to create anionic vacancies on and in ceria. Cerium suboxides (CeO<sub>x</sub> with  $1.5 < x < 2$ ) are generally formed, while cerium hydrides are sometimes observed [13]. Some studies have been devoted to the reactivity of H<sub>2</sub>O or CO<sub>2</sub> on reduced ceria catalysts [14–18]. These studies showed that the oxygen vacancies could be filled by oxygen from water or carbon dioxide. Padeste et al. showed that oxygen storage capacity of ceria (measured by CO<sub>2</sub> formation upon CO pulses) was considerably lowered by the presence of water [16]. Similarly, Trovarelli et al. have reported that oxygen vacancies produced during prereduction of Rh/CeO<sub>2</sub> or CeO<sub>2</sub>-promoted Rh/SiO<sub>2</sub> were annihilated by oxygen from CO<sub>2</sub> under CO<sub>2</sub> methanation conditions [19]. However, Otsuka et al. showed that CO<sub>2</sub> was significantly less reactive than H<sub>2</sub>O [14]. Moreover, CO<sub>2</sub> reaction with reduced ceria may lead to complex features: different species of carbonates or hydrogenocarbonates (or even carbonites) generally appear preceding the CO formation. For these reasons, we have limited our investigation to the reoxidation of reduced Rh/CeO<sub>2</sub> by steam.

## 2. Experimental

### 2.1. Materials and catalyst preparation

The support used was a high-surface-area ceria (HSA) provided by Rhodia Rare Earths (BET area, 60 m<sup>2</sup> g<sup>-1</sup>; grain size, about 50 μm; no internal porosity; main impurity, La ≈ 2000 ppm). In order to avoid possible sintering of the oxide during the pretreatment of the catalyst, the support was pretreated at high temperature before impregnation: reduction under H<sub>2</sub> at 900 °C followed by calcination

under air at 450 °C. The BET surface was then reduced to 23 m<sup>2</sup> g<sup>-1</sup>.

The catalyst was prepared by impregnation of the pre-treated support (5 g) with an aqueous solution of rhodium III nitrate Rh(NO<sub>3</sub>)<sub>3</sub> from Fluka. The slurry was gently shaken at room temperature on an oscillating table for 16 h. The supernatant solution was evaporated to dryness on a sand bath maintained at 60 °C. The catalyst batch was subsequently dried at 120 °C and calcined in an air flow at 450 °C for 4 h before storage. After impregnation, the metal content was 3.7 wt% in rhodium.

### 2.2. Oxidation of prereduced Rh/CeO<sub>2</sub> by steam

Prereduction and steam oxidation experiments were carried out in a chromatographic microreactor described elsewhere [11,20]. The catalyst sample (typically 0.1 g) was reduced in a flow of pure hydrogen (less than 5 ppm impurity; 30 cm<sup>3</sup> min<sup>-1</sup>) at  $T_R$  for 1 h. H<sub>2</sub> was then replaced by Ar (less than 1 ppm impurity, same flow rate) and the catalyst sample was cooled down to  $T_{OX}$ . Once the temperature was stabilised, pulses of water (1 μl, i.e., 56 μmol) were injected every 10 min at this temperature ( $T_{OX}$ ). The hydrogen formed in the reaction was analysed by GC (carrier gas: Ar) on a 5 Å molecular sieve column using a thermal conductivity detector calibrated by reference to a pulse of pure H<sub>2</sub> (loop volume: 0.256 cm<sup>3</sup>). Nonreacted water was trapped in the molecular sieve column, which required regeneration every 50 pulses.

The following nomenclature has been chosen to denote the catalyst at different stages of reaction: RhCeRT<sub>R</sub> is the catalyst just reduced at  $T_R$  (°C), while RhCeRT<sub>R</sub>WT<sub>OX</sub> denotes the catalyst reduced at  $T_R$  and treated in pulses of water at  $T_{OX}$ . For instance RhCeR980W500 is the catalyst reduced at 980 °C and treated in pulses of water (typically five pulses of 1 μl) at 500 °C.

### 2.3. Oxidation of Rh/CeO<sub>2</sub> samples reduced in D<sub>2</sub> by H<sub>2</sub>O

Specific experiments were carried out on catalyst samples prereduced in deuterium (99.9% D<sub>2</sub>) in order to measure to what extent the hydrogen formed in the reaction may come from the reduction gas stored in the solid or from steam. Similar conditions were used except that H<sub>2</sub> was replaced by D<sub>2</sub> with the same flow rate for the catalyst reduction step.

### 2.4. In situ X-ray diffraction analyses

In situ XRD analyses were carried out in a SIEMENS D500 diffractometer equipped with a pretreatment chamber able to reach very high temperatures (1400 °C). X-radiation was produced by an anode made of copper ( $K_\lambda = 0.15406$  nm) operating at 30 mA and 40 kV. About 40 mg of catalyst powder was deposited on a Ta sheet which could be heated by the Joule effect. Care was taken to have a regular thickness of the catalyst layer with the minimum of

Ta directly accessible to X-rays. The pretreatment chamber was then evacuated to about  $10^{-3}$  mbar for 1 h and a flow of pure  $H_2$  was admitted in the chamber. The catalyst was reduced in situ from room temperature to 1000 °C. X-ray diffractograms were recorded at different temperatures of reduction.

### 2.5. Electron microscopy

Transmission electron microscopy in bright field mode was carried out in a Philips CM120 electron microscope operating at 120 kV with a theoretical resolution of 0.35 nm. The freshly treated sample was ultrasonically suspended in ethanol, deposited on a Cu grid previously covered with a thin layer of carbon. Selected area electron diffraction (SAED) patterns were taken on several particles. Three samples were examined: RhCeR500, RhCeR980, and RhCeR980W980.

## 3. Results

### 3.1. Effect of the reduction temperature

A first set of experiments was carried out at different temperatures of reduction ( $T_R$ ) while a constant temperature of oxidation by steam ( $T_{OX} = 500$  °C) was maintained. The amounts of hydrogen,  $Q_H$ , formed upon each pulse of water are reported in Fig. 1.

$Q_H$  remains relatively small and does not exceed  $100 \mu\text{mol H g}^{-1}$  up to a 500 °C reduction temperature. By contrast, considerable amounts of  $H_2$  can be formed when the catalyst is reduced above 500 °C:  $Q_H$  values are much higher than those observed with a 5% Rh/SiO<sub>2</sub> sample even when this catalyst was reduced at 980 °C [12]. However, with the sample weights used here in each experiment

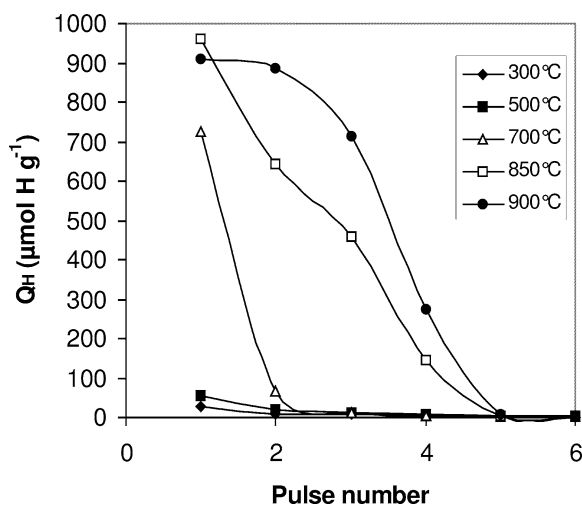


Fig. 1. Amounts of hydrogen formed as a function of the pulse number ( $1 \mu\text{l H}_2\text{O}$ ) injected on the Rh/CeO<sub>2</sub> catalyst reduced at different temperatures (300–900 °C).

Table 1

Cumulative amounts of  $H_2$  formed ( $Q_T$  in  $\mu\text{mol at H g}^{-1}$ ) in the first five pulses of water injected at 500 °C on the Rh/CeO<sub>2</sub> catalyst sample prerduced for 1 h at  $T_R$  (°C)

$T_R$ (°C)	300	500	700	850	900
$Q_T$ (5 pulses) ( $\mu\text{mol H g}^{-1}$ )	47	103	812	2213	2790

(0.1 g),  $H_2$  production virtually ceases after the 5th pulse. The major part of (if not all) the reduced sites of ceria are thought to be titrated by water at 500 °C.

The cumulative amounts of hydrogen formed in the first five pulses ( $Q_T$ ) are reported in Table 1. Arrhenius plots of  $Q_T$  vs  $T$  (not shown) give a straight line with a very good coefficient of correlation (0.9994) inasmuch as the first point at  $T_R = 300$  °C is excluded from the correlation. The activation energy deduced from this graph ( $E_a = 62.5 \text{ kJ mol}^{-1}$ ) is a measurement of the activation energy for reduction of ceria by  $H_2$  in Rh/CeO<sub>2</sub> catalysts. The following equation can thus be given for the amount of reduced sites of ceria created after reduction in  $H_2$  for 1 h at  $T_R$ ,

$$Q_T (\mu\text{mol g}^{-1}) = 1.76 \times 10^6 \exp\left(-\frac{7517}{T}\right), \quad (4)$$

where  $T$  is the reduction temperature in K. The value obtained at 300 °C ( $47 \mu\text{mol g}^{-1}$ ) is significantly higher than the theoretical value ( $3.5 \mu\text{mol g}^{-1}$ ) calculated by Eq. (4). A likely explanation is that a small number of sites (about  $40 \mu\text{mol g}^{-1}$ ) can be reduced at very low temperatures according to a kinetic law not represented by Eq. (4). These reactive species are probably located at the *ceria surface* while reduction of *inner layers of ceria* would be better represented by Eq. (4).

At low reduction temperatures (300–500 °C), only a very small fraction of the pulse (3% at 300 °C and 7% at 500 °C) is decomposed, but the amount of  $H_2$  formed upon the first pulse corresponds to the major part of the total  $H_2$ . At these temperatures, one pulse is almost sufficient for dosing the reduced sites. At 850 and 900 °C, the titration of reduced sites requires several pulses of water:  $H_2O$  conversion is close to 80% at the first pulse and it is still very high at the second one (Fig. 1). These results show that the reaction of steam at 500 °C is very fast and is only limited by the number of moles of water in the pulse when this latter is overpassed by the number of sites to be titrated.

### 3.2. Effect of the temperature of oxidation by steam, $T_{OX}$

A series of experiments were carried out by changing the temperature of oxidation by steam ( $T_{OX} = 100, 500, 700, \text{ and } 850$  °C) while maintaining the temperature of reduction at a constant value ( $T_R = 850$  °C). The results are shown in Fig. 2. A slight increase of  $Q_H$  can be observed. However, a significant amount of hydrogen ( $2064 \mu\text{mol at H g}^{-1}$ ) is already obtained when  $H_2O$  is admitted to react

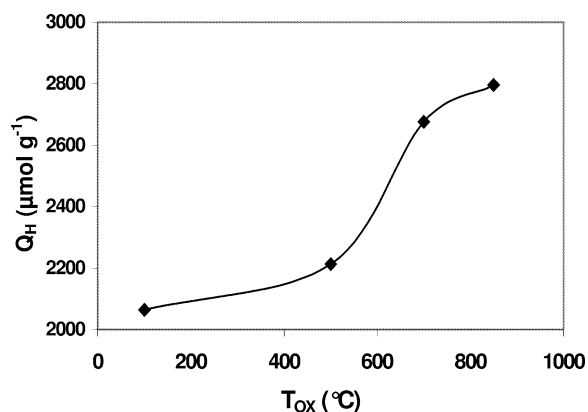


Fig. 2. Effect of  $T_{OX}$  on the amount of hydrogen formed by reaction of steam (five  $\text{H}_2\text{O}$  pulses) on Rh/CeO<sub>2</sub> prerduced at 850 °C.

at temperatures as low as 100 °C. At 850 °C,  $Q_H$  stabilizes around 2800  $\mu\text{mol at H}^{-1}$ .

These results clearly indicate that steam can fill in anionic vacancies of reduced ceria at low temperatures: at 100 °C, 74% of the  $\text{Ce}^{3+}$  ions generated by reduction at 850 °C are reoxidized after five pulses of  $\text{H}_2\text{O}$ .

### 3.3. Number of vacancies titrated by $\text{H}_2\text{O}$

Each anionic vacancy in the reduced catalyst is associated with two  $\text{Ce}^{3+}$  ions (Eq. (2)) and gives rise to two atoms of H (one molecule of  $\text{H}_2$ ) by reaction with steam (Eq. (3)). The reduction percentage ( $R\%$ ) can thus be calculated by

$$R\% = 100 \frac{Q_H}{N_{\text{Ce}}}, \quad (5)$$

$N_{\text{Ce}}$  being the number of Ce atoms in one gram of catalyst (5545  $\mu\text{mol g}^{-1}$ ; see Appendix A). The general formula of the reduced compound is Rh/CeO<sub>2-x</sub>, where  $x$  is

$$x = \frac{R\%}{200}. \quad (6)$$

$R$  and  $x$  values measured by  $\text{H}_2\text{O}$  titration are reported in Table 2 for various temperatures of reduction  $T_R$  and of oxidation by steam  $T_{OX}$ . Table 2 also gives the equivalent number of reduced layers of ceria  $n_L$  at  $T_R$  (see Appendix A). Between 300 and 500 °C, the reduction of ceria is restricted to the surface ( $n_L < 1$ ). Above 500 °C, the number of reduced layers increases to reach 13–14 layers at the highest temperatures. There is a significant increase of the percentage of  $\text{Ce}^{4+}$  reduced to  $\text{Ce}^{3+}$  between 700 °C (14%) and 850 °C (40–48%), while the increase of  $R$  observed between 850 and 980 °C is very small. It seems as if the percentage of Ce reduction would tend to about 50%, in agreement with the XPS results of Laachir et al. [21], who reported a 48% reduction at 927 °C for a ceria of 115  $\text{m}^2 \text{g}^{-1}$ . This limit of reduction does not depend on the presence or absence of rhodium in the catalyst. Temperature-programmed reduction (TPR) of ceria shows generally two reduction peaks: the low-temperature peak (400–550 °C) has been ascribed to the

Table 2

Percentage of reduced ceria, general formula and number of reduced layers in the Rh/CeO<sub>x</sub> after reduction at  $T_R$  (the titration was carried out at  $T_{OX}$ )

$T_R$ (°C)	$T_{OX}$ (°C)	$Q_H$ ( $\mu\text{mol at H g}^{-1}$ )	$R\%$ <sup>a</sup>	General formula <sup>b</sup>	Number of reduced layers <sup>c</sup>
300	500	47	0.85	CeO <sub>1.996</sub>	0.2
500	500	103	1.86	CeO <sub>1.991</sub>	0.4
700	500	812	14.6	CeO <sub>1.927</sub>	3.2
850	100	2064	37.2	CeO <sub>1.814</sub>	9.3
850	500	2213	39.9	CeO <sub>1.800</sub>	10.1
850	700	2685	48.4	CeO <sub>1.758</sub>	12.9
850	850	2795	50.4	CeO <sub>1.748</sub>	13.5
900	500	2790	50.3	CeO <sub>1.748</sub>	13.5
980	980	2870	51.7	CeO <sub>1.741</sub>	14.0

<sup>a</sup> From Eq. (5).

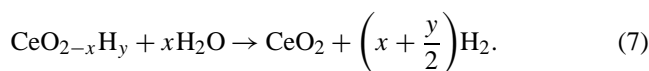
<sup>b</sup> From Eq. (6).

<sup>c</sup> From Eq. (A.3).

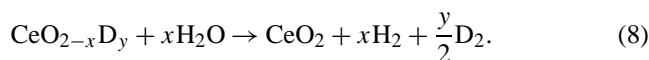
reduction of the ceria surface, while the reduction of the bulk would start at about 600 °C [2,22]. The presence of a noble metal is known to favour the reducibility of the ceria surface [23–25], but that of the bulk is virtually unaffected by Rh or Pt [24,26]. It is thus conceivable that the same reduction percentage in the bulk of ceria can be observed at about the same temperature whether there is a noble metal in the catalyst or not.

### 3.4. Water decomposition on the catalyst reduced in $\text{D}_2$

Hydrogen formation may arise from the reoxidation of  $\text{Ce}^{3+}$  with correlative filling of anion vacancies by the oxygen of  $\text{H}_2\text{O}$  (Eq. (3), back reaction). It may also arise from the displacement, by water, of a certain amount of  $\text{H}_2$  stored in the catalyst during its reduction. This reaction can be written as



To discriminate between the two possible routes ( $\text{H}_2$  from  $\text{H}_2\text{O}$  decomposition and  $\text{H}_2$  from H storage), the same experiments—reduction, degassing, oxidation by  $\text{H}_2\text{O}$  pulses—were repeated, replacing  $\text{H}_2$  used for ceria reduction with  $\text{D}_2$ . Reaction (7) becomes



The catalyst sample was reduced in a flow of pure  $\text{D}_2$  at 850 °C during 0.5 h and degassed in a flow of argon at the same temperature for 0.5 h. Pulses of  $\text{H}_2\text{O}$  were injected every 10 min at 500 °C (7 pulses; 1  $\mu\text{l/pulse}$ ). The MS analysis of the different hydrogen isotopomers ( $\text{H}_2$ , HD, and  $\text{D}_2$ ) is represented Fig. 3.

As for samples prerduced in  $\text{H}_2$ , oxidation is total after the 6th pulse of water. The main product obtained is  $\text{H}_2$  accompanied by small amounts of HD upon the first pulse of  $\text{H}_2\text{O}$ .  $\text{D}_2$  formation is virtually nil. These results show that hydrogen storage in the catalyst cannot be excluded but remains negligible under our experimental

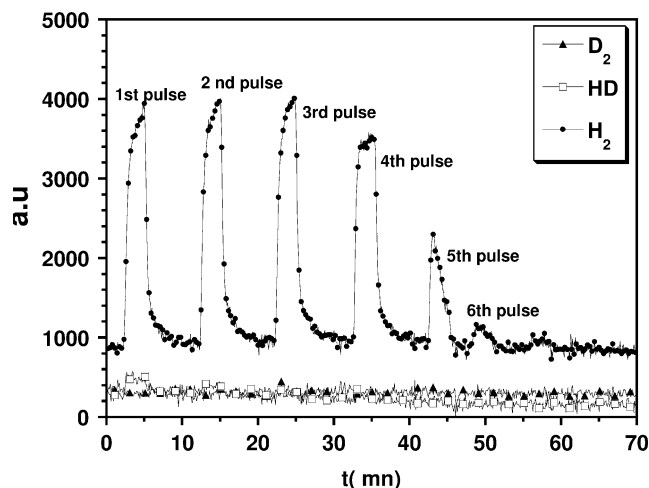


Fig. 3.  $\text{H}_2$ , HD, and  $\text{D}_2$  formed upon  $\text{H}_2\text{O}$  pulses injected on Rh/CeO<sub>2</sub> reduced in  $\text{D}_2$ .

conditions. A similar result was obtained with Rh/SiO<sub>2</sub> catalysts reduced at high temperatures in  $\text{D}_2$ : no D-labeled hydrogen was found in the products of reaction with pulses of  $\text{H}_2\text{O}$  [12].

### 3.5. Characterisation by powder X-ray diffraction (XRD)

It was difficult to characterise reduced CeO<sub>2</sub> or Rh/CeO<sub>2</sub> samples by ex situ XRD because of the reoxidation of ceria in air even at ambient temperatures. For this reason, the catalyst samples were examined by in situ XRD, the reduction (from ambient temperature to 1000 °C) being carried out in the diffraction chamber of the apparatus. These diffractograms were compared to those recorded after reaction with steam.

The diffractograms obtained by in situ reduction showed only one phase, the cubic fluorite phase of CeO<sub>2</sub> (ICDD file 34-0394;  $a = b = c = 0.541134$  nm), for those catalyst samples reduced between 25 and 800 °C under  $\text{H}_2$ . The shift of the peaks to the lower  $2\theta$  values is mainly due to the thermal expansion coefficient of ceria for the catalysts reduced between 25 and 500 °C. In this temperature range, a negative shift of 0.16° on the (111) peak of ceria at 28.5° and of 0.27° on the (220) peak at 47.5° was observed: from these values, a linear thermal expansion factor of  $2.29 \times 10^{-5} \text{ K}^{-1}$  can be derived. This value is slightly higher than those reported in the literature for CeO<sub>2</sub> ( $1.15 \times 10^{-5} \text{ K}^{-1}$  between ambient and 500 °C), which can be ascribed to the presence of  $\text{Ce}^{3+}$  and oxygen vacancies in the ceria network [27]. At 800 °C, an increased shift can be observed (−1.15° between 500 and 800 °C on the peak at 47.5°) which is due to two conjugated factors, thermal expansion and significant formation of oxygen vacancies, in agreement with Perrichon et al. [28] and Lamonier et al. [29,30]. No peak width broadening is noticed when the reduction temperature is increased from 25 to 800 °C (peak width 0.47° at  $2\theta = 28.5^\circ$ , and 0.57° at  $2\theta = 47.5^\circ$ ), which

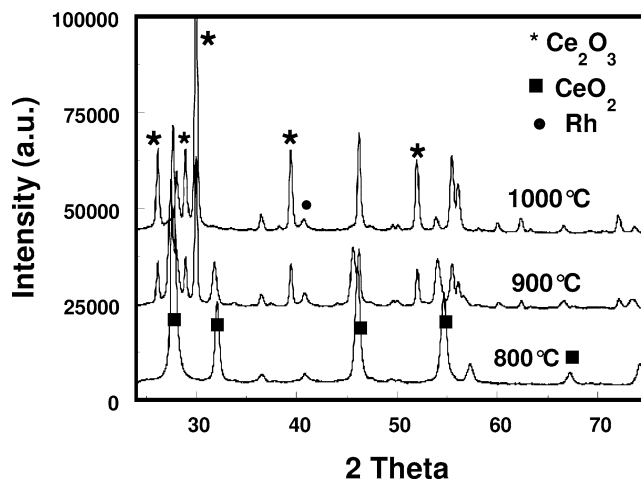


Fig. 4. In situ X-ray diffractograms of Rh/CeO<sub>2</sub> reduced between 800 and 1000 °C.

proves that the catalyst sample was very stable. Taking into account the peak width broadening of the apparatus, the mean size of CeO<sub>2</sub> crystallites can be estimated at about 22 nm. This value is smaller than the mean diameter of ceria particles deduced from the BET area of catalyst (36.5 nm; see Appendix A), which strongly indicates that individual particles are composed of several monocrytals of ceria.

The diffractograms recorded above 800 °C are shown in Fig. 4.

The reduction of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub> can be observed (ICDD file 23-1048; hexagonal structure;  $a = b = 0.393646$  nm and  $c = 0.615680$  nm). Small amounts of a phase identified as CeO<sub>1.83</sub> or Ce<sub>6</sub>O<sub>11</sub> appear in the diffractogram recorded at 900 °C (ICDD file 32-0196; monoclinic;  $a = 0.6781$  nm,  $b = 1.11893$  nm, and  $c = 1.5823$  nm;  $\alpha = \gamma = 90^\circ$  and  $\beta = 125.04^\circ$ ).

A catalyst sample reduced at 980 °C and treated in five pulses of water at this temperature was characterised by XRD, which confirmed that ceria was totally reoxidised into the fluorite form of CeO<sub>2</sub>. No significant sintering of ceria was observed, its mean crystallite size being close to 25 nm after  $\text{H}_2\text{O}$  pulses.

### 3.6. Electron microscopy and diffraction

Rh particles of cubic or hexagonal shape, some apparently truncated, have been observed in the catalyst reduced at 500 °C (TEM picture not shown). This is in agreement with the experimental HREM pictures and image simulations reported by Bernal et al. showing truncated cubooctahedron particles in a 2.4% Rh/CeO<sub>2</sub> ( $4 \text{ m}^2 \text{ g}^{-1}$ ) reduced at 350 or 500 °C [31,32]. The mean particle size of Rh is 2.7 nm with sizes in the range 1.7–4.3 nm. After reduction at 980 °C, TEM pictures (Fig. 5) reveal a definite increase of the mean particle size at about 8.7 nm.

Nevertheless, the size distribution is rather heterogeneous, with sizes ranging from 3.4 to 16.5 nm. Particle

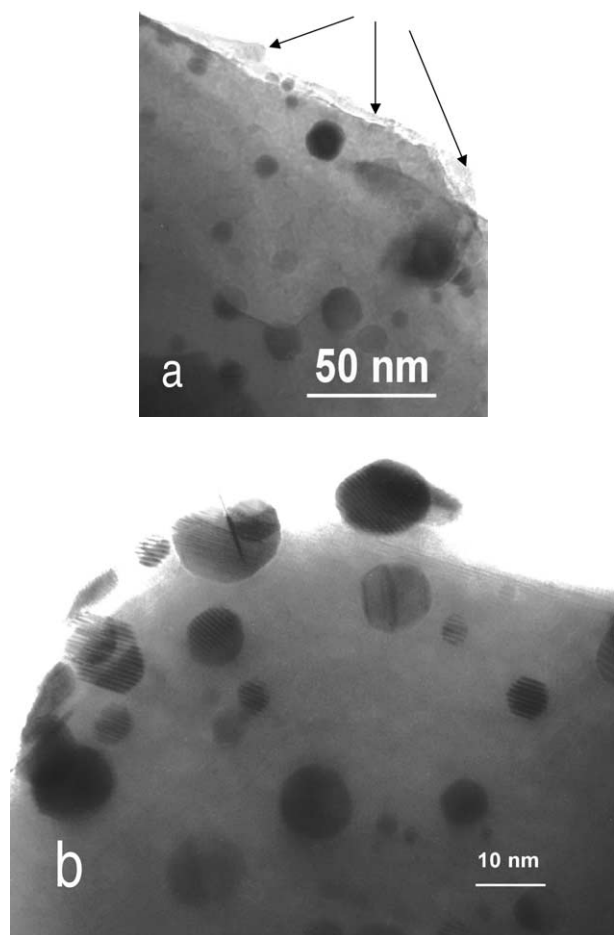


Fig. 5. TEM micrographs of Rh/CeO<sub>2</sub> reduced at 980 °C: (a) low magnification, (b) high magnification.

shapes are similar to those observed on RhCeR500. However, the high-magnification image (Fig. 5b) clearly evidences moiré patterns likely due to epitaxial phenomena between the support and the Rh particles, in agreement with the HREM studies of Bernal et al. [31,32]. A thin layer of amorphous CeO<sub>2-x</sub> moieties at the surface of ceria crystallites appears in Fig. 5a (arrows). This thin layer seems not to cover the metal particles. Water treatment at 980 °C (Fig. 6) does not lead to additional sintering of Rh, the mean particle size being even lower (7.8 nm) than after reduction, with a relatively narrow distribution (4.1–10.9 nm, Fig. 6a).

Ce-containing crystalline phases detected by selected area electron diffraction are reported in Table 3. Cubic ceria is not reported in the table: this is the major phase in all instances (except RhCeR980). Cubic suboxides CeO<sub>2-x</sub> with  $0 < x < 0.25$  cannot be distinguished from CeO<sub>2</sub>. As of 500 °C, some patches of hexagonal Ce<sub>2</sub>O<sub>3</sub> start to be detected, whereas this phase was not yet visible by XRD. After reduction at 980 °C, electron diffraction clearly shows the presence of intermetallic compounds between Rh and Ce (CeRh and Ce<sub>5</sub>Rh<sub>4</sub>, in particular) as well as a relatively high number of Ce<sub>2</sub>O<sub>3</sub> particles (Table 3 and Fig. 7). After a subsequent treatment in steam, all the intermetallic particles

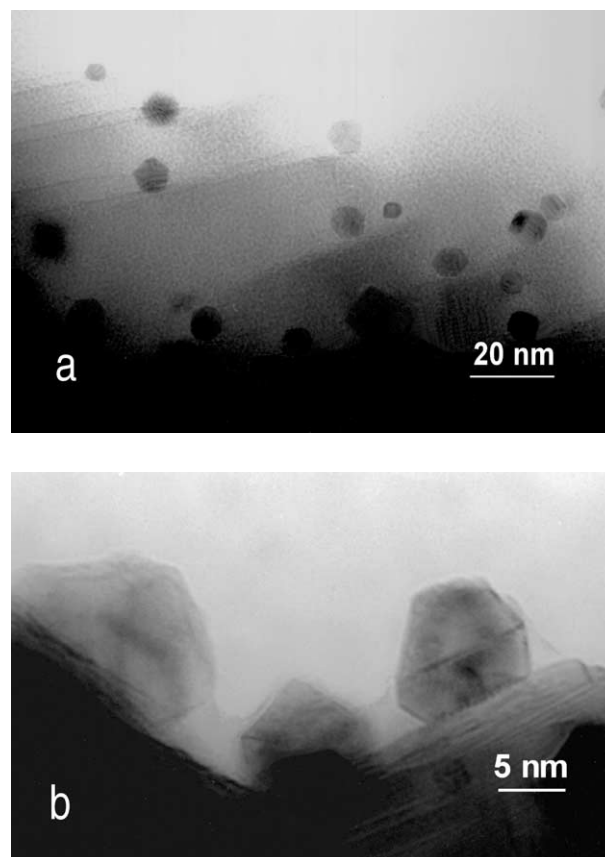


Fig. 6. TEM micrographs of Rh/CeO<sub>2</sub> reduced at 980 °C, then treated in steam at the same temperature: (a) low magnification, (b) high magnification.

disappear but some hexagonal oxide particles (Ce<sub>2</sub>O<sub>3</sub>) still remain visible.

## 4. Discussion

### 4.1. Thermodynamics of the reduction of ceria by H<sub>2</sub>

Thermochemical data of CeO<sub>2</sub> and suboxides of cerium have been reported by Barin [33] and by Karapetyants and Karapetyants [34]. The Gibbs free energy of formation follows a linear relationship with the temperature (in K)

$$\Delta G_f^0 = a + bT. \quad (9)$$

Numerical values of  $a$  and  $b$  for the different oxides are reported in Table 4. Data of Barin [33] lead to a monotonic increase of  $a$  and a decrease of  $b$  with  $x$ . Data of Karapetyants and Karapetyants [34] are obviously outside of this tendency, which shows that the two set of data are not coherent. A possibility could be to normalise the coefficients  $a$  and  $b$  deduced from Karapetyants's data with those of Barin. However, as there remained some doubt about the former, only the later set of data were considered for calculating equilibrium constants of the reaction:

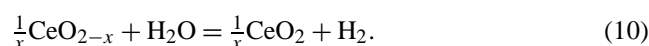


Table 3

Identification by electron diffraction of Ce-containing phases formed after different treatments (CeO<sub>2</sub> not reported)

Sample	Phase	Zone axis	Structure
RhCeR500	Ce <sub>2</sub> O <sub>3</sub>	[110]	Hexagonal
RhCeR980	Ce <sub>2</sub> O <sub>3</sub>	[110]	Hexagonal
	Ce <sub>5</sub> Rh <sub>4</sub>	[321]	Orthorhombic
	Ce <sub>5</sub> Rh <sub>4</sub>	[110]	Orthorhombic
	CeRh	[120]	Orthorhombic
	Ce	[010]	Quadratic
RhCeR980W980	Ce <sub>2</sub> O <sub>3</sub>	[110]	Hexagonal

The reaction is strongly shifted to the right over a large temperature range:  $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$  ratios at equilibrium are very high at low temperatures and become lower than one around 875 °C for CeO<sub>1.83</sub> and CeO<sub>1.72</sub>, while still higher temperatures (about 1050 °C) are required to shift the equilibrium to the left for CeO<sub>1.5</sub>. This means that the reaction of reduced ceria with steam is possible in a very large range of temperatures. Conversely, high temperatures are necessary to reduce ceria, but the reduction to suboxides is significantly more easy than the reduction to Ce<sub>2</sub>O<sub>3</sub>.

#### 4.2. Mechanism of the reduction of ceria by H<sub>2</sub>

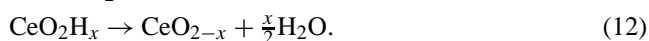
The reduction of CeO<sub>2</sub> into CeO<sub>2-x</sub> oxides has been studied by many authors. Most of them concluded that the reduction proceeded in two steps: first the surface layers at a temperature  $T_S$  and then the bulk of the oxide at  $T_B$  [2,22–24,35]. The presence of a noble metal decreases  $T_S$  (from ≈ 600 to ≈ 200 °C) but has no or little effect on  $T_B$  (> 600 °C). Contrasting with this general agreement about the surface or the bulk reduction, the mechanism of the reaction still remains a matter of debate. El Fellah et al. [36] proposed a four-step model: (i) formation of hydroxyl groups by dissociation of chemisorbed H<sub>2</sub>, (ii) formation of anionic vacancies and reduction of the neighbouring cations, (iii) desorption of water by recombination of H<sub>2</sub> and OH groups, (iv) diffusion of the surface vacancies in the core of the solid. Another mechanism was established by Ferriro et al. [37] and by Cunningham et al. [38], who suggested

Table 4

Linear coefficients of the relationship between the Gibbs free energy of formation of CeO<sub>2-x</sub> oxides (kJ mol Ce<sup>-1</sup>) and the temperature in K (Eq. (9))

$x$	Oxide formula	$a$	$b$	Ref.
0	CeO <sub>2</sub>	-1086.7	0.2062	[31]
1/6	CeO <sub>1.83</sub> (Ce <sub>6</sub> O <sub>11</sub> )	-1028.1	0.1824	[31]
2/11	CeO <sub>1.81</sub> (Ce <sub>11</sub> O <sub>20</sub> )	-1055.2	0.2388	[32]
2/9	CeO <sub>1.78</sub> (Ce <sub>9</sub> O <sub>16</sub> )	-1042.5	0.2354	[32]
2/7	CeO <sub>1.72</sub> (Ce <sub>7</sub> O <sub>12</sub> )	-990.88	0.1706	[31]
1/3	CeO <sub>1.67</sub> (Ce <sub>6</sub> O <sub>10</sub> )	-995.86	0.2184	[32]
1/2	CeO <sub>1.50</sub> (Ce <sub>2</sub> O <sub>3</sub> )	-894.61	0.1382	[31]

the incorporation of H<sub>2</sub> in the cerium oxide to form ceria bronzes according to the following reactions:



The insertion of H<sub>2</sub> as a hydride into ceria-based materials has also been reported by Lamonier et al. [29,30]. The catalysts were characterised by different techniques: in situ XRD, in situ XPS, and thermogravimetry. The amounts of H stored in the catalysts were measured by the ability of the solid to hydrogenate isoprene in the absence of gaseous hydrogen. The results can reasonably be explained by an heterolytic dissociation of H<sub>2</sub> according to the reaction



The authors did not observe Ce<sub>2</sub>O<sub>3</sub> nor suboxide-like Ce<sub>6</sub>O<sub>11</sub> in a ceria reduced at 800 °C. A hydride phase of general formula Ce<sub>x</sub><sup>4+</sup>Ce<sub>1-x</sub><sup>3+</sup>O<sub>y</sub><sup>2-</sup>(OH<sup>-</sup>)<sub>z</sub>H<sub>r</sub><sup>-</sup>□<sub>u</sub> has been proposed by C. Lamonier to explain the significant shift of 2θ values observed for the (311), (220), and (111) peaks of the fluorite structure between 600 and 800 °C.

#### 4.3. Phases formed by reduction of Rh/CeO<sub>2</sub> in H<sub>2</sub> at 800–1000 °C

In the present work, different phases were identified in Rh/CeO<sub>2</sub> reduced in H<sub>2</sub>. In situ DRX showed that a cubic-

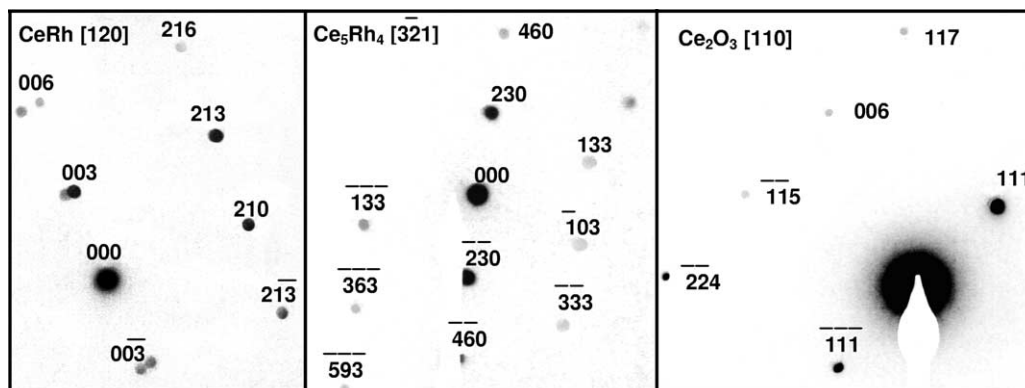
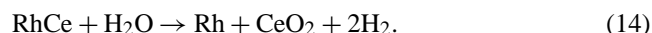


Fig. 7. Electron diffraction patterns of selected area on Rh/CeO<sub>2</sub> reduced at 980 °C.

like structure was maintained in the cerium oxide between ambient temperature and 800 °C. The peaks are shifted to lower angles as reduction temperatures are increased. Up to 700 °C,  $2\theta$  shifts can be ascribed to thermal expansion of the lattice. At 800 °C, an abrupt decrease of  $2\theta$  values suggests a profound change in the cubic structure of the support. Because of the relatively low accuracy of the in situ DRX technique, it is not possible to calculate precise crystallographic data of this new phase, intermediate between expanded lacunar ceria (cubic) and  $\text{Ce}_2\text{O}_3$  (hexagonal). In accordance with Perrichon et al. [28] this phase could be ascribed to a cubic form of  $\text{Ce}_2\text{O}_3$ . This is in line with the recent review of Trovarelli [39], who stressed the fact that  $\text{Ce}_2\text{O}_3$ , normally hexagonal, could have a cubic-like structure under certain conditions. Oxygen might be in slight excess in cubic Ce(III) oxide, whose formula would be  $\text{Ce}_2\text{O}_{3+\delta}$  with  $0 < \delta < 0.3$ .

If most of the cerium atoms are present as  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ions, a small proportion of them are reduced to the zerovalent state. These  $\text{Ce}^0$  atoms are generally combined with Rh to form rhodium cerides in agreement with the results obtained by Chojnacki et al. on model Rh/ $\text{CeO}_x$ / $\text{SiO}_2$  catalysts [13].  $\text{CeRh}$  and  $\text{Ce}_5\text{Rh}_4$  compounds were identified by electron diffraction, even though isolated  $\text{Ce}^0$  crystals could appear in the reduced catalyst (Table 3). Metallic rhodium was found in the catalyst after oxidation by water, so the reaction can be written as



Taking into account the metal loading in the catalyst, about 13% of the hydrogen produced could originate from Rh ceride compounds if all the Rh atoms were associated with Ce atoms in intermetallic compounds. The major part of  $\text{H}_2$  comes from reduced ceria not associated with Rh particles.

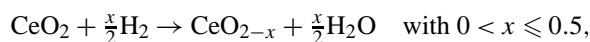
## 5. Conclusion

Water decomposition on reduced centres of ceria (the reverse reaction of the reduction) can be used to titrate anionic vacancies of this oxide, which has dominant redox properties. The number of vacancies is deduced from the amount of hydrogen produced in the reaction. Thermodynamics shows that water decomposition on reduced ceria to give hydrogen and  $\text{CeO}_2$  is possible at temperatures below 1000 °C. The method, applied to a Rh/ $\text{CeO}_2$  catalyst, shows that the reduction rate of ceria significantly increases above 500 °C (activation energy  $62.5 \text{ kJ mol}^{-1}$ ), but the reduction would be limited to  $\text{CeO}_{1.74}$ . In situ XRD reveals that the structure of the cerium oxide remains cubic up to 800 °C, a temperature at which a new cubic phase—possibly cubic Ce(III) oxide—is shown to appear. At 900 and 1000 °C, the support is composed of a mixture of two phases: cubic  $\text{CeO}_{2-x}$  and hexagonal  $\text{Ce}_2\text{O}_3$ . Electron diffraction also shows that Rh particles can react with fully reduced cerium to form Rh

cerides (mainly  $\text{CeRh}$  and  $\text{Ce}_5\text{Rh}_4$ ). After reaction with water, only  $\text{CeO}_2$  and  $\text{Rh}^0$  are identified by XRD and electron diffraction in the catalyst: reduced ceria and  $\text{Ce}^0$  atoms of Rh cerides are fully reoxidised into  $\text{CeO}_2$ . This reaction occurs at temperatures as low as 100 °C and reaches its maximum at about 850 °C. The amount of  $\text{H}_2$  produced at 100 °C is, however, not negligible: it represents 74% of the maximum yield observed at 850 °C. The formation of rhodium cerides and the high temperature required to titrate all or almost all oxygen vacancies are the main limitations of this relatively simple technique.

## Appendix A. Determination of the number of reduced centres of ceria

During the reduction of ceria by  $\text{H}_2$  the following reaction can occur,



which can be written as Eq. (3) given in the Introduction. Before reduction, the 3.7% Rh/ $\text{CeO}_2$  catalyst contains 4.56% rhodium oxide (as  $\text{Rh}_2\text{O}_3$ ) and 95.44%  $\text{CeO}_2$  (it is assumed that the number of vacancies in the oxidised sample is negligible). The total number of  $\text{Ce}^{4+}$  in the catalyst is  $5545 \mu\text{mol g}^{-1}$ , associated with  $11,090 \mu\text{mol O g}^{-1}$ . The number of O corresponding to the total reduction of  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$  would be  $2772 \mu\text{mol g}^{-1}$  (one O out of four). The maximum amount of  $\text{H}_2$  that the reaction with  $\text{H}_2\text{O}$  can produce is then  $5545 \mu\text{mol H g}^{-1}$ .

Taking into account the density of ceria ( $7.28 \times 10^6 \text{ g m}^{-3}$ ), the concentration  $N_{\text{O}}$  of oxygen atoms is  $5.09 \times 10^{28} \text{ at m}^{-3}$ . The surface concentration can be approximated by

$$S_{\text{O}} = N_{\text{O}}^{2/3} = 1.374 \times 10^{19} \text{ at m}^{-2},$$

in agreement with the surface density of O atoms deduced from crystallographic data ( $13.6 \text{ O nm}^{-2}$  for a fluorite  $d$  spacing of 0.541 nm) [40].

The total number of O surface atoms in the Rh/ $\text{CeO}_2$  catalyst ( $23 \text{ m}^2 \text{ g}^{-1}$ ) is  $3.16 \times 10^{20} \text{ at g}^{-1}$ . Assuming that one O atom out of four can give rise to anion vacancies, the amount of hydrogen recovered by reaction of steam with the surface layer of ceria (reduced to  $\text{Ce}^{3+}$ ) will be  $262 \mu\text{mol H g}^{-1}$ . The number of equivalent layers of reduced ceria titrated by steam would be

$$n_{\text{L}} = \frac{Q_{\text{H}} (\mu\text{mol at H g}^{-1})}{262}. \quad (A.1)$$

Assuming that there is no microporosity in the crystals of ceria, their particle size can be given as a function of the BET area of ceria ( $A$  in  $\text{m}^2 \text{ g}^{-1}$ ) and of its density  $\rho$  in  $\text{g m}^{-3}$

$$d (\text{m}) = \frac{6}{\rho A} \quad \text{or} \quad d (\text{nm}) = \frac{841}{A}. \quad (A.2)$$

With a surface area of  $23 \text{ m}^2 \text{ g}^{-1}$ , this equation leads to 36.5 nm for the mean diameter of the ceria particles in Rh/ $\text{CeO}_2$ . There are two O layers per lattice parameter unit



of the fluorite structure (0.541 nm), i.e., a maximum of  $\approx 67$  oxygen layers in each ceria particle. Equation (A.1) is valid only for semi-infinite flat surfaces. In a finite particle, the amount  $Q_H$  per layer regularly decreases from the external surface to the centre of the particle. For a spherical particle of diameter 36.5 nm, the cumulative amount  $Q_H$  is given by the equation

$$Q_H = 265n_L - 4.11n_L^2 + 0.022n_L^3$$

and the inverse function can be approximated by

$$n_L = \frac{Q_H}{282} \left( 1 + \frac{Q_H}{7639} \right) \quad \text{for } 20 \geq n_L \geq 0. \quad (\text{A.3})$$

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