

# Metal Particles Coverage Evidenced by $^1\text{H}$ NMR Spectroscopy in High Surface Rh/CeO<sub>2</sub> Catalysts

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H<sub>2</sub> reduction at increasing temperatures of high surface Rh/CeO<sub>2</sub> catalyst ( $S_{\text{BET}} \approx 55 \text{ m}^2/\text{g}$ ) has been followed with  $^1\text{H}$  NMR spectroscopy. Metal–support interaction produces an important decrease in intensity of the shifted NMR signal ascribed to hydrogen adsorbed on metal particles, disappearing when the sample is reduced at 773 K. Oxidation at 473 K of reduced catalysts restores the position of this line, but intensity displays lower values than initial ones, suggesting that some metal coverage has been produced. Consecutive 773 K reduction/473 K oxidation treatments showed that metal coverage increases with the number of cycles. To analyze the origin of this phenomenon, the influence of temperature, time, and type of reduction has been studied. From results reported in this work, it has been concluded that diffusion of reduced species from the support is the main factor responsible for the metal coverage produced. Elimination of the metal coverage requires the oxidation at 673 K of the catalyst.

## Introduction

Cerium oxide plays an important role as promoter in three way catalysts (TWC) used for elimination of pollutants produced in automobiles.<sup>1–3</sup> The promoting effect of cerium oxide is mainly related to oxidation/reduction changes ( $\text{Ce}^{4+}$ – $\text{Ce}^{3+}$  couple) produced during formation/annihilation of surface oxygen vacancies, that increases the oxygen storage capacity of this oxide. When hydrogen adsorption is analyzed in Rh/CeO<sub>2</sub> catalysts, spill-over of hydrogen adsorbed on the metal favors the reduction of CeO<sub>2</sub> at metal–support contacts. Reduction of Rh/CeO<sub>2</sub> catalysts with hydrogen at 473 K produces an increase of  $\text{Ce}^{3+}$  and OH groups; however, reduction at higher temperatures produces the partial elimination of oxygen and the progressive increase of  $\text{Ce}^{3+}$  species at the CeO<sub>2</sub> surface.<sup>4–7</sup>

High-temperature reduction of Rh/CeO<sub>2</sub> catalysts favors the interaction of the reduced support with supported metal particles, decreasing hydrogen adsorption capacity of rhodium particles (SMSI effect).<sup>8,9</sup> Two effects are usually accepted as causes of this phenomenon: (i) coverage of rhodium metal particles by CeO<sub>x</sub> ( $1 < x < 2$ ) suboxides and (ii) electronic perturbation of metal particles by the reduced support. At this moment, some discrepancies remain about the relative importance of these two phenomena in high-temperature reduced Rh/CeO<sub>2</sub> catalysts.<sup>5–18</sup> Bernal's group observed that coverage effects are not produced below 973 K;<sup>16–18</sup> however, previous results obtained in our group showed that appreciable metal coverage can be produced during reductions even at 673 K. On the other hand, the  $^1\text{H}$  NMR technique is capable of differentiating hydrogen adsorbed on the metal from that adsorbed on the support.<sup>19</sup> On the basis of this fact, the NMR technique is particularly suitable to follow the SMSI establishment.<sup>5,6,14,15,20–22</sup> In the case of Rh/TiO<sub>2</sub> catalysts, an estimation of electronic perturbation and coverage by suboxide layers of metal particles was obtained.<sup>21,22</sup>

In this work, the reduction of a high surface Rh/CeO<sub>2</sub> catalyst prepared by impregnation of CeO<sub>2</sub> with  $\text{Rh}(\text{NO}_3)_3$  has been investigated with the  $^1\text{H}$  NMR technique. In particular, the influence of temperature, time, and reduction type has been analyzed. It has been shown that migration of CeO<sub>x</sub> species from the reduced support enhances the electronic perturbation of metal particles. Elimination of metal–support interactions during oxidation of Rh/CeO<sub>2</sub> catalysts has also been analyzed.

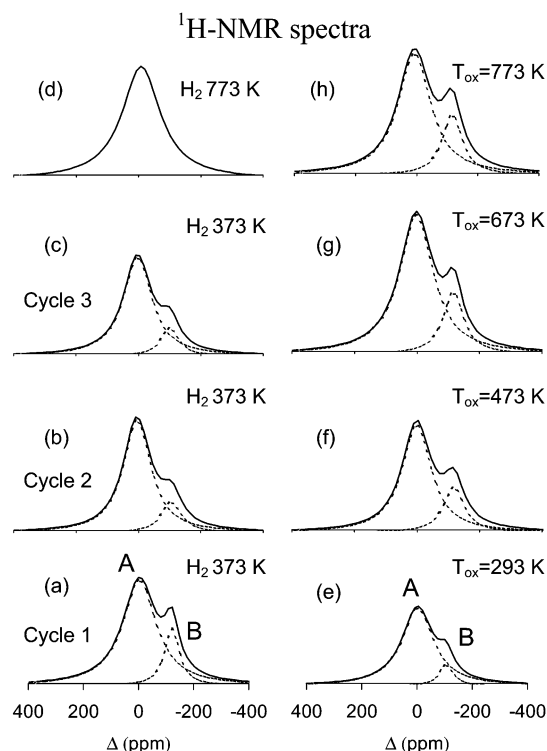
## Experimental Methods

Rh/CeO<sub>2</sub> catalysts were prepared by incipient wetness impregnation of CeO<sub>2</sub> (Rhodia,  $S_{\text{BET}} = 109 \text{ m}^2/\text{g}^{-1}$ ) with an aqueous solution of  $\text{Rh}(\text{NO}_3)_3$  to obtain a final Rh loading of 2.5 wt %. This salt was selected to avoid the blocking of electronic exchanges between metal particles and CeO<sub>2</sub> produced by chloride ions, when catalysts are obtained by  $\text{RhCl}_3$  impregnation.<sup>5,13,23</sup> The impregnated sample was first dried at 393 K for 24 h, then calcined at 673 K for 4 h (using a ramp up of  $4 \text{ K min}^{-1}$ ), and finally cooled in dry air to 295 K. The resulting precursor was reduced under flowing H<sub>2</sub> between 373 and 773 K.<sup>5</sup> The metal dispersion was determined by H<sub>2</sub> adsorption on the catalyst reduced at 473 K and outgassed at 523 K ( $\text{H}/\text{Rh} = 0.4$ ). This value corresponds to particles with a mean size of 2.5 nm. The BET surface area of the Rh/CeO<sub>2</sub> catalysts was  $55 \text{ m}^2/\text{g}$ .

Thermal treatments up to 773 K were carried out by placing the sample in Pyrex tubular cells provided with high-vacuum stopcocks. These cells allow the flow of gases through the catalyst as well as the outgassing of the sample. Reduction treatments at different temperatures and times were performed in conditions called “static” (closed cell with H<sub>2</sub> pressure of 150 Torr) or “dynamic” (H<sub>2</sub> flowing through the catalyst at about atmospheric pressure). Oxidation of the catalyst was always carried out under dynamic conditions.

$^1\text{H}$  NMR spectra were recorded at room temperature with an SXP 4/100 spectrometer equipped with an Aspect 2000 Fourier

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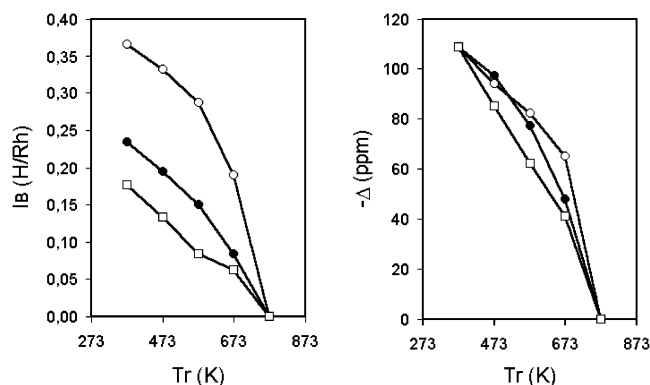
**Figure 1.**  $^1\text{H}$  NMR spectra of the Rh/CeO<sub>2</sub> catalyst reduced under flowing H<sub>2</sub> at 373 K in the first (a), second (b), and third (c) oxidation–reduction cycles. After reduction at 773 K (d), the sample was oxidized at 293 K (e), 473 K (f), 673 K (g), and 773 K (h). NMR spectra were recorded on samples outgassed at 423 K and exposed to H<sub>2</sub> (35 Torr).

transform unit. The NMR proton frequency was 75 MHz. Spectra were taken after  $\pi/2$  pulse excitations (3.5  $\mu\text{s}$ ). An interval of 1 s between successive accumulations was chosen to avoid saturation effects. The number of accumulations (1000) was selected to obtain a good signal-to-noise ratio ( $S/N > 20$ ). The intensities of the NMR lines were determined by comparing the integrated intensities with that of a known mica specimen.

## Results

The Rh/CeO<sub>2</sub> catalyst was reduced in flowing H<sub>2</sub> at 373, 473, 573, 673, and 773 K, 1 h each treatment. After the final reduction at 773 K, the sample was oxidized at 473 K and reduced in flowing H<sub>2</sub> at the above temperatures. After the second reduction cycle the sample was oxidized at 473 K and reduced in static conditions at the same temperatures. After each treatment, the sample was outgassed at 423 K to clean the metal surface, and exposed to H<sub>2</sub> (35 Torr) at 300 K before recording  $^1\text{H}$  NMR spectra.

$^1\text{H}$  NMR spectra of the Rh/CeO<sub>2</sub> catalyst, obtained after reduction at 373 K in the three mentioned cycles, are shown in Figure 1 parts (a), (b), and (c). Two lines are observed: line A centered at the resonance frequency, assigned to proton species located at the support, and line B upfield shifted due to adsorbed hydrogen on rhodium particles.<sup>14,15,19</sup> Taking into account that the intensity and the position of line B depend on the H<sub>2</sub> pressure and the reduction extent of the support,<sup>19–22</sup> NMR spectra were recorded on samples outgassed at 423 K and exposed to the same H<sub>2</sub> pressure (35 Torr). This pressure was chosen because of (i) the relative high amount of hydrogen adsorbed on metal particles and (ii) the high sensitivity of the position of line B to reduction treatments. In samples oxidized at 473 K, the intensity of line B decreases with the number of 773 K reduction/473 K oxidation cycles applied. Along the same treatments, the position



**Figure 2.** Variation of intensity ( $I_B$ ) and position of line B with reduction temperature in the first (open circles), second (closed circles), and third (open squares) oxidation–reduction cycles. After each reduction at 773 K, the Rh/CeO<sub>2</sub> catalyst was oxidized at 473 K. In all cases,  $I_B$  and  $\Delta$  values were measured in samples outgassed at 423 K and exposed to H<sub>2</sub> (35 Torr).

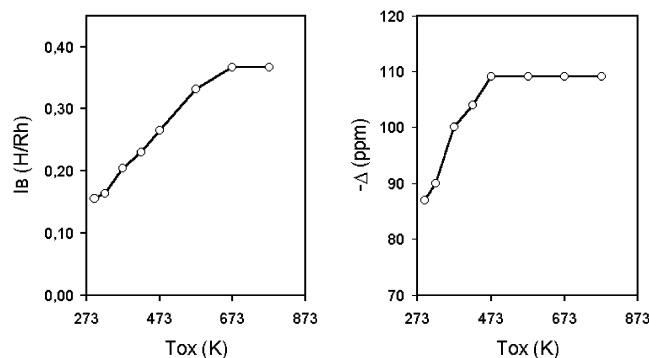
of line B does not change appreciably with the number of cycles (Figure 2). The  $^1\text{H}$  NMR spectra of the Rh/CeO<sub>2</sub> catalyst reduced at 773 K display only the line centered at the resonance frequency (line A) assigned to protons located on the support (Figure 1 (d)). The absence of the shifted line (line B), assigned to hydrogen adsorbed on metal particles, indicates that this adsorption has been fully suppressed by high-temperature reduction treatments (SMSI state).<sup>8,9</sup>

Figures 1 (e), (f), (g), and (h) show  $^1\text{H}$  NMR spectra of the sample reduced at 773 K, when it is oxidized in flowing O<sub>2</sub> at increasing temperatures, 293, 473, 673, and 773 K. After each of these oxidation treatments, the catalyst was reduced at 373 K outgassed at 423 K and exposed to H<sub>2</sub> (35 Torr). In all cases, line B is detected, increasing the intensity and separation from line A when oxidation temperature increases. Oxidation at 673 K (Figure 1 (g)), produces a small increase of line B without a change in position ( $\Delta = -109$  ppm). Above 673 K, the intensity of line B does not further increase with oxidation treatments (Figure 1, part h).

## Discussion

Intensity ( $I_B$ ) and position ( $\Delta$ ) of line B as a function of reduction temperature, corresponding to three consecutive reduction/oxidation cycles, are analyzed in Figure 2. The analysis of the intensity ( $I_B$ ) allows an estimation of the hydrogen adsorption on the metal, and the analysis of the position ( $\Delta$ ) allows the study of the changes produced in the hydrogen–metal interaction.<sup>20–22</sup> In Rh/CeO<sub>2</sub>, reduction treatments at increasing temperature decrease the  $I_B$  and  $\Delta$  values, indicating the progressive establishment of metal–support interactions. The decrease of  $\Delta$  shows the modification in the hydrogen–rhodium interaction induced by the support reduction (electronic effect). The oxidation at 473 K produces the total recuperation of  $\Delta$  (–109 ppm), indicating that the electronic perturbation disappears with this treatment. On the contrary,  $I_B$  decreases in subsequent reduction/oxidation cycles, indicating that oxidation at 473 K does not restore the adsorption capacity of the metal. The same observations were reported in Rh/TiO<sub>2</sub> catalysts.<sup>21,22</sup>

Reduction of the sample at increasing temperature produces a decrease of  $I_B$  and  $\Delta$  parameters and the elimination of the line B during 773 K reduction (Figure 1 (d)). These results differ from those reported during high-temperature reduction of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, in which metal sintering occurred.<sup>24</sup> In the latter catalyst, the shift of line B decreases in an asymptotic way to



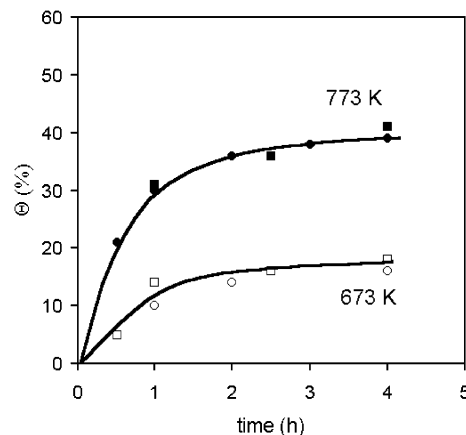
**Figure 3.** Plot of intensity ( $I_B$ ) and position ( $\Delta$ ) of line B vs oxidation temperature. The sample was first reduced at 773 K and then oxidized at increasing temperatures (1 h). After the oxidation treatments, the sample was reduced in  $H_2$  (50 Torr) at 373 K (1 h) and outgassed at 423 K. Values of  $I_B$  and  $\Delta$  were measured at  $p(H_2) = 35$  Torr.

the value of  $-120$  ppm measured in large ( $100 \text{ \AA}$ ) particles. However, in Rh/CeO<sub>2</sub>, the intensity and shift of line B decrease drastically during reduction treatments, disappearing at 773 K. The oxidation at 673 K recovered the starting  $I_B$  and  $\Delta$  values, indicating that no agglomeration of metal particles was produced in the Rh/CeO<sub>2</sub> catalysts along the three reduction/oxidation cycles analyzed. These results differ from those reported in Rh–Ce catalysts supported on silica, where some redispersion of the Rh was produced during oxidation–reduction cycles.<sup>25</sup>

The reduction at increasing temperatures of Rh/CeO<sub>2</sub> produced a progressive decrease of the hydrogen–metal interaction and hydrogen adsorption capacity of the metal. In particular, reduction at 773 K produced the total elimination of hydrogen adsorption on the metal. To eliminate metal–support interactions, which reduce hydrogen adsorption on metal particles, the sample was oxidized at increasing temperatures. The evolution of  $I_B$  and  $\Delta$  versus oxidation temperature is given in Figure 3. In samples oxidized at 293 K, the  $I_B$  and  $\Delta$  values are still very low, indicating that this treatment does not restore the adsorption and electronic properties of the metal particles. Oxidation treatments in the range 293–473 K produce a significant increase of hydrogen adsorption and the recuperation of the metal behavior, as deduced from the increase of the  $I_B$  and  $\Delta$  values. Above 473 K, a plateau of  $\Delta$  is detected ( $\Delta = -110$  ppm), indicating that the electronic properties of the metal are not further modified. Between 473 and 673 K,  $I_B$  still increases, and at 673 K,  $I_B$  attains a plateau, indicating that hydrogen adsorption on the metal is fully recovered and the SMSI eliminated. Subsequent oxidation at 773 K does not change the  $I_B$  value.

In line with the above observations, the increase of  $I_B$  and  $\Delta$  produced during oxidations between 293 and 473 K has been mainly ascribed to the suppression of the electronic perturbation of the metal. However, the increase of  $I_B$  detected in the range of 473–673 K, without changes in  $\Delta$ , has been ascribed to the progressive elimination of CeO<sub>x</sub> overlayers that are physically blocking the metal surface. In Rh/CeO<sub>2</sub> catalysts, these overlayers are fully removed by oxidation at 673 K. From NMR results, the most efficient treatment to restore hydrogen adsorption capacity of the metal consists of oxidation of the sample at 673 K followed by reduction at 373 K.

When oxidation is carried out at 473 K, metal particles remain partly covered by CeO<sub>x</sub> species. An estimation of the metal covered in reduced samples can be done with <sup>1</sup>H NMR spectroscopy.<sup>21</sup> For that, differences of  $I_B$  measured in samples oxidized at 473 ( $I_{B,O473}$ ) and 673 K ( $I_{B,O673}$ ) after each reduction treatment have been used for determining the metal surface



**Figure 4.** Effect of the reduction time on the metal surface covered by CeO<sub>x</sub> species in the Rh/CeO<sub>2</sub> catalyst, reduced in  $H_2$  at 673 and 773 K in static (squares) and dynamic (circles) conditions. The covered surface ( $\Theta$ ) was deduced by subtraction of the  $I_B$  values of samples oxidized at 673 and 473 K after each reduction treatment. These values were normalized with respect to that of the sample oxidized at 673 K.

covered by CeO<sub>x</sub> overlayers ( $\Theta = (I_{B,O673} - I_{B,O473})/I_{B,O673}$ ). To minimize the possible loss of these species during oxidation at 473 K, this treatment was applied for short times (1 h). On this basis, the influence of temperature and time of reduction on the extent of metal surface covered by CeO<sub>x</sub> overlayers has been analyzed.

A plot of  $\Theta$  versus the time used in reduction treatments of Rh/CeO<sub>2</sub> at 673 and 773 K in static and dynamic conditions is shown in Figure 4. It is observed that  $\Theta$  increases with reduction time, quickly at short times and slowly at times higher than 2 h. The observed behavior is characteristic of a diffusion process. Higher  $\Theta$  values are obtained when the reduction in  $H_2$  is carried out at higher temperatures. In particular, the metal surface covered by CeO<sub>x</sub> species is 15 and 40% after 4 h of reduction at 673 and 773 K, respectively. No influence of the type of treatment, static or dynamic, was observed (squares and circles of Figure 4).

Important differences in metal coverage have been detected during the reduction of Rh/CeO<sub>2</sub> and Rh/TiO<sub>2</sub> catalysts.<sup>21</sup> Similar plateaus ( $\Theta = 40\%$ ) were attained at lower reduction times in Rh/CeO<sub>2</sub> (2 h) than in Rh/TiO<sub>2</sub> (12 h). The higher reducibility of CeO<sub>2</sub> explains also the total elimination of line B, produced during the reduction at 773 K in static conditions of Rh/CeO<sub>2</sub>, that was not produced in Rh/TiO<sub>2</sub> catalysts. The second difference refers to smaller  $\Theta$  values found after reduction at 773 K for Rh/CeO<sub>2</sub> (40%), as compared with those of Rh/TiO<sub>2</sub> (60%), under the same conditions. We think that the higher reducibility of CeO<sub>2</sub> induces a faster and more intense electronic metal–support interaction, which makes the detection of the metal coverage in Rh/CeO<sub>2</sub> more difficult.

In previous works, Bernal et al. obtained HRTEM images showing the coverage of rhodium metal particles by CeO<sub>x</sub> species.<sup>16–18</sup> They concluded that metal decoration is only produced when the sample is reduced in the range of 973–1173 K, requiring an oxidation at 973 K to eliminate the metal coverage. However, results of our group showed that both phenomena, hydrogen adsorption loss and recovery, can be produced at milder temperatures, 673–773 K. The main difference in these two works is the surface area of the analyzed samples, low in the case of Bernal et al. ( $S_{BET} = 11 \text{ m}^2/\text{g}^{16}$  and  $4 \text{ m}^2/\text{g}^{17}$ ) and high in our case ( $S_{BET} = 55 \text{ m}^2/\text{g}$ ). In relation to this point, it has been recently shown that reduction of high surface samples is produced at 770 K, but reduction of low surface CeO<sub>2</sub> samples require temperatures near 1100 K.<sup>26</sup>

Differences in surface reducibility of used supports explain results reported on Rh/CeO<sub>2</sub> catalysts.<sup>27,28</sup> Migration of CeO<sub>x</sub> ( $1 < x < 2$ ) moieties will be produced at higher temperatures in low surface thermally stable Rh/CeO<sub>2</sub> catalysts. If the metal coverage is not important, the extent of the SMSI effect will decrease, and electronic perturbation will be preferentially detected.<sup>16–18</sup> In high surface samples, both phenomena are important and cannot be differentiated easily (Figure 1d). From these considerations, differences observed in high and low surface catalysts underline the importance of the textural characteristics of the supports used. In the case of metastable high surface supports, surface reactivity will be higher than in stabilized low surface supports. From this fact, the choice of a particular support must be done according to the working conditions of the application devices. Supports used in low-temperature methane oxidation<sup>29</sup> or in high-temperature autoexhaust converters (TWC)<sup>3</sup> should be clearly different.

## Conclusions

Evidences for coverage of rhodium metal particles by CeO<sub>x</sub> species in high surface Rh/CeO<sub>2</sub> catalysts reduced at 673 and 773 K are presented. From <sup>1</sup>H NMR data, the total elimination of metal hydrogen adsorption, produced in catalysts reduced at 773 K, results from the electronic perturbation and the partial decoration of metal particles with CeO<sub>2</sub> overlayers.

Oxidation of Rh/CeO<sub>2</sub> catalyst produces the elimination of the metal electronic perturbation in the range of 273–473 K, but the metal coverage is only eliminated after oxidation at 673 K. In Rh/CeO<sub>2</sub> catalysts, electronic and coverage effects are difficult to differentiate, requiring partial oxidation of Rh/CeO<sub>2</sub> catalysts to detect the metal decoration. The comparison of the intensity of the NMR line B of reduced samples after oxidations at 473 and 673 K allowed an estimation of the metal coverage extent. The coverage of the metal particles depends on the reducibility of the support, increasing with the temperature and time of reduction.

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