# Microstructural and Chemical Properties of Ceria-Supported Rhodium Catalysts Reduced at 773 K

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This work reports on the chemical and microstructural characterization of a series of $Rh/CeO_2$ catalysts. The volumetric adsorption and FTIR spectroscopic studies show the occurrence of considerable changes in the chemistry of the $H_2-(Rh/CeO_2)$ system upon increasing the reduction temperature from 623 to 773 K. However, the H/Rh values determined from hydrogen isotherms at 191 K suggest that the rhodium microcrystals remain chemically active after reduction at 773 K. The major effect of the high-temperature reduction treatment would be the blocking of the spillover process, much slower on the catalysts reduced at 773 K. In agreement with this, no dramatic effect of the reduction temperature on the catalytic activity for benzene hydrogenation has been found. These observations contrast with some recent results in the literature, in accordance with which ceria-supported metal catalysts exhibit the so-called SMSI effect. The high-resolution transmission electron microscopy (HRTEM) micrographs reported here for $Rh/CeO_2$ catalysts show clean, well-faceted rhodium particles. No evidences of metal decoration phenomena like those earlier reported for $Rh/TiO_2$ could be obtained from them. However, HRTEM images of the metal/support interface reveal an epitaxial growth of the rhodium microcrystal on ceria. The structural nature of this epitaxial relationship is rather singular leading to the regular appearance of rhodium dislocations at the metal/support interface. In addition to several other observations also based on the HRTEM images, the occurrence of such an epitaxy might well be interpreted as being due to some kind of strong metal–support interaction. The ensemble of results presented here suggests that the nature of this rhodium–ceria interaction is different from that referred to as the classic SMSI effect.

## Introduction

Since Tauster et al.'s pioneering works on the so-called strong metal–support interaction (SMSI) effect,[1,2] it is generally acknowledged that reducible oxides are good candidates to exhibit this kind of phenomenon. This is the case of ceria, an oxide, which according to the literature can undergo reduction processes when treated with $H_2$[3–7] or CO[8–10] under relatively mild conditions. In fact, several authors have reported the occurrence of strong metal–support interactions on $Pt/CeO_2$,[11] $Ni/CeO_2$,[12,13] $Ir/CeO_2$,[14] and $Rh/CeO_2$.[15]

In some cases,[13,15] the behavior of the $M/CeO_2$ catalysts has been described in terms of what might be called a classic strong metal–support interaction (SMSI) effect, similar to the one seen on titania-supported metal catalysts.[16–21] In several other cases[11,14] alternative interpretations of the strong metal–support interaction phenomena have been proposed. Furthermore, some hydrogen adsorption studies carried out on $Pt/CeO_2$[22] and $Rh/CeO_2$[23–25] catalysts, reduced at 773 K, do not suggest the occurrence of the strong inhibition effects expected for catalysts in the SMSI state.[26]

The results above clearly indicate that the actual nature of metal–support interactions in ceria-supported metal phases is far from being well understood. Moreover, some recent studies from our laboratory[27–29] show that the chemistry of the $H_2-(Rh/CeO_2)$ system should be considered rather complex, thus introducing some further difficulties for the characterization of ceria-supported metal catalysts. As has been outlined by a number of authors,[22,30] the development of a characterization methodology that could be fruitfully applied to the so-called three-way catalysts represents a major challenge. In this respect, it would be recalled that ceria-supported noble metal catalysts are being very intensively investigated as model systems of the TWCs.[31]

For all the reasons above, it seemed interesting to us to initiate

a research program aimed at investigating both the chemical and microstructural properties of a series of $Rh/CeO_2$ catalysts. Three ceria samples, with quite different Brunauer–Emmet–Teller (BET) surface areas, as well as two metal precursor salts, $Rh-(NO_3)_3$ and $RhCl_3$, have been used in the preparation of our catalysts. The reduction temperatures were also varied, always including 773 K. Conventional characterization techniques like hydrogen volumetric adsorption and FTIR spectroscopy, as well as high-resolution transmission electron microscopy (HRTEM) have been extensively applied. The benzene hydrogenation was used as a test reaction to investigate the catalytic behavior of the samples. Some interesting conclusions have been drawn from our study about both the chemistry of the $H_2-(Rh/CeO_2)$ system and the nature of the rhodium–ceria interactions.

## Experimental Section

A major part of this work has dealt with catalysts which will be hereafter referred to as $Rh/CeO_2$-HSA. The rhodium loading was 2.9% by weight. They were prepared by the incipient wetness impregnation technique from an aqueous solution of $Rh(NO_3)_3$. The ceria used, $CeO_2$-HSA, with a purity of 99.9%, was a high surface area sample, 130 $m^2 \cdot g^{-1}$, supplied by Rhône-Poulenc Minerale Fine. As deduced from the nitrogen physisorption studies carried out at 77 K, the $CeO_2$-HSA samples exhibit microporosity, the amount of nitrogen condensed in micropores being equivalent to 16 $cm^3(NTP) \cdot g^{-1}$. After the impregnation treatment, the sample was dried in air, at 383 K, for 10 h, and further stored in a desiccator until its reduction in situ.

In addition, we have studied three other ceria-supported rhodium catalysts referred to as $Rh(2.4\%)/CeO_2$-BS (BET surface area, 11 $m^2 \cdot g^{-1}$), $Rh(1.9\%)/CeO_2$-BS (BET surface area, 7 $m^2 \cdot g^{-1}$), and $Rh/CeO_2$-JM (BET surface area, 49 $m^2 \cdot g^{-1}$). The first one, $Rh(2.4\%)/CeO_2$-BS, was prepared following the same procedure reported above. The metal loading was 2.4%. The

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**TABLE I: Volumetric Study of Hydrogen Chemisorption on Rh/CeO₂-HSA Catalysts**

| treatment | | BET[a] | H/Rh[b] | H/Rh[b] | H/Rh[b] | H/Rh[b] |
|---|---|---|---|---|---|---|
| redn temp (K) | evac temp (K) | surface area | isot 191 K | isot 295 K | 20 h 295 K | 1 h 473 K |
| 623 | 623 | 130 | 1.41 | 3.97 | 5.23 | 5.60 |
| 773 | 773 | 62 | 0.82 | 0.75 | 0.84 | 2.28 |
| 623[c] | 623 | 62 | | 0.83 | 1.52 | 2.11 |

[a] BET surface area in $m^2 \cdot g^{-1}$ as determined from $N_2$ adsorption at 77 K. [b] Apparent H/Rh ratio referred to the total amount of Rh in the catalyst. [c] The catalyst was reduced and evacuated at 773 K, reoxidized at 673 K with pure $O_2$, for 1 h, evacuated at 673 K, for 1 h, and further treated as indicated.

support was a commercial 99.9% pure sample from Alpha Ventron. The second catalyst sample, Rh(1.9%)/CeO₂-BS, with a metal loading of 1.9%, was also prepared by the incipient wetness impregnation technique, but RhCl₃ was used as the metal precursor salt. In the case of the Rh/CeO₂-JM catalyst, the rhodium precursor was RhCl₃. We used an aqueous solution and the incipient wetness impregnation technique. The metal loading was 3%. In this latter case, the support, CeO₂-JM, was prepared in our laboratory by calcining, at 873 K, for 4 h, a cerium hydroxycarbonate phase obtained by precipitation with an aqueous solution of ammonium carbonate from a solution of Ce(NO₃)₃. To eliminate residual carbonates and improve the textural stability of this oxide sample, it was further treated with flowing hydrogen at 773 K for 4 h and finally reoxidized in air at 773 K for 4 h.

Hydrogen volumetric adsorption measurements were carried out in a high-vacuum system equipped with a capacitance gauge, MKS Baratron, Model 220 BHS. In the case of conventional isotherm experiments, the time elapsed between successive adsorption measurements was routinely 20 min. The standard procedure for reducing the catalysts consisted of heating the precursor/support systems, prepared as indicated above, in a flow of $H_2$ (flow rate, 1 $cm^3 \cdot s^{-1}$), at a heating rate of 10 $K \cdot min^{-1}$, up to the selected reduction temperature. The catalysts were held for 1 h at this temperature, they were further pumped off at the reduction temperature for 1 h, and finally, they were cooled to 295 K under high vacuum.

The FTIR spectroscopy study was carried out with the help of a conventional quartz cell, which allowed the thermal treatment under controlled atmospheres, including flowing gases and high vacuum ($P < 10^{-4}$ Pa), of self-supporting disks pressed into 18 mm diameter wafers, weight ca. 40 mg. The spectra were recorded on a Philips instrument, Model PU9800; 100 scans at 4-$cm^{-1}$ resolution were routinely averaged.

The high-resolution transmission electron microscopy (HR-TEM) images were obtained with a JEOL JEM-2000-EX instrument, equipped with a top entry specimen holder and an ion pump. The structural resolution was better than 0.21 nm. The samples to be investigated were prepared as reported elsewhere.[23]

The catalytic activity measurements were carried out in a flow microreactor, under differential conditions. The standard experimental conditions were as follows: benzene partial pressure, 4.0 KPa (30 Torr); hydrogen partial pressure, 97.2 KPa (730 Torr); flow rate, 1 $cm^3 \cdot s^{-1}$; reaction temperature, 303 K. The analysis of the reaction products was performed by gas chromatography. The hydrogen was further purified before its use by passing it through a deoxo catalyst and a zeolite trap.

## Results and Discussion

**Hydrogen Chemisorption Studies.** Table I summarizes the results of our volumetric study of the hydrogen adsorption on the Rh/CeO₂-HSA catalysts. In the particular case of the ordinary isotherm experiments, the apparent H/Rh ratios reported in Table I were all determined from the experimental point corresponding

to $P_{H2} = 250$ Torr. In spite of the limitations inherent to this way of reporting our results, no corrections like those applied in refs 22, 24, and 25 to eliminate the so-called reversible hydrogen were introduced by us. These corrections may lead in the case of Rh/CeO₂ catalysts to a meaningless estimate of the metal dispersion and even introduce some further confusion. A number of reasons justify the criteria followed in this work. First of all, the isotherms recorded at 298 K for Rh/CeO₂-HSA catalysts may account for hydrogen adsorption taking place on both the metal and the support.[23,27–29,32] Second, because the two adsorption processes above take place at quite different rates, the ordinary isotherms lead to rather ill-defined situations, which do not represent in general true equilibrium states.[27–29] Third, in accordance with our own results, the longer the evacuation time at 298 K, the larger the amount of hydrogen eliminated from the catalyst after the first isotherm. Thus, the amounts of $H_2$ evacuated after pumping off the catalyst reduced at 623 K for 5, 60, and 600 min were H/Rh = 1.1, 1.3, and 2.2, respectively. This suggests that we cannot establish a precise evacuation time just leading to the elimination of the so-called reversible hydrogen. Furthermore, with the help of a magnetic balance, we have shown in ref 28 that large amounts of hydrogen chemisorbed on ceria can be eliminated from some Rh/CeO₂-HSA catalysts by simple evacuation at 298 K. In other words, the hydrogen eliminated by pumping off the Rh/CeO₂ catalysts, at room temperature, does not necessarily correspond to chemically insignificant very weakly adsorbed species, as usually is meant for reversible adsorbed hydrogen.[22]

In contrast to what might be expected for a catalyst in the SMSI state,[26] the amount of $H_2$ chemisorbed at 298 K by the Rh/CeO₂-HSA reduced at 773 K, H/Rh = 0.75, is far from negligible. Moreover, this H/Rh value underestimates the true hydrogen/metal ratio because data in Table I are all referred to the total amount of rhodium present in the catalyst, but only part of the metal is actually accessible to $H_2$ after reduction at 773 K. In effect, associated with the reduction treatment at 773 K there is a decrease of the catalyst BET surface area, from 130 to 62 $m^2 \cdot g^{-1}$, and presumably, an important metal loss via an encapsulation process. If a simple linear correction is applied, the H/Rh ratio would reach a value around 1.4. This rough correction actually overestimates the true H/Rh value because of the microporosity exhibited by the CeO₂-HSA sample.

The H/Rh value reported in Table I for the catalyst reduced at 623 K, H/Rh = 3.98, is much larger than the one obtained for the sample reduced at 773 K. This suggests that there is a relative inhibition of the chemisorptive properties of the Rh/CeO₂-HSA catalyst upon increasing the reduction temperature from 623 to 773 K. The question arising is whether the loss of chemisorption capability observed can be attributed to the operation of a classic SMSI-like effect. In this respect, it would be recalled that several authors have proposed the occurrence of such an effect on Ni/CeO₂[13] and Rh/CeO₂[15] catalysts.

The very large H/Rh value reported in Table I for the catalyst reduced at 623 K clearly shows the occurrence, at room temperature, of strong spillover phenomena. The same can be concluded from the results reported in some earlier studies.[23,27–29,32] With the help of a Faraday balance[27,28] and temperature programmed desorption studies,[29] it has also been shown that, at room temperature, the spillover rate of $H_2$ on the Rh/CeO₂-HSA catalysts reduced at 623 K or lower temperatures is slow. Specifically, 20 h long exposure times to $H_2$ ($P_{H2}$, 300 Torr) were needed to reach an apparent saturation of the catalyst at 298 K.[27,28] Since the spillover process may be blocked by lowering the adsorption temperature, low-temperature chemisorption studies might well be used to directly estimate metal dispersions. We have proposed in ref 29 that volumetric adsorption studies at 191 K can fruitfully be used for this purpose.

As can be deduced from Table I, for Rh/CeO₂-HSA reduced at 773 K, the H/Rh values determined from both 191 and 298
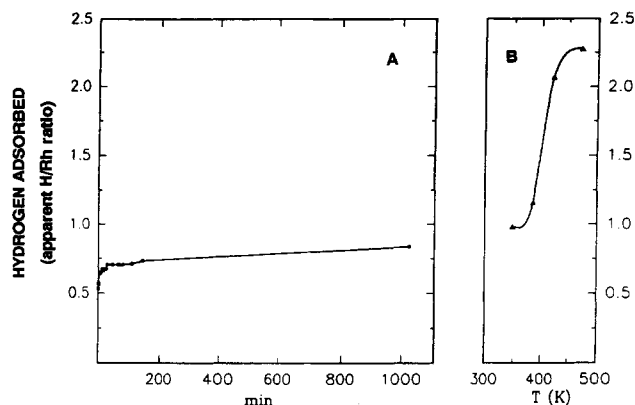
**Figure 1.** Volumetric study of hydrogen chemisorption on Rh/CeO₂-HSA reduced at 773 K. (A) Evolution of the amount of chemisorbed H₂ with time ($T$, 295 K; $P_{H2}$, 250 Torr). (B) Evolution of the amount of chemisorbed H₂ with temperature: treatments at 350, 385, 425, and 473 K (time, 1 h; $P_{H2}$, 250 Torr).

K isotherms are very close to each other. On the contrary, for the catalyst reduced at 623 K, the value estimated from the low-temperature isotherm is much smaller. This suggests that, after reduction at 773 K, the metal remains chemically active. Furthermore, in this particular case, it seems that the hydrogen adsorption would only take place on the metal at both 191 and 298 K. If the correction due to the support sintering discussed above is taken into account, the H/Rh ratio for the Rh/CeO₂-HSA catalyst reduced at 773 K would be 1.4, a value similar to the one estimated from the low-temperature isotherm for the sample reduced at 623 K. Since H/Rh values larger than unity have already been reported in the literature[33,34] for highly dispersed rhodium catalysts, the results above are consistent with catalysts exhibiting very high metal dispersion; in other words, no significant metal sintering or chemical deactivation of the rhodium crystallites seems to occur upon increasing the reduction temperature from 623 to 773 K. These observations are in good agreement with the FTIR spectroscopy, catalytic activity measurements, and HRTEM images reported below.

In summary, the main differences we can notice between the Rh/CeO₂-HSA catalysts reduced at 623 and 773 K would be as follows: the amount of exposed rhodium present in the catalysts, smaller in the latter case because of support sintering, and the negligible rate, at room temperature, of the hydrogen spillover on the catalyst reduced at 773 K. Since the spillover rate is generally considered to be faster on highly hydroxylated surfaces,[35,36] the differences we have observed between the two catalysts above might well be due to the lower concentration of hydroxyl groups on the ceria surface of the catalyst reduced and evacuated at 773 K.

We have also carried out a series of additional essays aimed at completing the classic isotherm studies discussed above. Figure 1 accounts for a volumetric experiment from which we have obtained some further details about the chemistry of the hydrogen adsorption on Rh/CeO₂-HSA catalyst reduced at 773 K. After completing the ordinary isotherm at 298 K, the catalyst was held in contact with H₂ for a long time, 18 h; then, it was submitted to a series of cyclic treatments consisting of heating the catalyst up to several increasing temperatures, 350, 385, 425, and 473 K, for 1 h, and cooling it again to 298 K, always under hydrogen. The amount of hydrogen adsorbed by the catalyst was determined after each of these cycles. The results reported in Figure 1, some of which are also included in Table I, clearly support the suggestion that for the catalyst reduced at 773 K, the spillover rate at 298 K is very small, making it necessary to heat to 425 K to observe a significant increase of the amount of adsorbed hydrogen.

The chemisorptive behavior of the Rh/CeO₂-HSA catalyst reduced at 773 K has also been studied by FTIR spectroscopy. The experiment was parallel to the one depicted in Figure 1. We
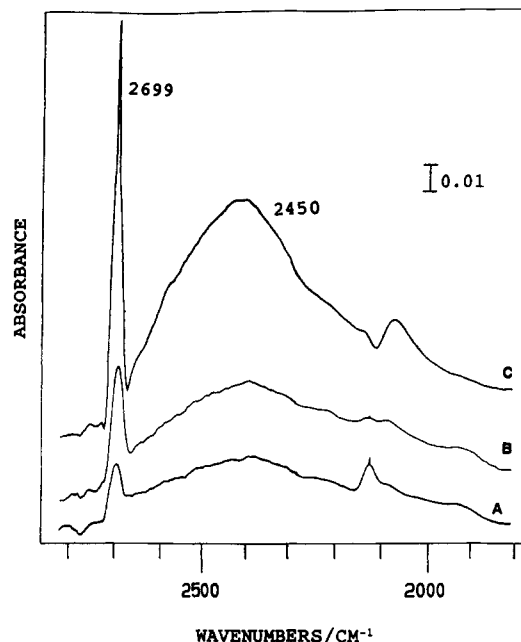


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**Figure 2.** FTIR study of D₂ ($P_{D2}$, 300 Torr) interaction with a Rh/CeO₂-HSA catalyst reduced at 773 K. Influence of the temperature of treatment: (A) 295 K, (B) 373 K, and (C) 473 K.

have obtained the spectra corresponding to the catalyst reduced and evacuated at 773 K, cooled under high vacuum to 298 K, and further treated for 1 h with 300 Torr of D₂ at 295 K (Figure 2A), 373 K (Figure 2B), and 473 K (Figure 2C). The spectra were recorded after cooling the catalyst to 298 K, under deuterium pressure. The O–D stretching region of the three spectra in Figure 2 is characterized by two main features: a narrow band at 2699 cm⁻¹ and a second one, much broader, centered at around 2450 cm⁻¹. These two bands can be correlated to those appearing at around 3650 and 3280 cm⁻¹ in the O–H stretching region. In accordance with the literature,[3,10,37,38] the band peaking at 2699 cm⁻¹ can reasonably be assigned to isolated OD species, whereas the low-frequency one would correspond to deuterium-bonded OD groups. The evolution undergone by the FTIR spectra reported in Figure 2 gives us some further very substantial experimental support to the conclusions drawn from the volumetric study. In effect, FTIR spectroscopy allows us to track the hydrogen chemisorption on ceria, thus confirming that even at 373 K the spillover rate on the Rh/CeO₂-HSA catalyst reduced at 773 K is very slow.

It is well-known that upon oxidizing and further rereducing at milder temperature a catalyst under SMSI state there should be a significant recovery of its chemisorptive properties.[1] We have carried out this type of experiment on the Rh/CeO₂-HSA catalyst reduced at 773 K. First, we reoxidized the sample at 673 K, with pure oxygen ($P_{O2}$, 760 Torr), for 1 h; then we rereduced it at 623 K, as usual. The bottom part of Table I accounts for the behavior of this catalyst. After recording the ordinary isotherm, at 298 K, the amount of chemisorbed hydrogen is slightly larger, H/Rh = 0.83, than that obtained for the sample reduced at 773 K, H/Rh = 0.75. Upon prolonging the hydrogen treatment at 298 K, for 20 h, the difference becomes larger, H/Rh = 1.52 for the catalyst reoxidized and further reduced at 623 K versus H/Rh = 0.84 for that reduced at 773 K. Finally, the H/Rh values obtained after activating the hydrogen adsorption at 473 K are again quite close to each other: 2.1 for the catalyst reoxidized and reduced at 623 K and 2.3 for the catalyst simply reduced at 773 K. This behavior is in complete agreement with that of a catalyst whose loss of chemisorption capability is due to support sintering and blocking of the spillover process, with no contribution of an SMSI-like phenomenon.

We have also studied the hydrogen volumetric adsorption on several other Rh/CeO₂ catalysts. Low (BS) and medium (JM)

**TABLE II: Volumetric Study of Hydrogen Chemisorption on Rh/CeO$_2$-BS and Rh/CeO$_2$-JM Catalysts**

| treatment | | BET$^a$ | H/Rh$^b$ | H/Rh$^b$ | H/Rh$^b$ | H/Rh$^b$ |
|---|---|---|---|---|---|---|
| redn temp (K) | evac temp (K) | surface area | isot 191 K | isot 295 K | 20 h 295 K | 1 h 473 K |
| Rh(NO$_3$)$_3$/CeO$_2$-BS (2.4 % Rh) | | | | | | |
| 523 | 523 | 11 | | 0.36 | | 0.51 |
| 523 | 773 | 11 | | 0.27 | 0.32 | 0.49 |
| 623 | 623 | 12 | 0.31 | 0.36 | 0.68 | 0.67 |
| 773 | 773 | 7 | 0.27 | 0.27 | 0.32 | 0.49 |
| RhCl$_3$/CeO$_2$-BS (1.9% Rh) | | | | | | |
| 773 | 773 | 7 | 0.26 | 0.21 | | |
| RhCl$_3$/CeO$_2$-JM (3% Rh) | | | | | | |
| 523 | 523 | 49 | 0.84 | 0.87 | | |
| 623 | 623 | 49 | 0.99 | 0.71 | | |
| 773 | 773 | 49 | 0.88 | 0.71 | | |

$^a$ BET surface area in m$^2$·g$^{-1}$ as determined from N$_2$ adsorption at 77 K. $^b$ Apparent H/Rh ratio referred to the total amount of Rh in the catalyst.

**TABLE III: Catalytic Activity Data for Benzene Hydrogenation on Rh/CeO$_2$ Reduced at 473 K and 773 K**

| catalyst | redn temp (K) | catalytic activity (mmol(C$_6$H$_{12}$)·g$^{-1}_{Rh}$·s$^{-1}$) |
|---|---|---|
| Rh/CeO$_2$-HSA | 473 | 0.25 |
| Rh/CeO$_2$-HSA | 773 | 0.10 |
| Rh(2.4%)/CeO$_2$-BS | 773 | 0.17 |

surface area ceria samples were used as supports. Likewise, rhodium nitrate and rhodium chloride have been investigated as metal precursor salts. Table II summarizes the results of this study.

In accordance with Table II, the H/Rh values determined from the low-temperature isotherms do not depend on the reduction temperature. Since support sintering is insignificant for these series of catalysts, it can be concluded, as already noted for the Rh/CeO$_2$-HSA catalysts, that the rhodium remains chemically active and the metal dispersion unmodified after reduction at 773 K; i.e., the Rh/CeO$_2$ samples investigated here do not seem to show the classic SMSI effect.

It has been shown in ref 39 that the chloride ions can notably modify the redox properties of ceria. In accordance with this, we have also included in the present study some catalysts prepared from RhCl$_3$. As it has already been commented, no strong inhibition of H$_2$ chemisorption on rhodium can be observed, even for the catalysts reduced at 773 K. However, the results in Table II indicate that the chloride ions depress the hydrogen adsorptive properties of ceria. In particular, we may notice that, in spite of the relatively high surface area of the Rh/CeO$_2$-JM catalysts, 49 m$^2$·g$^{-1}$, and the high metal dispersion of these catalysts, deduced from both HRTEM and volumetric adsorption studies, the spillover effects do not seem to be relevant, independent of the reduction temperature. In conclusion, the use of RhCl$_3$ as the metal precursor seems to disturb the mechanism of hydrogen transfer from the metal to the support, the chemisorptive properties of the support itself, or even both, to a much larger extent than the chemical properties of the metal.

**Catalytic Activity.** We have also studied the behavior of our catalysts toward the hydrogenation of benzene. This reaction has been used in earlier studies on ceria-supported metal catalysts.[11,13] Table III summarizes our results. The catalysts were reduced in situ with flowing hydrogen in the same way as in the chemisorption and FTIR experiments discussed above. After the reduction treatment, for 1 h, at either 473 or 773 K, the catalyst was cooled to room temperature in flowing hydrogen. Under the conditions used here, the only reaction product we observed was cyclohexane. The catalytic activity was found to increase during approximately the first hour. After this transient step, the activity was constant for hours. The results reported in Table III represent the behavior of the stabilized catalysts.
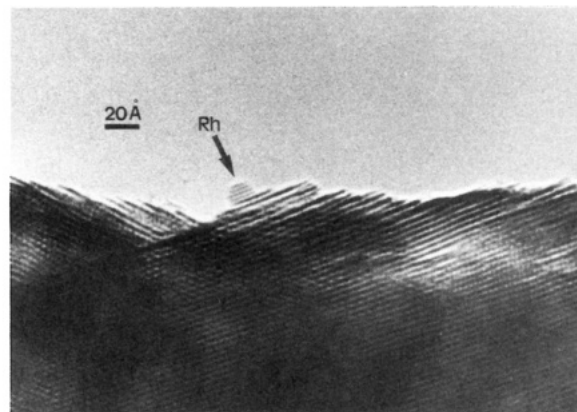


**Figure 3.** HRTEM image corresponding to the Rh/CeO$_2$-HSA catalyst reduced at 773 K.

No strong changes of catalytic activity can be noted in Table III upon increasing the reduction temperature from 473 to 773 K. For Rh/CeO$_2$-HSA the activity decreases by a factor less than 3, the actual variation being even smaller because support sintering and inherent metal encapsulation occurred after reduction at 773 K. Likewise, the catalytic activity for the Rh(NO$_3$)$_3$/CeO$_2$-BS sample does not suggest any inhibition effect associated with the reduction treatment at 773 K. Preliminary studies carried out by us for the acetone hydrogenation on the same catalysts led us to quite the same conclusion.

Some recent studies dealing with the hydrogenation of both benzene on Ni/CeO$_2$[13] and acetone on Rh/CeO$_2$[15] have reported a dramatic loss of catalytic activity upon increasing the reduction temperature. In both cases[13,15] the effect was observed for reduction temperatures lower than the highest value used here, 773 K. The authors[13,15] conclude that the ceria-supported metal catalysts show the SMSI effect. In the present case, in agreement with the results obtained by Naccache et al.[11] for benzene hydrogenation on Pt/CeO$_2$, the influence of the reduction temperature on the catalytic activity ought to be considered rather modest. This reinforces the conclusions drawn from the chemisorption studies, in accordance with which, the reduction treatment at 773 K does not induce strong perturbations on the chemical properties of the rhodium microcrystals.

**High-Resolution Transmission Electron Microscopy Studies.** The high-resolution transmission electron microscopy technique of surface profile imaging[40] has been used to investigate the microstructural properties of our catalysts. Figure 3 shows a representative image of the Rh/CeO$_2$-HSA catalyst reduced at 773 K. As in the case of the sample reduced at 623 K, the metal crystallites can hardly be observed, those identified being smaller than 1.5 nm. This suggests, in good agreement with the volumetric studies commented on above, that rhodium is ultradispersed, and also that no significant sintering of the metal crystallites takes place upon increasing the reduction temperature from 623 to 773 K. If images like that depicted in Figure 3 are analyzed in more detail, some further very interesting observations can be made. First of all, our HRTEM images do not suggest the occurrence of partial covering of the rhodium particles by the support, an effect well-known to occur on titania-supported metal catalysts in the SMSI state.[21,41,42] The absence of metal decoration effects, in addition to being very consistent with the chemisorption and catalytic activity results discussed above, is in complete agreement with some HRTEM studies reported earlier.[21,23,40,43,45] In brief, the high-resolution transmission electron microscopy images give substantial experimental support to the proposal that our ceria-supported rhodium catalysts, even after reduction at the highest temperature investigated here, 773 K, do not exhibit the classic SMSI effect.

Figures 4 and 5 account for the HRTEM study of Rh (2.4%)/CeO$_2$-BS reduced at 773 and 623 K, respectively. Because of the
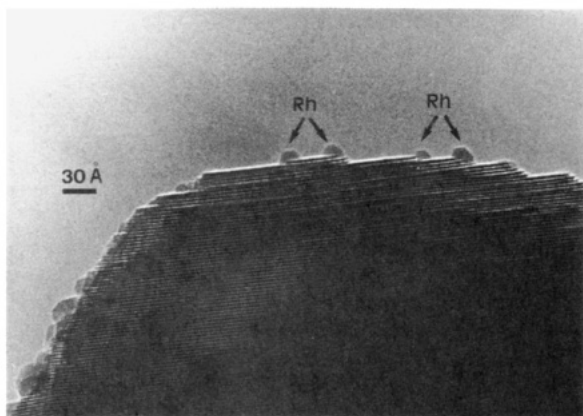
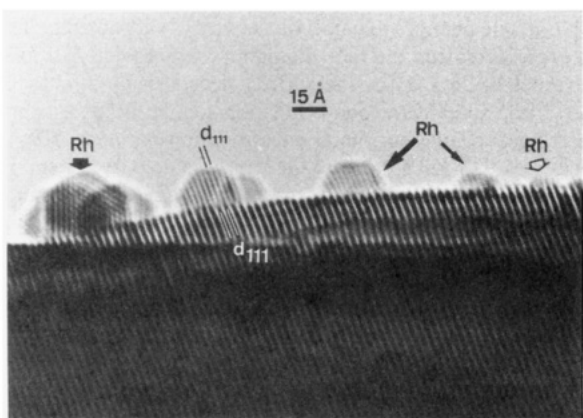**Figure 4.** HRTEM image corresponding to the Rh(2.4%)/CeO₂-BS catalyst reduced at 773 K.



**Figure 5.** HRTEM study of the Rh(2.4%)/CeO₂-BS catalyst reduced at 623 K.

low surface area of the $CeO_2$-BS sample, the particle size and surface concentration of the rhodium microcrystals is much higher than in the case of the Rh/CeO₂-HSA catalysts, thus allowing a more detailed microstructural study of the metal/support interface. There are a number of aspects to be commented on in relation to these two figures. The rhodium particles in Figures 4 and 5 look like clean, well-faceted microcrystals, thus confirming the absence of metal decoration effects. The mean crystal size of rhodium is only slightly modified by the reduction temperature, i.e., within the experimental range investigated here, there is no significant metal sintering. Though twinning is considered to be a usual mechanism of stabilization of very small metal particles,[44] the frequency of twinned rhodium crystallites is very low in the case of Rh/CeO₂ catalysts. This had already been noted in ref 44. Finally, there is an epitaxial growth of the metal crystallites on the support. The occurrence of such a structural relationship between rhodium and ceria has already been reported in the literature.[43-45] As it has been shown in ref 44 with the help of nanodiffraction techniques, this epitaxial relationship consists of the parallel growth of planes $(h,k,l)$ of rhodium on the same sort of $(h,k,l)$ planes of ceria. This type of structural relationship can also be deduced from the images presented in Figures 4 and 5. Moreover, the HRTEM technique provides some further very interesting details about the microstructure of the rhodium/ceria interface. Figure 5 shows the metal/support system in orientation $\langle 110 \rangle$. It can be seen that planes {111} of rhodium ($d_{111}$ Rh, 0.220 nm) grow parallel to planes {111} of the support ($d_{111}$ CeO₂, 0.312 nm). Similar observations have been reported in ref 45. In spite of the existence of some, in principle, less-strained possibilities for matching rhodium and ceria structures,[45] the epitaxial relationship experimentally observed consists of three planes of ceria fitted to four planes of rhodium, thus creating regular metal dislocations at the interface. This particular type

of epitaxial relationship, the almost complete absence of twinned metal crystallites, as well as the resistance of the metal particles to sintering, might well be considered as indications of some kind of strong metal–support interaction. The nature of this interaction, however, would not be like that referred to as the classic SMSI effect.[1,26]

**Conclusions.** The chemical and microstructural properties of 10 different Rh/CeO₂ catalysts have been investigated. In contrast with that expected for catalysts exhibiting the SMSI effect, reduction with flowing hydrogen, at 773 K, does not induce on any of the samples studied here the suppression of the hydrogen absorption on the metal, drastic effects on the catalytic behavior, nor decoration of the metal particles. It would be noted, however, that the chemisorptive properties of the catalysts are notably modified upon increasing the reduction/evacuation temperature. All the evidence gathered in this work indicates that the differences of chemical behavior observed are mainly due to changes of the spillover rate, much slower on the catalyst reduced at 773 K. Likewise, the use as metal precursor of RhCl₃ instead of Rh-(NO₃)₃ seems to modify significantly the behavior of the Rh/CeO₂ catalysts. As in the case of the effects induced by the increase of the reduction/evacuation temperature, chemical modifications occurring at the support, rather than the inhibition of the adsorptive properties of the metal, seem to be responsible for the changes observed. In the particular case of Rh/CeO₂-HSA catalysts, the support sintering can also be a very disturbing factor in chemisorption studies.

The HRTEM technique has proven to be a very powerful tool for investigating the actual nature of the metal–support interactions in ceria-supported rhodium catalysts. Direct experimental information about the micromorphology and mean size of the metal particles can also be obtained. This constitutes an essential piece of information because, as the chemisorption results reported here show, the conventional characterization techniques cannot be straightforwardly applied. The HRTEM images have not shown any evidence of metal decoration phenomena. This substantially reinforces the chemical observations commented on above, in accordance with which none of the Rh/CeO₂ catalysts investigated here shows the classic SMSI effect. The HRTEM images presented here, as well as the series of electron microscopy studies reported earlier,[43-45] indicate that the nature of the interaction between rhodium and ceria, in particular the epitaxial relationship observed, has quite singular characteristics.

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