

## Reversibility of Hydrogen Chemisorption on a Ceria-Supported Rhodium Catalyst

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This work reports on some new aspects of the chemistry of hydrogen-ceria systems. It is shown that, at room temperature, in the presence of highly dispersed rhodium, ceria chemisorbs large amounts of hydrogen. As deduced from magnetic measurements carried out *in situ*, this spillover process leads to the reduction of ceria to an extent of 21% of the total amount of cerium ions present in the sample, which is roughly equivalent to the complete surface reduction of the oxide. It is found that over a highly hydroxylated sample the reduction of ceria induced by the spillover process is partly reversible even at 295 K. If the sample is pumped off at 773 K, the initial oxidation state of ceria is almost completely recovered. Both the rate and extent of hydrogen chemisorption on ceria were found to be sensitive to the specific pretreatment applied to the catalyst. Over bare ceria, hydrogen chemisorption at 298 K was negligible, temperatures as high as 473 K being necessary to activate the process. In contrast to the rhodium-containing catalyst, over pure ceria the desorption of hydrogen leads to a much larger extent to water formation, thus revealing a deeper irreversible reduction of the oxide. © 1992 Academic Press, Inc.

### INTRODUCTION

Cerium dioxide is an important component of the so-called "three-way catalysts" (1, 2). It is generally considered that ceria plays an important role in two ways: [a] as a textural promoter (3, 4) and [b] as an oxygen storage system (5, 6).

From a fundamental point of view, many questions concerning these ceria-containing catalysts still remain open to discussion. Two aspects, closely related to each other, are outlined here. First, the redox chemistry of ceria is rather complex (7, 9). Second, due to the reactivity of ceria towards classic probe molecules like H<sub>2</sub> and CO (10-16), on the one hand, and the likely occurrence of strong meta-support interaction phenomena in M/CeO<sub>2</sub> systems (17-20), on the other hand, there are considerable difficulties in establishing a suitable methodology for the characterization of this kind of system (21, 22), and therefore of three-way catalysts.

This work reports on hydrogen interac-

tion with a ceria-supported rhodium catalyst. In particular, it is shown that highly dispersed rhodium plays an important role in determining both the intensity and the reversibility of the reduction process induced by hydrogen on ceria. The relevance of these phenomena in the achievement of a better understanding and a finer characterization methodology of ceria-supported catalysts will also be discussed.

### EXPERIMENTAL

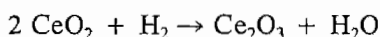
The catalyst investigated here, 2.9% rhodium loading, was prepared by the incipient wetness impregnation technique from an aqueous solution of Rh(NO<sub>3</sub>)<sub>3</sub>. The ceria used was a high surface area sample, 130 m<sup>2</sup> g<sup>-1</sup>, obtained from Rhône-Poulenc Minérale Fine. After the impregnation treatment, the sample was dried at 383 K, in air, for 10 h, and further stored in a desiccator.

Hydrogen adsorption measurements were carried out volumetrically at room temperature in a conventional high vacuum

system equipped with a capacitance gauge, MKS Baratron, model 220 BHS. The time spent between the successive isotherm points was routinely 20 min.

The experimental device used in Temperature Programmed Desorption studies with Mass Spectrometry as analytical technique (TPD-MS) was similar to that described in Ref. (23). The mass spectrometer was a VG Spectralab SX200 instrument, interfaced to a PC-type microcomputer. The experiments were run in a flow of He under the following conditions: total flow rate through the TPD reactor,  $1 \text{ cm}^3 \text{ s}^{-1}$ ; heating rate,  $0.1 \text{ K s}^{-1}$ .

The magnetic susceptibility measurements were carried out by means of a Faraday microbalance coupled to an ultra high vacuum system equipped with a quadrupole mass spectrometer to analyse the residual gases. Details concerning the equipment and the calibration procedures are given elsewhere (14, 24). All the susceptibility values were corrected for the ferromagnetic impurities (6–12 ppm). The susceptibility of the initial sample was  $-0.18 \times 10^{-6} \text{ emu cgs}$  (to be multiplied by 12.56 to obtain SI units in  $\text{m}^3 \text{ g}^{-1}$ ) which is the expected value for a diamagnetic ceria sample containing only  $\text{Ce}^{4+}$  ions. As a result of the hydrogen treatments, the susceptibility of the sample became paramagnetic. This change was totally attributed to the formation of  $\text{Ce}^{3+}$  ions, with a magnetic moment of  $2.5 \mu_B$ . The magnetic contribution of rhodium was neglected (maximum value to be expected:  $3 \times 10^{-8} \text{ emu cgs}$  at 298 K). The extent of the reduction undergone by ceria was estimated on the ground of the reaction



by using for  $\text{Ce}_2\text{O}_3$  the Curie-Weiss law determined previously (14):

$$\chi = 4.8 \times 10^{-3} / (T + 160).$$

At 294 K, 100% reduction of  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$  would lead to a  $\chi$  value of  $10.6 \times 10^{-6} \text{ emu cgs}$ .

The electron microscope used in this work was a JEOL, JEM 2000 EX instru-

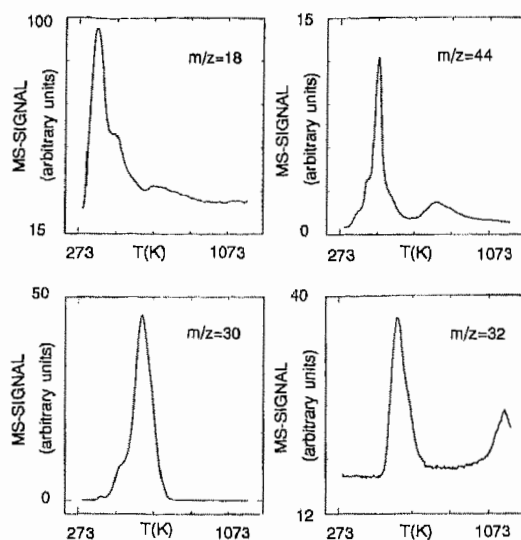


FIG. 1. TPD-MS study of  $\text{Rh}(\text{NO}_3)_3/\text{CeO}_2$ . The ( $m/z$ ) values on the figure account for the mass/charge ratios corresponding to the signals, in arbitrary units, recorded for  $\text{H}_2\text{O}$  (18),  $\text{NO}$  (30),  $\text{O}_2$  (32), and  $\text{CO}_2$  (44).

ment, equipped with a top-entry specimen holder and ion pump. Samples for high-resolution studies were prepared as reported elsewhere (17).

## RESULTS AND DISCUSSION

### Pretreatment of the Rh/Ceria Catalyst

The precursor-support system prepared as described above, hereafter referred to as sample A, was first studied by TPD-MS in a flow of He (Fig. 1). By monitoring the signals corresponding to sixteen mass/charge ( $m/z$ ) ratios we were able to establish the desorption traces for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_x$ , and  $\text{O}_2$  throughout the whole TPD experiment. According to Fig. 1, the most significant desorption processes take place below 773 K. In addition, the TPD spectra show two main features in the high-temperature region ( $T > 773 \text{ K}$ ): these are an oxygen peak ( $m/z$ : 32) observed at about 1150 K, reasonably due to the reduction of the oxidized Rh and/or the support, and a small  $\text{CO}_2$  peak ( $m/z$ : 44), presumably associated with the elimination of residual inner car-

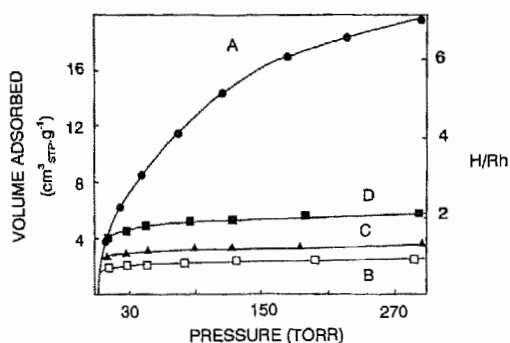


FIG. 2. Volumetric study, at 295 K, of hydrogen chemisorption on sample B of Rh/CeO<sub>2</sub>. (A) First isotherm of the series; (B) after evacuation for 5 min at 295 K; (C) after evacuation for 30 min at 295 K; (D) after evacuation for 10 h at 295 K.

bonate species not thoroughly decomposed during the preparation of ceria (14). In accordance with the results above, the following standard treatment was established to be applied to our precursor/support system (sample A): heating under high vacuum ( $10^{-6}$  Torr) from 295 to 773 K, at a rate of  $0.1 \text{ K} \cdot \text{s}^{-1}$ , the same as used in the TPD-MS experiments. The sample was held for 1 h at 773 K, and finally cooled to room temperature, always under high vacuum. The catalyst resulting from this treatment, hereafter referred to as sample B, had a BET surface area of  $120 \text{ m}^2 \text{ g}^{-1}$ .

#### Hydrogen Interaction with Catalyst B

The hydrogen volumetric isotherms, at 295 K, recorded for the so-called catalyst B are depicted in Fig. 2A. A number of aspects should be outlined from the analysis of this isotherm:

(a) The apparent H/Rh ratio is very high. Also worthy of note is that the value is larger than those observed for samples prepared from the same precursor/support system by reduction under flowing hydrogen at either 523 or 623 K. In these latter cases the H/Rh values were around 4.5.

(b) The shape of the isotherm depicted in Fig. 2A, compared to that of the isotherms shown in Figs. 2B to 2D, recorded after pumping the sample at 295 K for increasing

periods of time, strongly suggests that slow processes are taking place when catalyst B is put in contact with hydrogen for the first time.

(c) The amounts of hydrogen eliminated by pumping at room temperature are quite important, and are sensitive to the evacuation time.

An experiment parallel to the one described above, carried out on the same ceria support in the absence of rhodium, showed no measurable adsorption of hydrogen. The volumetric study of H<sub>2</sub>/CeO<sub>2</sub> interaction at increasing temperatures demonstrates, in effect, that temperatures as high as 473 K are necessary to detect hydrogen chemisorption on pure ceria (Fig. 3). This finding agrees fairly well with the results obtained from the study of the H<sub>2</sub>/CeO<sub>2</sub> system by means of magnetic susceptibility measurements (14).

To obtain some further insight into the nature of the processes associated with the interaction, at 295 K, between hydrogen and catalyst B, we have also investigated this interaction with the help of magnetic measurements. In these experiments we have tried to mimic the chemisorption studies. Accordingly, a portion of around 130 mg of catalyst A was calcined under high vacuum at 773 K for 1 h, then cooled under vacuum,

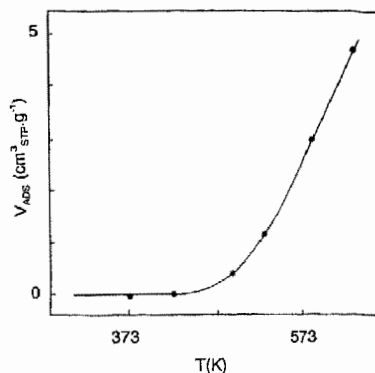


FIG. 3. Influence of the temperature on the amount of hydrogen adsorbed over the bare CeO<sub>2</sub> sample, calcined at 773 K, under high vacuum, for 1 h (initial hydrogen pressure: 300 Torr).

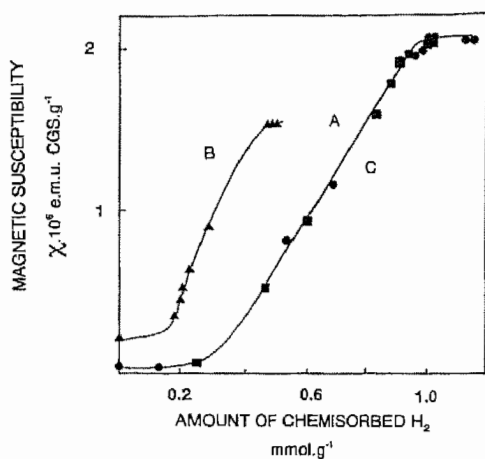


FIG. 4. Magnetic balance study of hydrogen interaction ( $P_{H_2}$ : 300 Torr) at 295 K with: (A) Sample B of Rh/CeO<sub>2</sub> (●). (B) The catalyst resulting from treatment [a] further evacuated under high vacuum, at 773 K, for 1 h, and then cooled to 295 K, also under high vacuum (▲). (C) Sample resulting from experiment [b], further evacuated under high vacuum at 773 K, treated with O<sub>2</sub> (140 Torr) at 295 K, pumped off at 773 K, and finally cooled to room temperature also under high vacuum (■).

and finally put in contact with hydrogen (300 Torr) at 295 K. Both the total weight and the magnetic susceptibility of the sample were monitored for about 27 h.

According to curve A in Fig. 4, the initial step of the chemisorption process implies a weight gain with no parallel modification of the magnetic susceptibility. In a second step, reduction of ceria does occur, as deduced from the increase of the magnetic susceptibility. Finally, a third step can be observed in which the hydrogen chemisorption takes place with no further reduction of ceria.

Table 1 summarizes the most interesting results obtained from this study. According to Table 1, the high vacuum pretreatment of the catalyst, at 773 K, induces a slight reduction of the ceria (2%). Also remarkable, after the exposure to H<sub>2</sub> for a long time (27 h), the total amount of hydrogen taken up by the sample was found to be 1.18 mmole H<sub>2</sub> per g of catalyst, which corres-

TABLE 1

Magnetic Balance Study of the Changes Undergone by an Rh(NO<sub>3</sub>)<sub>3</sub>/CeO<sub>2</sub> Sample Submitted to the Series of Treatments Indicated Below

Treatment	$\Delta W_t^a$	$\chi^b$	$n_{H_2}^c$	% Ce <sup>3+</sup>
Evacuation		-0.18		
T: 295 K; t: 2 h				
Evacuation		+0.04		2.1
T: 773 K; t: 1 h				
H <sub>2</sub> (300 Torr)	+2.36	+2.07	+0.60	21.2
T: 295 K; t: 27 h				
Evacuation	-0.63	+1.23	-0.22	13.3
T: 295 K; t: 24 h				
Evacuation	-7.55	+0.18	-0.28	3.4
T: 773 K; t: 1 h				
H <sub>2</sub> (300 Torr)	+1.19	+1.45	+0.34	15.4
T: 295 K; t: 24 h				
Evacuation	-0.19	+1.21	-0.06	13.1
T: 295 K; t: 72 h				
Evacuation	-0.36	+0.72	-0.13	8.4
T: 473 K; t: 1 h				
Evacuation	-0.41	+0.51	-0.06	6.5
T: 623 K; t: 1 h				
Evacuation	-1.03	+0.19	-0.08	3.5
T: 773 K; t: 1 h				
H <sub>2</sub> (300 Torr)	+0.98	+1.54	+0.36	16.2
T: 295 K; t: 24 h				
Evacuation	-0.08	+1.37	-0.04	14.6
T: 295 K; t: 15 h				
Evacuation	-0.52	+0.77	-0.16	9.0
T: 473 K; t: 1 h				
Evacuation	-0.45	+0.29	-0.12	4.4
T: 623 K; t: 1 h				
Evacuation	-0.70	+0.20	-0.02	3.6
T: 773 K; t: 1 h				
O <sub>2</sub> (140 Torr)	+7.10	-0.17	—	0.1
T: 295 K; t: 2 h				
Evacuation	-1.03	0.00	—	1.7
T: 295 K; t: 24 h				
Evacuation	-1.52	+0.02	—	1.9
T: 773 K; t: 24 h				
H <sub>2</sub> (300 Torr)	+2.01	+2.04	+0.52	20.9
T: 295 K; t: 24 h				

Note. The weight of catalyst used as reference was that corresponding to the sample heated under high vacuum at 773 K.

<sup>a</sup> Total weight variation of the sample expressed in mg g<sup>-1</sup> of catalyst.

<sup>b</sup> Magnetic susceptibility of the sample in e.m.u. (cgs) g<sup>-1</sup> × 10<sup>6</sup>.

<sup>c</sup> Estimate (in mmol g<sup>-1</sup> of catalyst) of the amount of hydrogen associated with the variation in the concentration of Ce(III) ions as determined from magnetic measurements.

ponds to an apparent H/Rh ratio of 8.5. As deduced from the magnetic measurements, the hydrogen consumption associated with the reduction of ceria was 0.60 mmol g<sup>-1</sup>, i.e., about 21% of cerium ions are present as Ce(III), which roughly corresponds to the complete surface reduction of the support (25). If this amount of hydrogen is referred to the number of rhodium atoms present in the sample, an apparent H/Rh ratio of 4.4 would be obtained.

By subtracting the contribution of ceria reduction from the total hydrogen consumption, an apparent H/Rh of 4.1 is obtained. This still represents a large amount of adsorbed hydrogen, which strongly suggests that, in addition to the chemisorption process, the interaction of H<sub>2</sub> with our Rh/CeO<sub>2</sub> system, at 295 K, leads to the reduction to the metallic state of oxidized forms of rhodium present in catalyst B.

It is known that for highly dispersed rhodium, H/Rh values larger than unity can be obtained (26, 27). In the present case, the high resolution transmission electron microscopy (HRTEM) study shows that for a sample of catalyst B treated with hydrogen at room temperature, as in the chemisorption study mentioned above (Fig. 5a) the rhodium microcrystals can hardly be observed, those detected being not larger than 1.5 nm. This contrasts with the results of the HRTEM study carried out on either a low surface area ceria-supported rhodium catalyst prepared in the same way (Fig. 5b) or Rh/CeO<sub>2</sub> catalysts prepared by reduction in flowing hydrogen at 623 K or 773 K (17, 28). In these latter cases epitaxially grown metal crystallites can be observed, thus indicating that for catalysts pretreated as described in the present work the rhodium phase is very highly dispersed. Then, in accordance with the literature (26, 27), it might tentatively be proposed that, when thoroughly reduced, the metal contribution to the apparent H/Rh ratio would be in our case around 1.5.

Preliminary XPS studies of our Rh(NO<sub>3</sub>)<sub>3</sub>/CeO<sub>2</sub> system, calcined under

high vacuum, at 723 K, indicates the occurrence of a significant reduction of the metal with formation of about two-thirds of the metallic rhodium (29). This result is in agreement with that reported by Munuera *et al.* (30) for RhCl<sub>3</sub>/TiO<sub>2</sub>, in the sense that upon treatment under high vacuum, at 773 K, about 60% of rhodium is reduced to Rh(O). The XPS study carried out on our sample also suggests that about 30% of Rh is present in the pretreated catalyst as Rh(III). This allows us to estimate that the contribution of the rhodium reduction process to the total hydrogen consumption would be approximately H/Rh = 1. It can therefore be concluded that there is some other process contributing to the total H/Rh ratio not considered as yet. In this respect we recall that our study with the magnetic balance shows the occurrence of a slow hydrogen adsorption, associated with which there is no reduction of ceria. This process might be interpreted as due to the appearance of some form of dissociative hydrogen adsorbed on the support. It should not be excluded, however, that this hydrogen consumption is associated with the slow reduction of an oxidized rhodium phase. If such is the case, the XPS data would give us an overestimate of the actual reduction level of rhodium. This seems to be possible, because the X-ray beam can induce some further reduction of the very highly dispersed rhodium phase. In this respect, it should also be mentioned that the XPS study of our precursor/support system evacuated under high vacuum has also shown the occurrence of some ceria reduction, an effect which, in accordance with the magnetic balance results, takes place to a lesser extent.

#### *Desorption Studies Carried Out on the Hydrogen-Catalyst B System*

We have also investigated the changes undergone by the hydrogen/catalyst B system, when pumped off under high vacuum. Upon evacuation at 295 K, there is a notable modification of the magnetic susceptibility val-

ues, thus indicating the occurrence of support reoxidation, even at room temperature (Table 1). This process is relatively slow: after pumping for 2 h, the magnetic susceptibility decreases from  $2.07 \times 10^{-6}$  emu cgs  $g^{-1}$  to  $1.41 \times 10^{-6}$  emu cgs  $g^{-1}$ , reaching the value of  $1.23 \times 10^{-6}$  emu cgs  $g^{-1}$  upon evacuation, at 295 K, for 24 h. This variation of the magnetic susceptibility, equivalent to  $0.22$  mmol  $H_2$   $g^{-1}$ , indicates that approximately 40% of initially reduced ceria can be reoxidized by pumping at room temperature. The total weight loss associated with the evacuation treatment, at 295 K, for 24 h, was found to be equivalent to  $0.31$  mmol  $H_2$   $g^{-1}$ . The occurrence of reversible hydrogen adsorption implying support reduction/reoxidation has also been reported for Rh/TiO<sub>2</sub> (31–33). However, the intensity of the process, at room temperature, seems to be smaller; thus, in accordance with the results reported in Ref. (31), the phenomenon is about three orders of magnitude less intense than that observed here.

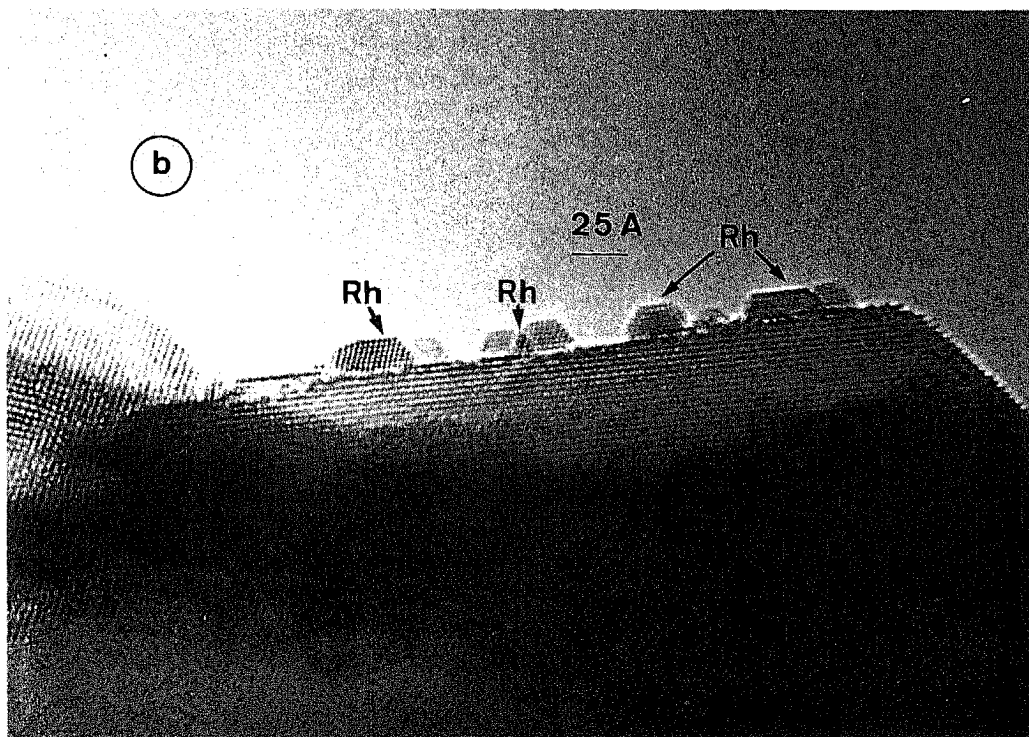
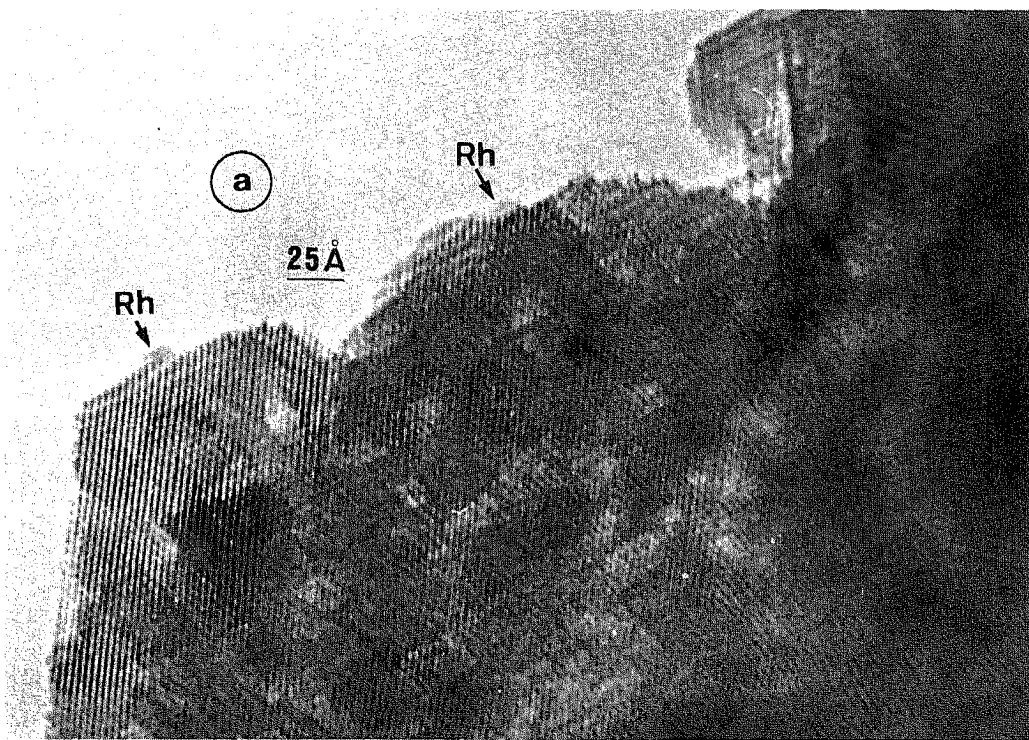
After evacuation at room temperature, the sample was heated (heating rate:  $0.1$  K  $s^{-1}$ ) under high vacuum up to 773 K, held for 1 h at this temperature, and then cooled to 295 K, always under high vacuum. After this treatment, the magnetic susceptibility of the sample,  $0.18 \times 10^{-6}$  emu cgs  $g^{-1}$ , suggests that, in the presence of rhodium, the reduction undergone by ceria is 90% reversible. In this respect it should also be noted that according to the TPD-MS spectra recorded after treating sample B with flowing hydrogen at 295 K (Fig. 6) there is a peak centered around 900 K, which might tentatively be ascribed to hydrogen adsorbed on ceria in a dissociative way. These forms would not be easily eliminated by pumping at 773 K. In other words, it cannot

be excluded that the hydrogen adsorption forms responsible for the reduction of ceria can be completely reversible. It must also be noted here that a number of papers dealing with Rh/TiO<sub>2</sub> catalysts (34, 35) have reported the formation of Ti<sup>3+</sup>-H species, associated with which there is a decrease of the Ti<sup>3+</sup>-ESR signal. The occurrence of hydride-like species has also been proposed in earlier studies of hydrogen adsorption over ceria (7, 13); thus one could not exclude the possibility of apparent reoxidation of ceria, actually due to the formation of some sort of diamagnetic Ce<sup>3+</sup>-H species, not eliminated upon evacuation at 773 K. The peak appearing above 773 K in the H<sub>2</sub>-TPD diagram depicted in Fig. 6 would give some support to this interpretation. There is, however, some other experimental evidence suggesting that the high temperature hydrogen adsorbed form is not related to Ce<sup>3+</sup>-H species. In effect, the peak centered at around 900 K mentioned above can also be observed on H<sub>2</sub>-TPD traces recorded for Rh/CeO<sub>2</sub> catalysts reduced under flowing H<sub>2</sub> at 623 K. In this latter case, however, the magnetic balance studies show that evacuation at increasing temperatures, from 773 K upwards, does not induce further reduction on ceria, as might expected after elimination of the high-temperature hydrogen adsorbed form.

In contrast with the results reported above, the reversibility of the H<sub>2</sub>-CeO<sub>2</sub> interaction is much lower when no metal is supported on ceria. Magnetic balance studies (14) have shown that hydrogen desorption from pure ceria takes place via an irreversible way, i.e., water formation, to a much larger extent. As an example, a bare high surface area ceria sample treated with hydrogen at 623 K and further evacuated,

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FIG. 5. HRTEM images corresponding to: (a) Sample B of Rh/CeO<sub>2</sub> treated with flowing H<sub>2</sub> at 295 K, for 15 h. (b) A low surface area ceria ( $11$  m<sup>2</sup>  $g^{-1}$ ) supported rhodium (metal loading: 2.4%) catalyst prepared and treated in the same way as that studied in (a).



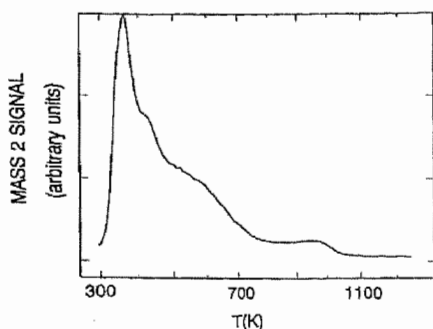


FIG. 6. Study by TPD-MS of hydrogen desorption from an Rh/CeO<sub>2</sub> sample prepared by heating in a flow of He, at 773 K, for 1 h, sample A (precursor/support system), further cooled to 295 K, under a flow of He, and then treated with flowing H<sub>2</sub> for 15 h.

under high vacuum at 773 K, exhibits a magnetic moment equivalent to a reduction to Ce(III) of 23% of Ce(IV) ions. Assuming that the recorded weight loss just corresponds to the elimination of water (14), this observed reduction level would be in good agreement with that estimated from gravimetric measurements. If the same reduction/evacuation treatment is applied to our Rh/CeO<sub>2</sub> system, the final reduction level reached by ceria, as determined from magnetic measurements, is only 5%. Accordingly, the mechanism of hydrogen elimination from ceria depends critically on the presence of a transition metal highly dispersed on the oxide.

#### *Behavior of Catalyst B after Successive Hydrogen Treatments*

The magnetic balance has also been used to study the behavior of the Rh/CeO<sub>2</sub> catalyst resulting from the hydrogen treatment, at room temperature, of sample B and its further evacuation under high vacuum, at 773 K, for 1 h. After cooling the catalyst to 295 K, under high vacuum, it was placed again in contact with H<sub>2</sub> (300 Torr) at room temperature. Compared to the catalyst not treated with hydrogen before (sample B), the one investigated now shows some nota-

ble differences. The amount of hydrogen adsorbed in the first step of the process, i.e., that occurring with no reduction of ceria (curve B in Fig. 4) is smaller, approximately one half of that observed for the initial catalyst (Fig. 4A). Also, as seen from Fig. 7, the adsorption rate is much lower in the case of the sample pretreated with H<sub>2</sub> at 295 K and further evacuated at 773 K. A third aspect worthy of note is the total amount of adsorbed hydrogen. After 20 h of interaction at 295 K, this amount is considerably smaller than that found for catalyst B. Likewise, the reduction level reached by ceria, as determined from magnetic measurements, is now lower. According to Table 1, this second hydrogen treatment, at 295 K, leads to a value of magnetic susceptibility of  $1.45 \times 10^{-6}$  emu cgs g<sup>-1</sup>, equivalent to a reduction level of ceria of 15%, significantly lower than that determined for catalyst B, viz. 21%.

Comparison of the results reported in Figs. 4A and 4B shows that the initial step of the hydrogen adsorption, that occurring without ceria reduction, is in the second case shorter, which suggests that this step is associated with hydrogen/rhodium interaction, the rhodium being either in a metallic or oxidized state. The larger hydrogen con-

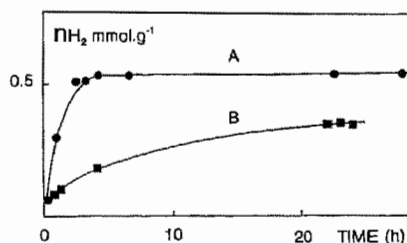


FIG. 7. Study of the hydrogen interaction with Rh/CeO<sub>2</sub> catalysts at 295 K: Variation with time of the amount of chemisorbed hydrogen associated with the reduction of ceria (as determined from the magnetic measurements): (A) catalyst B; (B) catalyst resulting from treatment [a], further evacuated at 773 K, for 1 h, and then cooled to 295 K under high vacuum.



sumption observed for sample B (Fig. 4A) can thus be interpreted as due to the existence in this sample of easily reducible cationic rhodium forms, in addition to the microcrystals of the metallic phase.

It is generally acknowledged (36, 37) that spillover phenomena are much faster on highly hydroxylated surfaces. This probably explains why the rate of hydrogen adsorption on ceria is higher for sample B than for the sample resulting from a previous treatment with hydrogen (Fig. 7). In the first case the reduction by H<sub>2</sub> of oxidized rhodium would lead to the formation of hydroxyl groups just in the vicinity of the metal crystallites which would increase very much the spillover rate.

Concerning the amount of H<sub>2</sub> taken up by the catalyst after this second treatment, Table 1 shows that it is significantly smaller than that reported for the initial catalyst. The difference can in part be interpreted as due to the hydrogen consumption associated with the reduction of rhodium; however, the magnetic measurements clearly indicate that the reduction level induced on ceria is also lower. At first sight this smaller uptake of hydrogen might be thought to be due to the occurrence of some sintering of the high surface area ceria sample. However, as shown below, the behavior of the catalytic system can be completely recovered by simple reoxidation at room temperature, which suggests that chemical rather than textural reasons are responsible for the differences observed here.

The change resulting from this second hydrogen treatment when pumped off the sample at 295, 473, 623, and 773 K has also been studied and Table 1 summarizes the results. In this case, the decrease in Ce<sup>3+</sup> content, from 15 to 13%, i.e., the extent of the reoxidation of ceria induced by evacuation, at room temperature, is smaller. This suggests that, compared to the initial, more hydroxylated sample, back-spillover phenomena are now less intense. After pumping at 473 K, however, the reoxidation of ceria reaches

45%, this value becoming 58% upon evacuation at 623 K. The final reduction level (3.5% Ce<sup>3+</sup>) resulting from the evacuation at 773 K agrees fairly well with the starting one (3.4% Ce<sup>3+</sup>), thus suggesting the occurrence of a cyclic reproducible behavior. This has been confirmed by further hydrogen adsorption-desorption treatments carried out on the sample, in accordance with which from the second cycle onwards no further differences can be observed.

#### *Behavior of the Reoxidized Catalyst*

We have also investigated by means of the magnetic balance the behavior of the catalyst resulting from the experiments reported above and further treated with oxygen ( $P_{O_2}$ : 140 Torr), at 295 K. The reaction is fast leading to the practical disappearance of the residual magnetic moment existing on the catalyst. The total amount of chemisorbed oxygen was 0.22 mmol g<sup>-1</sup> (Table 1). This value, equivalent to an O/Rh ratio of 1.6, is in good agreement with that determined from volumetric adsorption measurements. Upon evacuation, under high vacuum, at 295 K, for 24 h, the amount of oxygen eliminated represents about 15% of the total adsorbed oxygen, thus indicating that this chemisorption process is essentially irreversible at room temperature.

After reaction with O<sub>2</sub>, the catalyst was evacuated at 773 K for 1 h, then cooled under high vacuum, and, finally, treated with hydrogen (300 Torr), at 295 K, following the procedure established in this work. As can be deduced from the data depicted in Fig. 4C, also reported in Table 1, there is a complete recovery of the behavior found for sample B.

It can reasonably be concluded from these observations that oxygen adsorption, at room temperature, in addition to reoxidizing ceria and eliminating the hydrogen adsorbed forms retained after evacuation at 773 K, also induces rhodium reoxidation. The occurrence at such a low temperature of reduction/oxidation of rhodium crystallites has

earlier been observed on highly dispersed Rh/Al<sub>2</sub>O<sub>3</sub> catalysts (38). This is consistent with our own results in the sense that the catalyst investigated here also shows very high metal dispersion.

As commented on above, the reoxidation treatment at 295 K followed by evacuation at 773 K leads our Rh/CeO<sub>2</sub> system to a situation similar to that found for the initial catalyst untreated with hydrogen (sample B). The complete recovery of the hydrogen chemisorptive capabilities of the catalyst after such a mild reoxidation treatment allows us to exclude any major role to the presumable textural modifications undergone by the support. Thus, the differences of behavior observed here between the first hydrogen treatment and the succeeding ones ought to be interpreted as due to chemical changes which have occurred in the Rh/CeO<sub>2</sub> system.

#### CONCLUSIONS

The analysis of the results presented and discussed above allows us to draw a number of interesting conclusions concerning the chemistry of the interaction between hydrogen and Rh/CeO<sub>2</sub> catalysts.

First, our results show that, in the presence of rhodium, ceria can easily and reversibly be reduced at room temperature. Compared to the effects reported for Rh/TiO<sub>2</sub> (31), over Rh/CeO<sub>2</sub> the intensity of the reaction is much larger, roughly corresponding to the complete surface reduction of the oxide.

It is obvious from the present work that the use of hydrogen chemisorption studies at 295 K to characterize this type of catalyst, and specifically to determine metal dispersions, has very severe limitations. Due to the occurrence of intense spillover phenomena, the experimental H/Rh values are much larger than those expected for true hydrogen adsorption on the metal. A further element of complication proceeds from the kinetics of the spillover process, which are very sensitive to the specific pretreatment conditions. As already suggested in the liter-

ature (36, 37), the hydroxyl content of the oxide support seems to have a significant influence. The same is true for the reverse reaction, i.e., the so-called back-spillover process, so that the larger the OH concentration the faster the reaction. Thus, it has been found that upon prolonged evacuation at 295 K of the catalyst sample heated at 773 K, and further treated with H<sub>2</sub> at 298 K, ceria reoxidizes to a very large extent (ca. 40%). This demonstrates that for Rh/CeO<sub>2</sub> systems, weakly retained hydrogen forms cannot simply be ascribed to chemisorption on the metal or even to forms, usually referred to as reversible forms, the chemical interest of which is implicitly assumed to be negligible. This suggests that hydrogen chemisorption studies carried out at 295 K on ceria-supported rhodium catalysts are kinetically controlled, so that both the pretreatments applied to the catalyst and the specific protocol used in the chemisorption measurements can determine the final result of the study.

Also interesting is that the occurrence of back-spillover at rather low temperatures prevents a net separation between the desorption processes from the metal crystallites, typically observed in the low temperature range of the TPD diagrams, i.e., below 473 K, and those recorded at high temperature, ascribed to the hydrogen interaction with the support. In accordance with the results presented here, such a simple, straightforward interpretation of H<sub>2</sub>-TPD diagrams should be used cautiously in the case of ceria-supported metal catalysts.

Regarding the mechanism of hydrogen desorption from ceria, our data suggest that it depends very much on the presence of a transition metal dispersed on it. When rhodium is present, the hydrogen desorption process leads to a concentration of oxygen vacancies in the structure of ceria much lower than that found for the oxide in the absence of the metal. This can be explained as due to the relative weight of irreversible desorption of hydrogen leading to the formation of water, and its reversible elimination

as H<sub>2</sub>, the dispersed rhodium favoring the latter process via the back-spillover mechanism. The presence of a supported metal can thus indirectly contribute to an increase in the resistance of ceria against sintering under reducing conditions. This type of textural effect associated with the presence of metal crystallites highly dispersed on ceria has recently been reported by Havil (39).

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