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Hydrogen Chemisorption on Ceria: Influence of the Oxide Surface Area and Degree of Reduction

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The chemisorption of hydrogen on two ceria samples (CeO_2-BS, 4 m^2 g^{-1}; CeO_2-SM, 56 m^2 g^{-1}) reduced at temperatures ranging from 623 to 1173 K has been studied by Fourier-transform infrared (FTIR) spectroscopy and temperature-programmed desorption followed by thermal conductivity (TPD-TC) and mass spectrometry (TPD-MS). The concentration of the oxygen vacancies created by the reduction treatments was determined by using a combination of O_2 pulses and temperature-programmed oxidation. According to our TPD-MS study, hydrogen can be desorbed from ceria as both H_2 (reversible adsorption) and H_2O (irreversible adsorption), the relative contribution of these two forms depending on the reduction temperature. For samples reduced at 773 K or higher temperatures, H_2 was the only desorption product. From this observation, some earlier TPD-TC and TPR-TC results could be better understood. Upon reduction at 773 K, the amount of H_2 chemisorbed per mole of CeO_2 was ten times larger for CeO_2-SM than for CeO_2-BS. Likewise, the molar chemisorptive capability of CeO_2-SM strongly decreased (45 times) with the reduction temperature. No simple relationship could be observed between the amount of chemisorbed hydrogen and the total concentration of oxygen vacancies in the oxide. In contrast to earlier results on the contribution of a massive bronze-like phase when chemisorbing H_2 at 195–500 K, the results reported here show that the hydrogen chemisorption on reduced ceria is a surface-related process. Furthermore, the highest value for the hydrogen chemisorption we have obtained, 7.1 H atom nm^{-2} (BET), suggests a pure surface process.

Ceria-containing metal catalysts have been investigated intensively because of their close relationship to the so-called three-way catalysts (TWC).[1,2]

It is generally considered[3-5] that this family of catalysts, even the simplest M/CeO_2 binary systems (where M = metal), exhibit a number of characterization problems that are hard to overcome. On the one hand, as several authors have suggested, these catalysts may show strong metal–support interaction (SMSI) effects.[6-9] On the other hand, conventional hydrogen or carbon monoxide chemisorption studies very often lead to apparent H : M and CO : M ratios much larger than unity.[10-13] This is a consequence of the strong chemisorption capability of ceria for the classic probe molecules: H_2[11,14-16] and CO.[17-20]

It has been proposed that the interaction of hydrogen with ceria leads to a bronze-like massive phase, the stoichiometry of which would be $CeO_2H_{0.17}$.[14,15] Earlier studies of hydrogen chemisorption on several different Rh/CeO_2 catalysts carried out at our laboratory, however, suggested to us the existence of a relationship between the amount of hydrogen chemisorbed on the support and the BET surface area of the corresponding ceria sample.[21] In effect, it was found in ref. 21 that the larger the support surface area, the larger the amount of chemisorbed hydrogen. It can also be deduced from ref. 21 that the amounts of hydrogen retained by different ceria supports were always lower than that needed to reach a surface monolayer.

The controversial nature of the results above prompted us to investigate further the H_2/CeO_2 system. For this purpose, we have studied the interaction of H_2 with two cerium dioxide samples, with quite different textural properties, reduced at a number of temperatures ranging from 623 to 1173 K. The experimental techniques used were temperature-programmed desorption with analysis of the evolved gases by either a thermal conductivity detector (TPD-TC) or mass spectrometry (TPD-MS), as well as FTIR spectroscopy. Likewise, a combination of oxygen pulses at 295 K and temperature-programmed oxidation (TPO-TC) was used to determine the degree of reduction induced on ceria by the series of treatments applied. From our results some interesting conclusions about the influence of the surface area and reduction level of ceria on its hydrogen chemisorptive properties have been drawn.

Experimental

Cerium Dioxide Samples

Two ceria samples, hereafter referred to as BS and SM have been used. The BET surface areas, as determined from N_2 adsorption at 77 K, were 4 m^2 g^{-1} for CeO_2-BS and 56 m^2 g^{-1} for CeO_2-SM. The first sample, CeO_2-BS, was a commercial oxide, with a purity of 99.9%, from Alpha Ventron. The second one, CeO_2SM, was prepared in our laboratory from a high-surface-area CeO_2 (130 m^2 g^{-1}), 99.9% pure, kindly provided by Rhône-Poulenc. 15 g of the starting oxide were heated in a flow of H_2 (60 cm^3 min^{-1}), at 823 K, for 4 h; then, the sample was treated with flowing He, for 1 h, at 823 K; and finally, after its cooling in a flow of inert gas, it was heated in a flow of O_2 (60 cm^3 min^{-1}) up to 773 K. In this way, a ceria sample of medium surface area and no microporosity could be obtained.

Experimental Techniques

The TPD studies reported in this work were carried out in two different experimental devices. One of them, which is similar to that described in ref. 22, was equipped with a thermal conductivity detector (TPD-TC). In this system, the water formed along the TPD experiment, if any, was eliminated before the TC detector by passing the gases coming out from the reactor through a little zeolite column. The second TPD device, which used mass spectrometry as the analytical technique (TPD-MS), was similar to one described elsewhere.[23] The spectrometer was a VG Sensorlab instrument, interfaced to an AT-type microcomputer. The accuracy of the quantitative analysis of evolved hydrogen was significantly better with the TPD-TC device. Before use, the gases, N-50 type (99.9990%), from SEO, were further purified by passing them through either a series of deoxo and zeolite traps (H_2, Ar) or a zeolite trap only (O_2). The TPD experiments were run in the following conditions: Ar flow rate 60 cm^3 min^{-1} and heating rate 10 K min^{-1}.

The TPR-MS study was performed on the same TPD-MS device above. The experiments were carried out in a flow of pure hydrogen under the following conditions: flow rate 60 cm^3 min^{-1}, heating rate 10 K min^{-1}.

The oxygen pulses at 295 K, as well as the temperature-programmed oxidation experiments, were carried out in the TPD-TC device. The gaseous mixture used was O_2(5%)–He. The flow rate of either pure He or the mixture O_2(5%)–He was always 60 cm^3 min^{-1}. The heating rate in the TPO experiments was 10 K min^{-1}.

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, of mass *ca.* 40 mg. The spectra were recorded on a Mattson instrument, model 5020; 100 scans at 4 cm^{-1} resolution were routinely averaged.

Results

To establish the most convenient pretreatment and reduction conditions, some preliminary TPD-MS and TPR-MS studies, summarized in Fig. 1, were carried out. The TPD-MS trace for H_2O ($m/z = 18$) corresponding to CeO_2-SM, Fig. 1(*a*), consists of a strong peak at 373 K, which can be assigned to weakly adsorbed H_2O, and a second very broad feature centred at 600 K, much less intense, associated with the oxide dehydroxylation. In accordance with this, the ceria samples were routinely dehydrated before the reduction treatment by heating them either in a flow of inert gas or under high vacuum, at 773 K for 1 h. This pretreatment is similar to that applied in ref. 14 for an NMR study of ceria dehydroxylation.

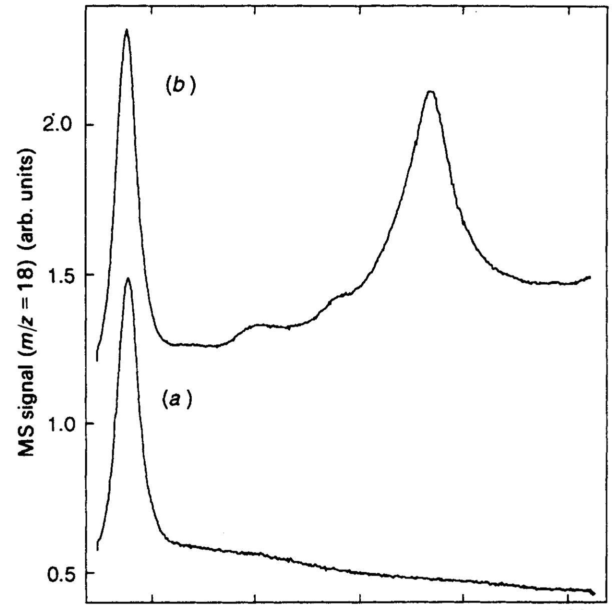

Fig. 1 TPD-MS (*a*) and TPR-MS (*b*) study of CeO_2-SM. Traces corresponding to H_2O ($m/z = 18$)

Comparison of the TPD-MS and TPR-MS results in Fig. 1(*a*) and (*b*), reveals that the differences observed can be interpreted as due to ceria reduction with an inherent creation of oxygen vacancies. As we have already discussed in ref. 11 and 12, the magnetic susceptibility measurements show that the interaction of hydrogen with ceria may lead either to water formation, *i.e.* to the irreversible reduction of ceria, or to chemisorption of hydrogen, which can further be desorbed as H_2, thus inducing a reversible reduction of the oxide.[11,12] Here, we study the relationship between the degree of irreversible reduction of ceria and its hydrogen chemisorption properties. Accordingly, it would be interesting to define the hydrogen treatments that lead to a wide range of degrees of irreversible reduction. In good agreement with ref. 11, 14 16 and 24, Fig. 1(*b*) shows that the reduction of CeO_2-SM starts at around 473 K. There is also a strong reduction peak at 900 K, which is similar to that reported in ref. 25 for some other ceria samples. This peak can be interpreted as due to bulk reduction of the oxide[16,25] with the formation of $CeO_{1.84}$ (reduction of CeO_2: 32%).[16] Experimental limitations obliged us to stop the TPR-MS experiment at 1273 K, thus preventing the recording of features starting at around 1200 K in Fig. 1(*b*). From the results above, the following series of reduction temperatures were selected 623, 773, 873, 973 and 1173 K.

Temperature-programmed Desorption Study

Hydrogen adsorption on a series of ceria samples reduced at the temperatures indicated above was investigated by means of TPD-TC and TPD-MS. The cerium oxides were treated with flowing hydrogen at the corresponding reduction temperature, then they were cooled to 295 K in a flow of H_2, and finally the TPD experiment was run. Some earlier studies carried out by us on both bare ceria[26] and Rh/CeO_2 catalysts[21,27] have shown that slow cooling in flowing H_2 always leads to the maximum amount of chemisorbed hydrogen observed in every case.

Fig. 2 reports the TPD-TC traces recorded for CeO_2-SM. The diagrams show a single hydrogen peak, the maximum of which is shifted to lower temperatures as the reduction temperature is increased. Thus, for the oxide reduced at 773, 873, 973 and 1173 K, the maximum occurs at 765, 740, 655 and 610 K, respectively. The same kind of effect has already been observed by Frety and co-workers[24] and ourselves.[26] Although the magnitude of the peak shift is significantly smaller, the low surface area sample, CeO_2-BS, does exhibit a similar behaviour.

Table 1 summarizes the quantitative results obtained upon integration of the TPD-TC traces corresponding to the two cerium oxides investigated here. The amounts of hydrogen are referred to mol CeO_2 as well as nm^2 BET surface area.

According to Fig. 2, the intensity of the hydrogen peak decreases as the reduction temperature increases. The only exception is the peak recorded for CeO_2-SM reduced at 623 K, not shown in Fig. 2, the area under which is about one half of that determined for the sample reduced at 773 K. To understand the origin of such a discontinuity, we have carried out some parallel TPD-MS experiments. Fig. 3 shows the traces for H_2 ($m/z = 2$) and H_2O ($m/z = 18$) corresponding to CeO_2-SM reduced at both 623 K [Fig. 3(*a*)] and 773 K [Fig. 3(*b*)]. There are notable differences from one case to the other. In effect, the diagram for the oxide reduced at 773 K shows no water peak, whereas for the sample reduced at 623 K, H_2O evolution does occur. Since, prior to reduction, the cerium oxide was dehydroxylated at 773 K, the water evolved along the TPD run ought to be assigned to ceria reduction induced by the chemisorbed hydrogen. For 773 K or higher

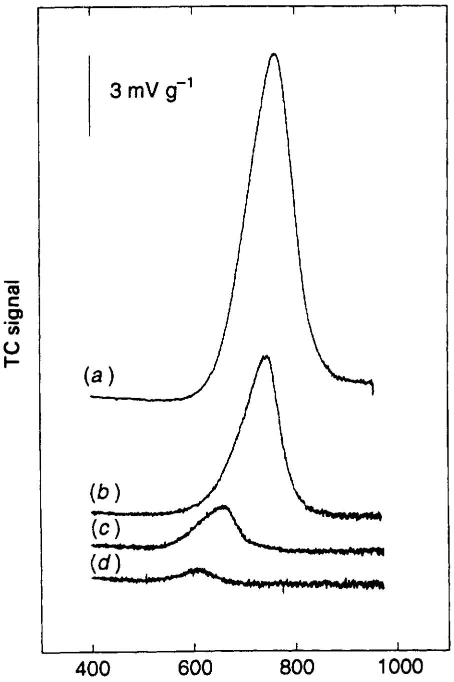

Fig. 2 TPD-TC traces for hydrogen evolution from CeO$_2$-SM reduced at 773 K (*a*), 873 K (*b*), 973 K (*c*) and 1173 K (*d*). The reduced samples were cooled further to 298 K in flowing H$_2$.

reduction temperatures, the reduction treatment itself would eliminate the surface oxygen ions responsible for the water peak in Fig. 3(*a*), and therefore, the hydrogen would be desorbed only as H$_2$. In other words, the TPD-MS study shows that, except for the lowest reduction temperature (623 K), the TPD-TC diagrams can be used to determine the total amount of hydrogen chemisorbed on the reduced ceria samples.

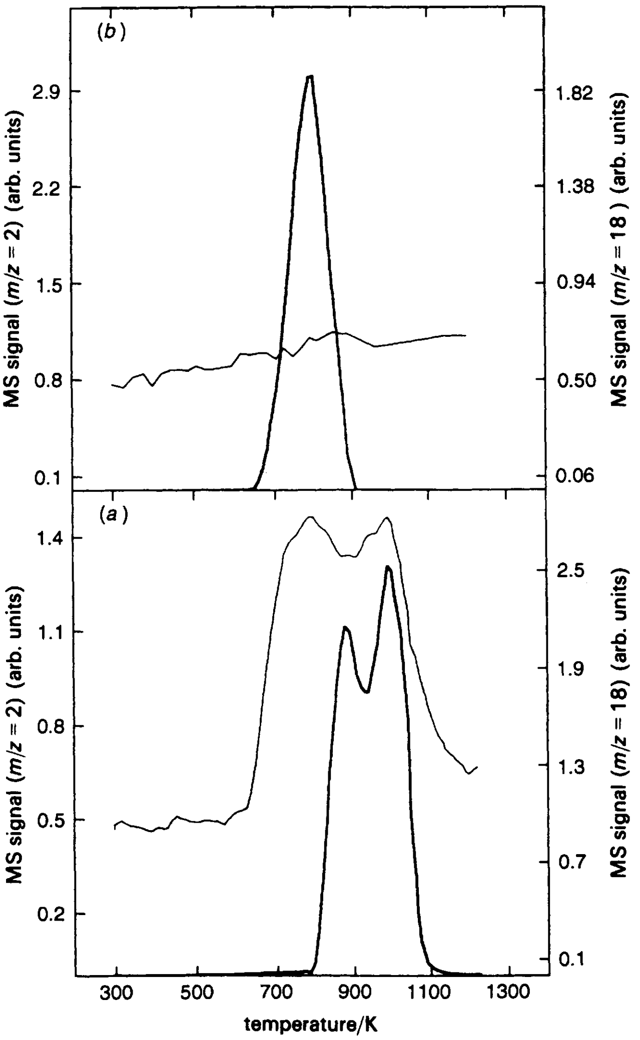

Fig. 3 Traces for H$_2$ ($m/z = 2$, bold line) and H$_2$O ($m/z = 18$, faint line) recorded from the TPD-MS study of CeO$_2$-SM reduced at 623 K (*a*) and 773 K (*b*), and further cooled to 298 K in a flow of H

Oxygen Pulses and Temperature-programmed Oxidation

The degree of irreversible reduction of ceria (expressed as percentage of CeO$_2$ transformed into Ce$_2$O$_3$) induced by the hydrogen treatments above has been estimated by determining the amount of O$_2$ taken up by the oxide. In ref. 28 this experimental approach has been proposed as an advantageous alternative to the usual TPR-TC studies.[29] The TPD H$_2$ results above are in agreement with this. In effect, they

Table 1 Amounts of hydrogen chemisorbed on different ceria samples reduced at temperatures ranging from 623 to 1173 K (data determined from TPD-TC experiments)

			amounts of H$_2$	
ceria sample	reduction temperature/K	BET surface area /m^2 g^{-1}	/mmol H$_2$ (mol CeO$_2$)$^{-1}$	/H atom nm^{-2}
CeO$_2$-SM	623	51.4	15.2 (34.8[a])	2.1 4.8[a])
CeO$_2$-SM	773	51.4	36.8	5.0
CeO$_2$-SM	873	13.4	13.6	7.1
CeO$_2$-SM	973	5.3	3.2	4.2
CeO$_2$-SM	1173	2.5	0.8	2.2
CeO$_2$-SM[b]	773	2.5	1.1	3.0
CeO$_2$-SM[c]	873	—	17.7	—
CeO$_2$-SM[c,d]	773	—	15.9	—
CeO$_2$-BS	773	4.0	3.3	5.9
CeO$_2$-BS	873	4.0	3.6	6.3
CeO$_2$-BS	973	—	2.2	—
CeO$_2$-BS	1173	—	0.4	—

[a] Total amount of chemisorbed hydrogen as determined by adding the amounts of hydrogen desorbed as H$_2$ (TPD-TC), and that desorbed as H$_2$O (TPD-MS). [b] Reduction at 1173 K, reoxidation at 773 K. [c] Experiments performed on a second CeO$_2$-SM sample. [d] Reduction at 873 K, reoxidation at 773 K.

clearly show that the hydrogen consumption peaks observed in a classic TPR-TC diagram cannot, in principle, be associated with the reduction of ceria with the creation of oxygen vacancies.

Taking into account that the reduced ceria can chemisorb, at room temperature, large amounts of O_2.[16,26,28,30] and that ceria reoxidation is not complete at 295 K,[16,28,30] we have combined a pulse technique, at 295 K, followed by TPO to estimate the total oxygen uptake.

Before running the oxidation experiment, the reduced samples were flushed with He at the reduction temperature, for 1 h, and cooled to 295 K, also in a flow of the inert gas. In accordance with Fig. 2 and 3, for 773 K or higher reduction temperatures, this treatment ensures the elimination of the hydrogen chemisorbed on the reduced oxide, a factor which can strongly disturb the estimate of the actual level of irreversible reduction reached by ceria.

Fig. 4 shows the results of a representative O_2 pulses–TPO experiment. The reduced ceria sample was treated with successive pulses of O_2(5%)–He until an apparent saturation was reached. Then the gas flow through the reactor was switched from He to O_2(5%)–He, and the TPO experiment was run. Table 2 summarizes the results we have obtained. As can be deduced from this table, the degree of reduction of CeO_2-BS varies from 4.9 to 62.7%, thus allowing one to investigate hydrogen chemisorption on ceria samples in a wide range of reduction states.

Table 2 Study by oxygen-pulse experiments and TPO of the degree of irreversible reduction of CeO_2-BS

reduction temperature /K	CeO_2 reduced to Ce_2O_3 (%)		
	pulses at 295 K	TPO	total
773	2.2 (5.5)	2.7 (6.7)	4.9 (12.2)
973	24.6 (61.6)	7.0 (17.5)	31.6 (79.0)
1173	45.2 (113.0)	17.5 (43.7)	62.7 (156.7)

O_2 uptake/mmol O_2 (mol CeO_2)$^{-1}$ is given in parentheses.

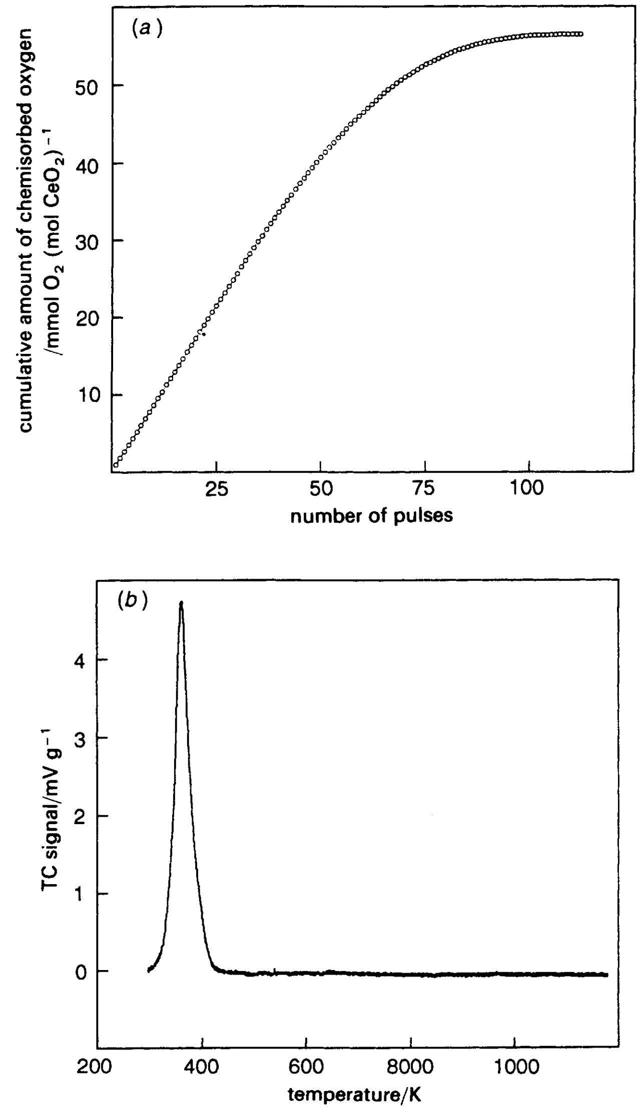

Fig. 4 Representative oxygen pulses experiment at 295 K (*a*) and TPO (*b*). Study of CeO_2-BS reduced with H_2 at 973 K, evacuated at 973 K and further cooled to 295 K in a flow of He.

FTIR Study of $H_2(D_2)$–CeO_2 Interaction

The interaction of hydrogen with CeO_2-SM was also investigated by FTIR spectroscopy. A self-supported ceria disk was first evacuated at 773 K, for 1 h, under high vacuum, and then reduced in a flow of H_2, at 623 K. The reduction protocol was the same as followed in the case of TPD H_2 studies. Finally, the sample was pumped off at several temperatures increasing from 295 to 773 K. The first experiment was followed by two successive series of reduction–evacuation treatments at 773 and 873 K.

Fig. 5 reports O—H stretching region of the spectra recorded for CeO_2-SM reduced at 623, 773 or 873 K, and further cooled to 295 K in a flow of H_2. For comparison, Fig. 5 also includes the spectrum of the oxide evacuated at 773 K. In good agreement with the results of ref. 16 and 18, the reduction treatment modifies significantly the ceria spectrum in this region. In effect, the unreduced sample, Fig. 5(*a*),

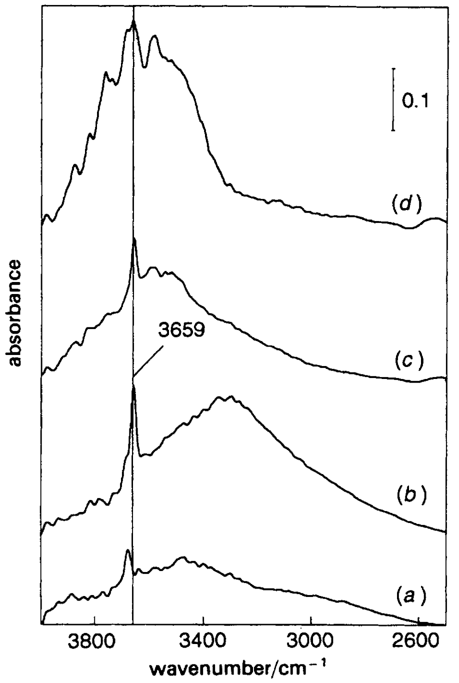

Fig. 5 FTIR spectra corresponding to a CeO_2-SM sample heated under high vacuum at 773 K for 1 h (*a*), and successively reduced with flowing H_2 at 623 (*b*), 773 (*c*) and 873 K (*d*). After the reduction treatment the sample was always cooled to 295 K under H_2 (P_{H_2} = 101 325 Pa).

shows a sharp band at 3678 cm^{-1} accompanied by a shoulder at 3659 cm^{-1}, which can be assigned to the so-called type II O—H species,[16] as well as a broader feature centred at around 3480 cm^{-1}. For the sample reduced at 623 K, Fig. 5(*b*), the spectrum of the high-frequency region is characterized by a sharp band at 3659 cm^{-1}, with a shoulder at 3684 cm^{-1}. As will be confirmed by the deuterium reduction experiments reported in Fig. 6, the same two features above are also characteristic of the oxide reduced at both 773 and 873 K.

The spectrum depicted in Fig. 5(*b*) also shows a broad band centred at 3225 cm^{-1}. This band reaches its highest intensity after reduction at 623 K. A quite similar low-frequency feature has been reported earlier for a ceria sample reduced with hydrogen at 573 K.[18]

The series of evacuation treatments at temperatures ranging from 295 to 773 K applied to the oxide reduced at 623 K, not shown in Fig. 5, led to the almost complete elimination of the O—H species.

If the spectra in Fig. 5(*b*) and (*c*) are compared, it can be noted that upon reduction at 773 K the band at 3659 cm^{-1} is recovered to a much larger extent than that at 3325 cm^{-1}. This suggests that the latter is associated with labile surface oxygen anions which are eliminated during the evacuation at 773 K, which followed the hydrogen treatment at 623 K. In this respect, note that, in accordance with the TPD-MS study reported in Fig. 3(*a*), the evacuation of CeO_2-SM reduced at 623 K, at temperatures higher than 623 K, leads to water formation, and therefore to the elimination of some lattice oxygen ions.

The spectrum in Fig. 5(*c*) also shows a broad feature centred at *ca.* 3600 cm^{-1}. The intensity of this band, which has been assigned to an electronic transition,[16] increases significantly after reduction at 873 K. This greatly affects the observation of other features also present in the same region of the spectrum, Fig. 5(*d*).

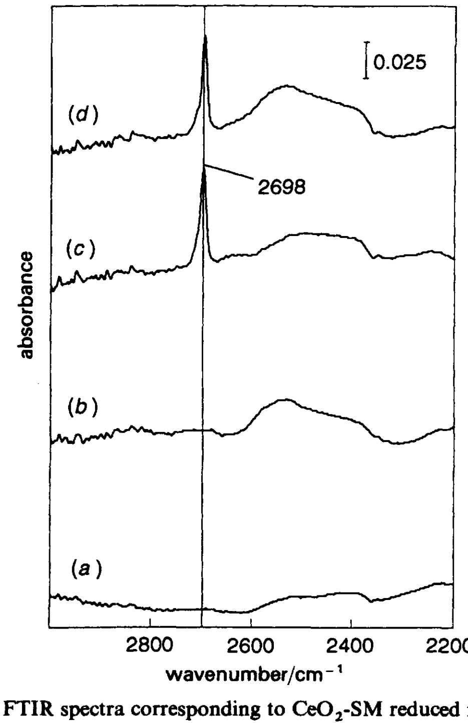

Fig. 6 FTIR spectra corresponding to CeO_2-SM reduced in flowing D_2 at 873 K (*d*), further oxidized in air at 773 K, evacuated at 773 K under high vacuum, and reduced in flowing D_2 at 773 K (*c*). In both cases the reduced sample was cooled to 298 K under D_2 (P_{D_2} = 101 325 Pa). The spectra corresponding to CeO_2-SM reduced with H_2 at 773 K (*a*) and 873 K (*b*) are also included for comparison.

To eliminate the difficulties above, we have carried out a parallel FTIR study in which D_2 was used instead of H_2. The oxide sample was first reduced at 873 K and cooled to 295 K under flowing D_2; then it was evacuated at several increasing temperatures up to 773 K, reoxidized in air at 773 K, evacuated, and finally, reduced again with D_2, at 773 K, and cooled to room temperature in a flow of D_2.

The features appearing at frequencies below 2600 cm^{-1} in Fig. 6(*c*) and (*d*) are similar to those observed after reduction with H_2 at 773 K [Fig. 6(*a*)] and 873 K [Fig. 6(*b*)], respectively. This allows us to conclude that the O—D stretching vibrations are not the major modes responsible for the bands found in the 2600–2200 cm^{-1} region, and therefore, that the O—D spectra for ceria reduced at 773 K [Fig. 6(*c*) and 873 K [Fig. 6(*d*)] are very similar to each other. In accordance with Fig. 6(*c*) and (*d*), these spectra consist essentially of a sharp band at 2698 cm^{-1}, which might well be correlated with the one observed at 3659 cm^{-1} in the O—H spectra reported in Fig. 5. This major feature 2698 cm^{-1}, also observed by us in spectra for D_2 chemisorbed on Rh/CeO_2 catalysts,[21] is accompanied by an unresolved shoulder on the high-frequency side, and a low-intensity band centred at 2650 cm^{-1}. Note that, the broad, strong band at 3600 cm^{-1} in Fig. 5(*c*) and (*d*) has no counterpart in the O—D stretching region of the spectra reported in Fig. 6(*c*) and (*d*), thus reinforcing the assignment to an electronic transition proposed in ref. 16.

Discussion

In Fig. 7 we have plotted the amount of hydrogen chemisorbed on CeO_2-SM *vs.* reduction temperature. For data referred to mol CeO_2 the amount of chemisorbed hydrogen strongly decreases with the reduction temperature. Thus, for CeO_2-SM reduced at 773 K, this amount is *ca.* 45 times larger than that determined after reduction at 1173 K. This variation is much smoother when data are referred to nm^2 BET surface area. In the latter case, values ranging from 7.1 H atom nm^{-2}, for ceria reduced at 873 K, to 2.2 H atom nm^{-2} after reduction at 1173 K have been obtained.

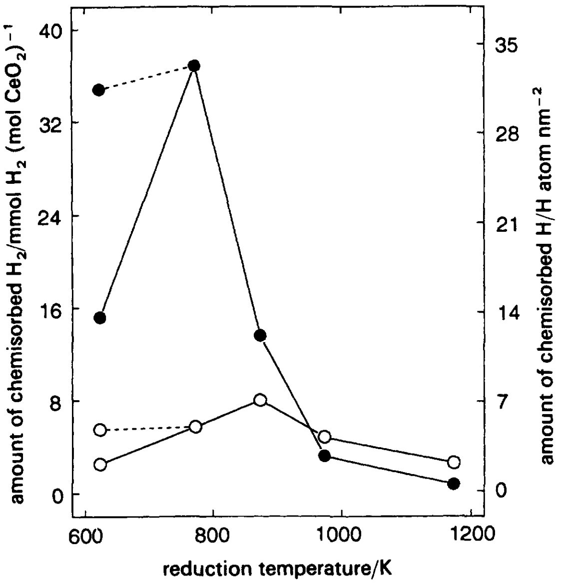

Fig. 7 Plots of the amount of H_2 chemisorbed on CeO_2-SM *vs.* reduction temperature. Data are referred to mol ceria (●) and nm^2 (BET) (○). For the sample reduced at 623 K, data corresponding to both the total amount of desorbed hydrogen ($H_2 + H_2O$) and that determined from TPD-TC (H_2) have been plotted.

Since the reduction treatments have an important effect on the BET surface area of CeO_2-SM, Table 1, the differences noted between the two plots in Fig. 7 might well be related to the sintering effects undergone by this oxide sample. In other words, the chemisorption of hydrogen on ceria seems to be a surface-related process. Furthermore, if the (110) plane of the fluorite-like structure of ceria is used as a reference to estimate the surface concentration of ions, the following values would be obtained 9.6 O^{2-} nm^{2-} and 4.8 Ce^{4+} nm^{-2}. This means that the whole series of data reported in Table 1 can be explained in terms of a purely surface process. In this respect, it is also interesting to analyse the results obtained for CeO_2-BS, an oxide sample with a much lower surface area and a higher textural stability. According to Table 1, the amounts of hydrogen chemisorbed on CeO_2-BS, if referred to mol CeO_2, are much smaller than those reported for CeO_2-SM. In contrast, the values per nm^2 are very close to each other. The results reported here are also in agreement with some earlier observations from the literature.[29] In effect, in ref. 29 a linear relationship has been observed between hydrogen consumption associated with the low-temperature TPR peaks and ceria surface area. In fact, they suggest the use of the TPR technique as a way of estimating ceria surface areas.[29]

As outlined above, the results obtained for CeO_2-SM reduced at 623 K show some singularities worthy of comment. According to Fig. 3(*a*), the hydrogen incorporated into CeO_2-SM during the reduction treatment is further desorbed as both H_2O and H_2. Upon integration of the trace for $m/z = 18$, we have estimated the amount of water evolved: 19.6 mmol $H_2O(mol\ CeO_2)^{-1}$. If this amount is added to the hydrogen desorbed as H_2, 15.2 mmol $H_2(mol\ CeO_2)^{-1}$, we should obtain 34.8 mmol $H_2(mol\ CeO_2)^{-1}$. This value is very close to that reported in Table 1 for CeO_2-SM reduced at 773 K, 36.8 mmol $H_2(mol\ CeO_2)^{-1}$. This is also observed in Fig. 7, where we have plotted both the amount of hydrogen desorbed as H_2 from the oxide reduced at 623 K, as determined by TPD-TC, and the value corrected by taking into account the amount desorbed as H_2O. Since the surface area of CeO_2-SM remains constant upon increasing the reduction temperature from 623 to 773 K, Table 1, the results above would indicate that, even in the case of the mildest reduction treatment, the total amount of chemisorbed hydrogen is determined by the surface area of the oxide.

All the results above, which were obtained from ceria samples reduced between 623 and 1173 K, contrast with the proposal made in ref. 14, where from H_2 chemisorption studies at 195–500 K, the formation of a bronze-like massive phase was suggested. Several other authors also seem to agree with this proposal.[16–24] Note, however, that the maximum intensity of the ^1H NMR signal in ref. 14, which is observed at 673 K, was found to correspond to 3.4×10^{20} H g^{-1}. This amount is equivalent to 5.9 H atom nm^{-2}, very close to our own results. If the stoichiometry $CeO_2H_{0.17}$ proposed in ref. 14 on the grounds of gravimetric studies is considered, we should obtain 9.6 H atom nm^{-2}, a value which does not allow us to exclude the surface nature of the chemisorption process. Since this latter value was determined after hydrogen treatment at 473 K,[14] it might be thought that for reduction temperatures lower than those investigated here, larger amounts of hydrogen would be chemisorbed. Some previous volumetric,[11,26] magnetic balance,[16,30] and TPR-TC[24,29] studies of the hydrogen interaction with bare ceria do not seem to support the above suggestion. On the contrary, all these studies show that the chemisorption process just starts at around 473 K, the hydrogen consumption increasing with the temperature. In contrast with this, when highly dispersed rhodium is present, the adsorption of hydrogen on ceria takes place well below 473 K.[11,12,21] In this latter case, on the other hand, the adsorption of hydrogen on ceria is, to a very large extent, reversible.[11] In spite of these, in principle, favourable conditions for observing a hydrogen-containing ceria bulk phase, the amounts of chemisorbed hydrogen were always found to be dependent on the BET surface area of the oxide used as support.[21] Furthermore, the largest amount of chemisorbed hydrogen we have ever determined can reasonably be interpreted as due to a purely surface process.[11]

It has previously been reported that the amount of hydrogen chemisorbed $(g\ ceria)^{-1}$ increases as the reduction temperature is increased from 673, to 773 and 873 K.[24] In ref. 24, however, the hydrogen desorption was studied, as usual, by TPD-TC, and the reducing agent was H_2(1%)–Ar, instead of the pure hydrogen used here. Consequently, the results discussed above for CeO_2-SM reduced at 623 K might well allow one to explain the differences noted between the observations made in ref. 24 and ours. It seems likely that the reduction treatments with H_2(1%)–Ar are mild enough to lead to ceria samples with a low degree of irreversible reduction. If this is so, part of the chemisorbed hydrogen would be desorbed as H_2O, and therefore it would not be detected by TPD-TC. In this respect, note that if the data in ref. 24 are referred to nm^2 BET surface area, we would obtain for the sample reduced at 873 K a value of 2 H atom nm^{-2}, thus suggesting that even at the highest reduction temperature, part of the hydrogen chemisorbed on the ceria sample, if saturated, is probably desorbed as H_2O. In any case, the largest amount of chemisorbed hydrogen reported in ref. 24 is far from that corresponding to surface saturation.

Compared with the CeO_2-SM sample, the influence of the reduction temperature on the BET surface area of CeO_2-BS is much smaller. Accordingly, this latter oxide was considered to be the most convenient sample for investigating the relationship between the degree of irreversible reduction of the oxide and the amount of chemisorbed hydrogen.

Table 1 shows that the amounts of H_2 chemisorbed by CeO_2-BS reduced at either 773 or 873 K are very close to each other. This is so, in spite of the notable difference in degree of reduction resulting from these two treatments. This suggests that there is no simple relationship between the total concentration of oxygen vacancies in the sample and its capability of chemisorbing hydrogen. Also in agreement with this observation, the amount of hydrogen chemisorbed by CeO_2-SM reduced at 873 K, and that determined for the sample resulting from its reoxidation a 773 K and further reduction at 773 K are very similar to each other (Table 1). For these two samples we should expect the same BET surface area, the only difference between them being the reduction level reached by ceria. The results of our FTIR study in Fig. 6 are also consistent with these observations. It can be concluded from comparison of Fig. 6(*c*) and (*d*) that both the frequencies and intensities of the O—D stretching bands are almost identical for CeO_2-SM reduced with D_2 at 873 K [Fig. 6(*d*)] and 773 K [Fig. 6(*c*)]. If the (110) plane of CeO_2 is used as a surface model, the complete irreversible surface reduction of CeO_2-BS would correspond to 0.7%, a value much smaller than those determined from the O_2 pulses–TPO experiments: 5% for the sample reduced at 773 K and *ca.* 20% after reduction at 873 K. Then, surface reconstruction at both 773 and 873 K is likely, and therefore the surface structures become close enough to explain the similarities observed. For the highest reduction temperatures investigated here, the formation of hexagonal cerium sesquioxide, A-Ce_2O_3, cannot be excluded.[30] This may modify the chemisorptive properties of the oxide, thus explaining the diminution of the adsorption capability observed here.

Conclusions

In accordance with our TPD-MS study, hydrogen can be desorbed from ceria in two ways leading, respectively, to H_2O and H_2. The relative amounts of these two forms depend on the reduction temperature, so that from 773 K onwards H_2 was the only desorption product. This observation suggests that the interpretation of the classic TPD-TC and TPR-TC experiments encounters some additional difficulties in the case of ceria-containing catalysts. Regarding the TPR experiments, our results show that the hydrogen consumption should not simply be assigned to the irreversible reduction of ceria leading to the creation of oxygen vacancies with H_2O evolution. In effect, part of the hydrogen incorporated into the oxide in the low-temperature region of the TPR spectra can be desorbed as H_2 at higher temperatures, thus introducing a further complicating element in their interpretation. It can also be deduced from our results that, depending on the prior reduction treatment applied to the oxide, the use of the TPD-TC traces to estimate the amounts of hydrogen chemisorbed on ceria can be very misleading, because the contribution of the hydrogen evolved as water is ignored.

Our TPD studies have also allowed us to define evacuation treatments ensuring the elimination of the hydrogen which might be retained by the oxide during the reduction treatment. In this way, the disruptive presence of chemisorbed hydrogen in the O_2 pulses–TPO experiments was prevented, and the concentration of oxygen vacancies in the reduced ceria sample determined. In summary, we have established a suitable experimental methodology to investigate hydrogen chemisorption on a series of ceria samples with a well defined degree of irreversible reduction.

The quantitative results reported in this work strongly suggest that hydrogen chemisorption on ceria is a surface process. Moreover, the results from the literature,[14,24] with no exception, can also be interpreted in the same way.

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