

Oxygen Titration of Spill-Over Hydrogen in Ceria and Ceria–Alumina Supported Platinum–Rhodium Catalysts: Application to the Determination of the Ceria Surface in Contact with Metal

S. Salasc,* V. Perrichon,*¹ M. Primet,* M. Chevrier,† and N. Mouaddib-Moral‡

* *Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634, CNRS/Université Claude Bernard Lyon 1, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France;* † *Technocentre Renault, 1 rue du Golf, 78288 Guyancourt Cedex, France;* and, ‡ *Renault, Centre de Lardy, 1 allée Cornuel, 91510 Lardy, France*

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Successive $O_2/H_2/O_2$ chemisorption measurements were performed at room temperature over Pt/CeO₂ catalysts of different BET surface areas after reduction at 573 K under H₂. It has been determined that about 4 μatom of oxygen per m² of ceria is required to fill the oxygen vacancies created by the reduction in agreement with the value deduced from the TPR profiles. The same value was also obtained from the H₂/O₂ titration, which shows that oxygen is able to titrate the hydrogen which has spilled over the ceria surface via the metallic particles. Thus, the consistency of the three techniques demonstrates the validity of this method of measuring both the total ceria surface area and the ceria surface in contact with the precious metals. The application of this methodology to the case of Pt and Pt–Rh /CeO₂–Al₂O₃ model three-way catalysts leads to a set of ceria surface areas deduced from O₂ chemisorption and O₂ titration much lower than those obtained by TPR. This behaviour has been attributed to the presence of chlorine ions originating from the precursor and to the formation of stabilised Ce³⁺ ions at the CeO₂/Al₂O₃ interface during reduction. After an ageing treatment at 1273 K under N₂ + 10% H₂O, an even greater difference was observed between the TPR ceria surface areas and those deduced from the chemisorption method. The results indicate an increased fraction of ceria without metal due to sintering and to the segregation between ceria and the metal particles. © 2000 Academic Press

Key Words: H₂/O₂ titration; O₂ chemisorption; Pt/CeO₂; PtRh/CeO₂–Al₂O₃; spill-over hydrogen; metal–ceria interaction; ceria–alumina interaction; three-way catalysts.

1. INTRODUCTION

The oxygen storage capacity has been established for several years as one of the key parameters of the activity in three-way catalysis. For this reason, it has been largely studied and a lot of effort has been devoted to its measurement. One of the basic methods to quantify the oxygen storage

capacity is the pulse technique performed at temperatures below 773 K with alternating injections of CO and O₂ as reactants (1,2), and it has been possible to establish a correlation between the oxygen storage capacity of commercial three-way catalysts and their catalytic activity (3). In our laboratory, we have developed a technique for measurement of this oxygen based on the analysis of temperature-programmed reduction (TPR) profiles under hydrogen. In particular, this method has made it possible to calculate the ceria surface area in ceria–alumina supported Pt–Rh catalysts (4). This method was also successfully applied to the case of commercial three-way monolithic catalysts at different stages of ageing, provided that some hypotheses were made on the mean oxidation state of the precious metals (5).

However, the ceria surface area or the oxygen storage capacity is probably not the only important parameter in the activity of three-way catalysts. The metal and its related characteristics, i.e., nature, content, chemical state, dispersion, and localisation, are among the parameters which need to be defined and may be determining for the activity. Peculiar contacts could be essential to increase the available oxygen of CeO₂-containing systems (6,7). However, the low dispersion (2–3%) measured on catalysts after ageing at 1273 K (8) raises the question of the nature of the active sites and of the precise localisation of the sintered precious metals on the support. Indeed, if the activity requires both metal sites and a high oxygen storage capacity, one of the key parameters will be the interaction between the metallic particles and the ceria surface. Consequently, to increase the knowledge about the three-way catalysts, it appears essential to quantify the interface between ceria and the metals and to determine the exact nature of this interaction. With this objective, we have developed a new method to measure the contact surface between ceria and the metals and this paper describes the obtained results.

The method is based on successive hydrogen/oxygen chemisorption in relation to the well-known spill-over phenomenon of hydrogen which occurs on the support

¹ To whom correspondence should be addressed. Fax: 33 4 72 44 81 14. E-mail: Vincent.Perrichon@univ-lyon1.fr.

when there is a direct interaction between the ceria surface and the precious metals. In the absence of metal, the chemisorption of hydrogen on ceria is activated and does not occur below 470 K (9,10). In the presence of a dispersed metal, the adsorption of hydrogen has been observed at room temperature and is not limited to the metallic particles, but concerns all the ceria surface (11–14). Therefore, one of the objectives of this study is to try to titrate by oxygen the hydrogen irreversibly adsorbed on the support. Insofar as the spill-over hydrogen requires the presence of metal atoms, this oxygen titration should then quantify the ceria surface in interaction with the precious metals. In addition, we have also performed the direct adsorption of oxygen on a catalyst reduced under mild conditions in order to obtain the total ceria surface area. Thus, with these two quantities of oxygen measured by direct chemisorption and by titration, one should be able to quantify directly the surface available oxygen and the available oxygen in interaction with the metals. In this paper, the validity of this method is first established with a series of Pt/CeO₂ catalysts. Then the method is applied to the case of Pt/CeO₂-Al₂O₃ model catalysts, in fresh or aged state.

2. EXPERIMENTAL

2.1. Materials

Most of the catalysts were those already used in a previous study (4). They were prepared by impregnation or coimpregnation of ceria or ceria-alumina supports with solutions of the metallic salts. The initial HSA CeO₂ support, from Rhodia, had a 127 m² g⁻¹ BET surface area. It was calcined at increasing temperature in order to obtain four other ceria samples with lower specific surface areas, down to 5 m² g⁻¹. The ceria-alumina support was prepared by grafting Ce(acac)₃ on an alumina support (Rhodia SCM129, S_{BET} = 107 m² g⁻¹) and calcining at 673 K (8,15). The final cerium content was around 19 wt%, representative of the cerium content in the industrial three-way catalysts.

These supports were impregnated with aqueous solutions of H₂PtCl₆ or/and RhCl₃. The metal contents were 0.5 wt% for the monometallic and 1 and 0.2 wt% for Pt and Rh, respectively, in the case of the bimetallic systems. The impregnated supports were dried overnight under vacuum at 383 K and then treated for 2 h at 773 K under flowing nitrogen.

In order to have free chlorine catalysts, a series of samples was prepared starting with platinum and/or rhodium acetylacetonate. In this case, the supports were impregnated in toluene at 343 K. Then, the solids were dried under vacuum at 313 K in a first step and then at 373 K. The further calcination was performed at 673 K under air. The obtained catalysts are presented in Table 1 with the corresponding chemical analysis of the metals and the BET surface area.

TABLE 1
Metal Content, BET Surface Area, and Accessible Metallic Area (H/M) of the Catalysts

Support	Catalyst	Pt (wt%)	Rh (wt%)	S _{BET} * (m ² g ⁻¹)	H/M (%)
Ceria	Pt/Ce	0.43		117	36
	Pt/Ce(80)	0.45		78	24/31 ^a
	Pt/Ce(60)	0.40		59	68/56 ^a
	Pt/Ce(30)	0.48		27	49
	Pt/Ce(5)	0.46		4.9	26
	Pt/Ce-acac	0.515		122	80
	Rh/Ce		0.51	124	41
	Pt-Rh/Ce	0.945	0.23	117	45
Ceria-alumina	Pt/CeAl	0.42		97	73
	Pt/CeAl-acac	0.49		96	>100 83 ^b
	Pt-Rh/CeAl	0.955	0.16	96	46
	Pt-Rh/CeAl-acac	1.05	0.225	97	>100 89 ^b

Note. Ce and CeAl refer to the ceria and ceria-alumina support.

* The BET measurements referred to the initial mass of the sample.

^aThe measure was doubled.

^bObtained by dynamic volumetry (see text).

Finally, the catalysts supported on ceria-alumina were aged for 5 h at 1273 K under flowing nitrogen (6 L h⁻¹) containing 10 vol% water vapour. The model catalyst 1Pt0.2Rh/CeO₂-Al₂O₃ was reduced for 5 h at 773 K before ageing.

2.2. Characterisation Methods

2.2.1. Chemisorption of oxygen and H₂/O₂ titration at room temperature: Principle of the method. The principle of the method is based on the results obtained previously in the study of the redox properties of ceria in the presence or in the absence of a metal. Indeed, for ceria, the surface is reduced by hydrogen for $T > 470$ –570 K (16). However, in the presence of precious metals, the surface cerium ions can be reduced at room temperature through the hydrogen migration on the support via the metallic particles (11–14). From previous magnetic balance results (14,17), it can be estimated that treatment at 573 K under H₂ reduces only the surface of ceria and the precious metals; the reduction of the bulk occurs only at higher temperature. Consequently, if after this reducing treatment an oxygen flux is sent at room temperature, the oxygen should fill the oxygen vacancies of the reduced ceria and should be adsorbed on the metallic particles. Thus, this oxygen chemisorption should lead to the determination of the total ceria surface if one takes into account the contribution of the precious metals in the measured quantity.

After this oxygen chemisorption, if a hydrogen flux is sent on the sample, always at room temperature, hydrogen should titrate the chemisorbed oxygen at the surface of the

metallic particles. It should also migrate via the spill-over on the surface of ceria particles which support precious metals. Since this spill-over phenomenon has been shown to affect the whole surface of the ceria grains which support metallic particles, by measuring the corresponding hydrogen quantity, it should be possible to quantify the corresponding ceria surface area.

A new surface reaction, potentially rich in information, can be added to this protocol. It involves sending an oxygen flux after this hydrogen chemisorption, assuming that almost none of the spill-over hydrogen is desorbed at room temperature. The oxygen then fixed during this step should correspond to the titration of the hydrogen chemisorbed on the metallic particles but could also include the titration of the hydrogen attached on the ceria. If this assumption is correct, the measurement of this titration oxygen should make it possible to quantify the quantity of hydrogen that migrated on the support and thus to determine the surface of ceria in contact with the metallic particles. In the following, the hydrogen and oxygen uptakes in the initial chemisorption or the subsequent titration steps will be denoted as HC, OC, HT, and OT. The corresponding adsorption treatments will also be referred to by the same symbols.

To clarify all these steps, the reactions involved in the succession of these supposed processes are given in Table 2 for the case of a platinum catalyst. The stoichiometry of the reactions has been confirmed by the results presented below. Similar reactions can be given for the case of rhodium.

2.2.2. Calculation method to obtain the ceria surface areas. To obtain the total ceria surface area, it is necessary to subtract the platinum (metal) contribution from the oxygen consumed during the OC step. This requires knowledge of the accessible metallic area (or dispersion). These values can be obtained by measuring the irreversible hy-

drogen chemisorption (HC) at room temperature on the catalysts after reduction at 573 K, which leads to reliable results in the case of ceria-alumina supported catalysts (8,18). For each HC or OC chemisorption, the H or O/Pt_s ratio can be considered equal to 1, where Pt_s represents a platinum surface atom. In other words, the oxygen quantity consumed by the Pt_s atoms during OC is identical to the hydrogen consumed during the hydrogen chemisorption HC (see Table 2). Thus, we obtain the quantity of oxygen directly related to ceria by subtracting HC from OC.

It is also possible to correlate the oxygen quantity determined during OT with the ceria surface in contact with platinum. From the equations presented in Table 2, the oxygen quantity consumed by the Pt_s atoms during OT is equal to 1.5 times that consumed during HC. Thus, to obtain the ceria surface area, it is necessary to subtract 1.5 HC from OT.

2.2.3. Experimental protocols. The successive chemisorption of hydrogen and oxygen was measured by dynamic volumetry using a thermal conductivity detector (19). For the hydrogen chemisorption, the mixture introduced in the reactor was 1% H₂/Ar with argon as reference. Similarly, the oxygen chemisorption was measured on the same apparatus using 1% O₂/He and He mixtures as flowing gases.

The experimental protocol to measure the different quantities is deduced from the method presented in Section 2.2.2. Each measurement is based on the irreversible adsorption of hydrogen or oxygen at room temperature. That requires the succession of two chemisorption steps, with the intermediary desorption step always at room temperature under an inert gas (Ar or He). Thus, after a treatment under vacuum at 723 K for 1 h, the sample (0.1–0.5 g) was reduced at 573 K under hydrogen for 12 h, desorbed under inert gas 2 h at the same temperature, and

TABLE 2

Presentation of the Reactions Involved during H₂/O₂ Chemisorption Cycles Carried Out at 298 K and of the Different Processes Which Are Supposed To Occur: Example of a Platinum Catalyst

Operations	Reactions involved ^a	Titrated species
	Reduction H ₂ —573 K	
Oxygen chemisorption: OC	Pt _s + 1/2 O ₂ → Pt _s O (OCeO□CeO) _s + 1/2 O ₂ → (OCeOOCeO) _s	O is fixed on Pt surface and fills the vacancies of reduced CeO ₂
Titration of adsorbed oxygen by hydrogen: HT	Pt _s O + 3/2 H ₂ → Pt _s H + H ₂ O _{ads}	H titrates O fixed on Pt and migrates over CeO ₂ (spillover)
	HH	
Titration of adsorbed hydrogen by oxygen: OT	(OCeOOCeO) _s ,Pt + H ₂ → (OCeOOCeO) _s ,Pt Pt _s H + 3/4 O ₂ → Pt _s O + 1/2 H ₂ O _{ads}	O titrates H fixed on Pt and doses the H spilled over CeO ₂
	HH	
	(OCeOOCeO) _s ,Pt + 1/2 O ₂ → (OCeOOCeO) _s ,Pt + H ₂ O	
	Reduction H ₂ —573 K	
Hydrogen chemisorption: HC	Pt _s + 1/2 H ₂ → Pt _s H	H is fixed on Pt surface

^as = surface.

cooled to room temperature. Then, the catalyst was put into contact with 1% O₂/He to measure the irreversible chemisorbed oxygen (OC). The other quantities HT and OT were obtained in the same way by repeating, several times if necessary, the successive adsorption with the 1% H₂/Ar and 1% O₂/He mixtures. An equilibrium must be obtained before going on to the next step.

A separate measurement could have been performed in the same apparatus to measure HC, the irreversible hydrogen chemisorption at room temperature, for evaluating the accessible metallic area. In fact, in the following, the HC values were obtained by static volumetry of the chemisorbed hydrogen according to the procedure already described (8,18) and after three reduction steps at 573 K under 2.7 kPa H₂ (18). A first and a second isothermal adsorption were performed, with an intermediary treatment of 15 min under vacuum at room temperature, in order to determine the irreversible adsorption. The two isothermal curves were drawn with 5–6 experimental points in the 0.5–3.5 kPa pressure domain, each equilibrium point being obtained after 10 min in contact with the catalyst.

Finally, in order to compare the OC–OT chemisorption methods with a more established technique, the ceria surface area was also measured with TPR under hydrogen for the various catalysts, according to the protocol already described (4). The TPR profile was obtained by heating 0.1 g of sample under a flux of 1% H₂/Ar up to 1073 K with a 20 K min⁻¹ heating rate. The sample was previously treated under air at 673 K for 1 h and then outgassed under argon for 1.5 h at 773 K.

3. RESULTS

3.1. Determination of the Accessible Metallic Area by Chemisorption of Hydrogen

As explained above, the HC values are necessary to calculate the contribution of the metals to the general chemisorption process. The accessible metallic areas were measured for each solid. They are given in Table 1, expressed as H/M in percentage. Although some questions may be raised on the evolution of the dispersion with the BET area of the ceria support in the Pt/CeO₂ series, we will not discuss the absolute metallic dispersions obtained for these catalysts. Some values which could have been considered as doubtful were doubled and led to almost the same results. The most relevant feature is the tendency for the catalysts prepared from the acetylacetonate complexes to give a H/M value much higher than the catalysts prepared from the chlorinated precursor. This is related to hydrogen spill-over processes on the support, which are supposed to not occur on a reduced catalyst but have been sometimes observed to a limited extent in the case of free chlorine catalysts. Some of these features have already been discussed (17) and will not be considered here. However, it is clear that the

TABLE 3

Results of the Chemisorption and Titration Operations Performed on Pt/CeO₂ Catalysts

Catalyst	OC	HT1	HT2	HT3	OT1	OT2
Pt/Ce	233	544	455	486	252	
Pt/Ce(80)	157	368	339	380	162	155
Pt/Ce(60)	114	292	277	268	132	137
Pt/Ce(5)	11	35	32	29	14	12

Note. All the results are expressed in micromoles of H₂ or O₂ per gram of catalyst.

conditions of adsorption and desorption may influence the amount of hydrogen fixed to the support. Separate experiments performed in dynamic volumetry with much longer equilibrium times for desorption led to about 83 and 89% dispersion values, for Pt/CeAl-acac and Pt–Rh/CeAl-acac samples, respectively. These values will be used in the following.

3.2. Study of Pt and/or Rh on Ceria

3.2.1. Study of Pt/CeO₂ catalysts of different specific surface areas: Relation between the oxygen quantities consumed during the successive chemisorptions and the ceria surface area. In order to establish the protocols and to verify the validity of the method, the study was started on Pt/CeO₂ catalysts before application to the case of CeO₂–Al₂O₃ supported catalysts. The results of the operations of chemisorption and titration are given in Table 3. The HT operation was repeated three times and the OT operation two times. The H/M values which were utilised for the metal contribution are those listed in Table 1.

Figure 1 summarises the results obtained with the Pt/CeO₂ catalysts. The oxygen quantities consumed during

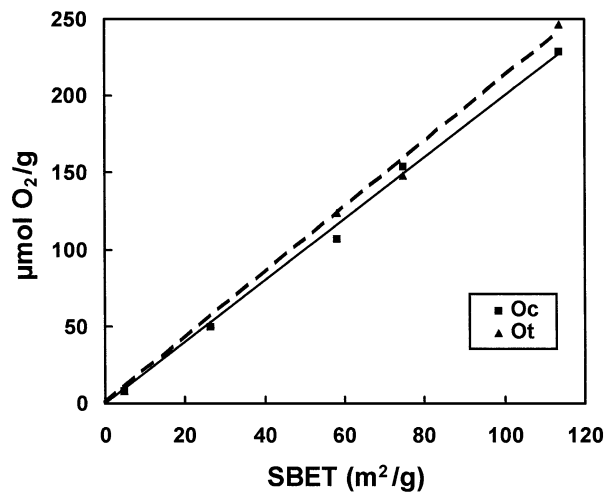


FIG. 1. Oxygen quantities consumed by the ceria of Pt/CeO₂ catalysts during the OC and OT operations vs the BET surface area.

the OC and OT steps have been corrected from the metal contributions and thus are due only to the ceria participation. By plotting these quantities vs the BET surface area, two straight lines are obtained, with slopes equal to 2.0 and 2.1, respectively, for the OC and OT steps, i.e., a mean correlation of 2 μmol of oxygen per square meter of ceria. In an equivalent manner, 4 μatom of oxygen is adsorbed per square meter of ceria.

This 4 μatom of oxygen is comparable to the 3.9 μmol of H₂ which was found necessary to reduce 1 m² per gram of ceria (4). It can be concluded that, after reduction at 573 K, the oxygen chemisorption doses the whole ceria and only that surface. Similarly, the values deduced from the OT step which represent the titration of the spill-over hydrogen by oxygen are also proportional to the ceria surface area with almost the same slope. Thus, the stoichiometry values of the reactions considered in Table 2 are verified. Consequently, the spill-over process involves one hydrogen atom per mole of surface cerium and the titration of this hydrogen by oxygen during OT corresponds to one oxygen for two surface cerium ions.

It is also noticed that there is an equivalence between the values deduced from OC which represent the total ceria surface and those issued from OT which titrate the hydrogen of spill-over and thus only the ceria surface in interaction with platinum. Therefore, it can be concluded that platinum has been impregnated on the whole ceria surface.

The same procedure could be used for the hydrogen quantities consumed during the HT operations. They are supposed to correspond to the titration of the oxygen fixed on platinum and to the migration of hydrogen on the ceria. However, the measured HT data are not very reproducible, with a tendency for the first hydrogen uptake HT1 to be higher than the subsequent HT. Moreover, using the basic assumptions given in Table 2, these quantities lead to an overestimation of the ceria surface area. Therefore, since these hydrogen titrations do not give reliable values of surface area, they will not be presented again in the remainder of this paper. It is certain that complementary studies would be necessary to examine in more detail this hydrogen overconsumption.

3.2.2. Influence of the nature of the precious metals and the metallic precursor: It was necessary to verify with rhodium the validity of the correlation established on the Pt/CeO₂ catalysts between the OC and OT quantities and the ceria surface area. Therefore, the oxygen chemisorption and the H₂/O₂ titration were applied to Rh/CeO₂ and Pt-Rh/CeO₂ catalysts. They were prepared from chlorinated precursors by impregnation of the HSA ceria. In the same way, in order to study the influence of the metallic precursor, a new Pt/CeO₂ catalyst was prepared from platinum acetylacetonate on the same HSA ceria.

The ceria surface areas calculated by applying the relation of 4 μatom of oxygen per square meter of ceria,

TABLE 4

Ceria Surface Area of Rh or Pt-Rh/CeO₂ ex-Chloride and Pt/CeO₂ ex-Acac Calculated from OC and OT

Catalyst	S_{BET} (m ² g ⁻¹)	S_{CeO_2} (m ² g ⁻¹)	
		OC	OT
Rh/CeO ₂ (115)	124	140	104
Pt-Rh/CeO ₂ (115)	117	140	117
Pt/CeO ₂ (115)-acac	122	132	123

after deduction of the metal contribution, are given in Table 4.

Some variation can be observed between the surface areas measured by each technique ($\pm 20\%$). However, considering the good homogeneity of the results for each technique, it can be concluded that, on ceria support, the ceria surface area measurement by OC and OT is not influenced by the nature of the precious metal, Pt or Rh, nor by that of the metallic precursor, chlorinated or not.

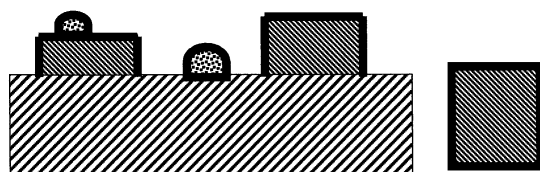
3.3. Application to Pt and/or Rh Catalysts Deposited on Ceria-Alumina

In order to appreciate the validity and the limits of the methods elaborated with catalysts deposited on ceria, the oxygen chemisorption and H₂/O₂ titrations were performed on catalysts deposited on a CeO₂-Al₂O₃ support. The values issued from OC should make it possible to obtain the total ceria surface, in contact with a precious metal or not, and the oxygen quantity consumed during the OT step should correspond to the titration of the hydrogen which has migrated on ceria through the precious metals and thus should quantify only the ceria surface supporting the precious metals. To illustrate these different possibilities, Fig. 2 presents a model of a Pt-Rh/CeO₂-Al₂O₃ catalyst and the scheme of the ceria surface areas measured by OC and OT.

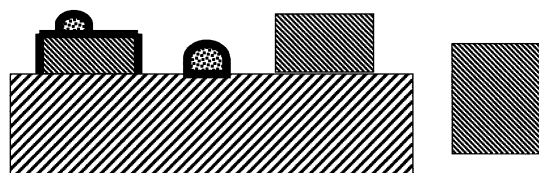
This study was carried out on two catalysts, mono- (Pt) and bimetallic (Pt-Rh). They were prepared from chlorinated precursors or from acetylacetonate precursors to study again the influence of chlorine with this ceria-alumina support. In addition, these catalysts were aged to study the possibilities of the method for application to the case of real catalysts.

3.3.1. Study of fresh catalysts: Influence of the metallic precursor: Table 5 gives, for the catalysts deposited on ceria-alumina, the ceria surfaces measured by oxygen chemisorption and H₂/O₂ titration. They were calculated from the relation established above that 4 μatom of oxygen corresponds to 1 m² per gram of ceria. In order to analyse the results in more detail, the table gives also the ceria surface areas deduced from TPR measurements.

The values of ceria surface area deduced from TPR are identical for the four samples. However, large differences



Surface measured by O₂ chemisorption : OC



Surface measured by O₂ during the titration : OT

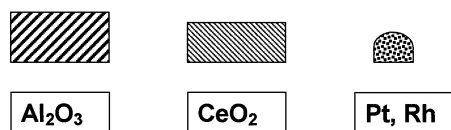


FIG. 2. Schematic representation of the ceria surface areas estimated from OC and OT in a Pt-Rh/CeO₂-Al₂O₃ model catalyst. The thick black lines represent the metal and ceria surfaces adsorbing oxygen during the O₂ chemisorption and O₂ titration steps.

are observed between the results from TPR and the OC and OT techniques. For the catalysts prepared from the chlorinated precursors, the ceria surface areas estimated by OC are much lower than those determined by TPR, 23–21 m² g⁻¹ instead of 65–68 m² g⁻¹. It can be noticed that the two techniques are supposed to measure the total ceria surface and should lead to the same results. In the case of free chlorine catalysts, the two sets of values are closer, but the total surface values determined by OC remain lower (45–44 m² g⁻¹). Thus, it seems that the reoxidation at room temperature during the OC step is only partial and affects only a fraction of the ceria surface. It must also be added

TABLE 5

Different Surface Areas Estimated by BET, TPR, OC, and OT in the Fresh Catalysts Deposited on Ceria-Alumina

Catalyst	S_{BET} (m ² g ⁻¹)	S_{CeO_2} total (m ² g ⁻¹)		$S_{\text{CeO}_2/\text{PM}}$ (m ² g ⁻¹)	
		TPR	OC	TPR (1st peak)	OT
Pt/CeAl	97	65	23	54	12
Pt/CeAl-acac	96	60	45	53	27
Pt-Rh/CeAl	96	68	21	51	6
Pt-Rh/CeAl-acac	97	60	44	51	25

TABLE 6

Different Surface Areas Estimated by BET, TPR, OC, and OT in the Aged Catalysts Deposited on Ceria-Alumina

Catalyst	S_{BET} (m ² g ⁻¹)	S_{CeO_2} total (m ² g ⁻¹)		$S_{\text{CeO}_2/\text{PM}}$ (m ² g ⁻¹)
		TPR	OC	
Pt/CeAl aged	54	16	4	0.5
Pt/CeAl-acac aged	53	15	5	0.8
Pt-Rh/CeAl aged	57	17	5	1.5
Pt-Rh/CeAl-acac aged	53	15	7	0.7

that the surface areas determined by OT are also well below those deduced from OC. Consequently, unlike the catalysts deposited on ceria, the impregnation of the precious metals is probably not uniform and leaves part of the ceria grains free of metal and thus not titrated by OT.

3.3.2. Influence of ageing. The ceria surface areas measured for the catalysts after ageing at 1273 K are given in Table 6. In agreement with results obtained previously on the same type of catalysts (20), the BET surface area is approximately divided by 2 compared to the case with the fresh catalysts, whereas the ceria surface area measured by TPR decreases by a factor 4, from about 64 to about 16 m² g⁻¹.

The accessible metallic area measured by static volumetry was found to be very low, less than 1%, and with a large uncertainty. Under these conditions, the values of HC were neglected in the calculation of the ceria surface areas in the OC and OT methods. As shown in Table 6, the results are homogeneous for each technique, showing that the nature of the precursor has no influence. However, the ceria surfaces determined by OC (around 5 m² g⁻¹) and OT (around 1 m² g⁻¹) remain much lower than those obtained from TPR, indicating that only a part of the ceria surface which was initially reduced can be reoxidised at room temperature. In addition, the comparison between the values obtained from OC and OT indicates that after the ageing an important part of the ceria surface is probably without precious metal.

4. DISCUSSION

Considering the model platinum-ceria catalysts, there exists a very good correlation between the ceria surface areas measured by BET, TPR, and the OC and OT operations. This result is summarised by the fact that approximately 4 μmol of hydrogen is required to reduce the whole ceria surface. Reciprocally, 2 μmol of O₂, or 4 μatom of O, is necessary to reoxidise the reduced ceria surface. The OT operation has confirmed this stoichiometry, thus validating the general scheme of the reactions occurring on the surface and involving the hydrogen spill-over. From this consistent

set of conclusions, we have concluded that the method is valid to quantify both the total ceria surface area and the fraction of the ceria surface in contact with the metallic platinum. We have also deduced that, with these Pt/CeO₂ samples, the platinum was homogeneously distributed in all the grains of ceria.

The application of this method to the case of Pt/CeO₂-Al₂O₃ catalysts is not so straightforward. If the reduction method (TPR) leads to the same values for the ceria surface area for each type of Pt and Pt-Rh catalysts, the reoxidation process at room temperature (OC) leads to lower values, and even much lower in the case of chlorinated precursors. To interpret these results, we can consider two components of the catalysts which are able to interact strongly with the ceria surface and thus modify the surface redox properties, i.e., the chlorine ions introduced with the metallic precursor and the alumina surface which supports the ceria.

These two parameters were investigated recently using magnetic measurements to follow the concentration of the reduced Ce³⁺ ions (17,21). It was shown that the chlorine ions remained fixed on the support after reduction and that they significantly modified the redox properties of the ceria phase. In particular, the reoxidation of the cerium species associated with chlorine was not effective at room temperature. This chlorine incorporation into oxygen lattice vacancies resulting from the reduction of surface oxygen was also recently shown on Rh/CeO₂ catalysts (22).

It was also shown on the same Pt/CeO₂-Al₂O₃ catalysts that a ceria-alumina interaction occurred after reduction by hydrogen at 573 K which stabilised a relatively large fraction of Ce³⁺ against reoxidation at room temperature (17). Indeed, magnetic results have shown that the Ce³⁺ ions stabilised by alumina and the chlorine ions trapped on the surface inhibit the reversibility of the redox processes on the ceria at room temperature. Consequently, in the present study, the ceria surface area obtained by OC is certainly underestimated, because for the ex-chlorinated precursors catalysts, the Ce³⁺ ions associated with Cl⁻ ions are not measured upon reoxidation at room temperature. Moreover, for all the catalysts on ceria-alumina, the Ce³⁺ ions stabilised at the interface with alumina are not reoxidised.

In the same manner, the surface determined by OT is certainly underestimated since the presence of chlorine has been shown to limit the extent of hydrogen spill-over (17,22). For example, magnetic susceptibility data have shown that, when hydrogen is introduced on a sample reoxidised at room temperature, there is a great increase of the Ce³⁺ percentage for Pt/CeAl-acac (from 20.5% to 35%) whereas for Pt/CeAl-Cl, the increase is low (from 31% to 35%). Thus, it is logical to obtain lower values for OT. However, it must be noted that, for the Pt/CeO₂ catalysts which were also prepared with chlorinated precursors, the presence of chlorine did not perturb the measurements since the

results are almost the same for OC and OT. These different behaviours may be related to the presence of aluminium ions in the catalysts prepared on the mixed supports (CeO₂-Al₂O₃) which modifies the redox behaviour of the solid. To support this working hypothesis, it can be remarked that oxygen storage capacity measurements on Rh/CeO₂ catalysts have shown that chlorine has no effect on the mobility and the storage of oxygen (23). To the contrary, if an alumina phase was present, the oxygen storage capacity was clearly decreased by the presence of chlorine.

One of the positive points of this limitation of the spill-over by the presence of chlorine is the possibility of measuring the metallic dispersion by hydrogen chemisorption in static volumetry. Without this effect, as is the case for the catalyst ex-acetylacetonate, the measured dispersion is higher than 100%.

For the aged catalysts supported on ceria-alumina, the nature of the precursor has no influence on the measurements. In fact, most of the chlorine was eliminated from the solid by the ageing treatment (5 h at 1273 K under N₂/H₂O mixture), as shown by chemical analysis which indicates a residual content below 5% of the introduced chlorine, whereas almost all the chlorine of the precursor remained fixed on the support in the fresh solids (4). Under these conditions, it is normal to obtain a good agreement of the results within each method. The ceria surfaces estimated by OC or OT are still much lower than those determined by TPR. We can suppose that the high-temperature treatment modifies the metal-support interactions and also induces the formation, during the reduction, of a great number of stabilised Ce³⁺ ions at the interface with alumina. These ions, which are stable against oxidation at room temperature (17), are not titrated by OC or OT. It can be noticed that, by XRD analysis, it was not possible to prove the formation of a CeAlO₃ phase, as was observed by Humbert *et al.* for similar catalysts after redox treatments at 1223 K (24). This is understandable if one considers these solids as poorly crystallised, particularly alumina, and if one considers that no reducing treatment was performed at high temperature.

In the aged solids, the low values of the ceria surface areas evaluated by OT compared to those deduced from OC also indicate that an important part of the ceria surface must be without precious metal particles. During the ageing, the sintering of the precious metals and ceria probably leads to a segregation between these two types of species.

Finally, the various methods used to quantify the different oxygen species on the catalysts lead to three specific conclusions. The TPR method makes it possible to measure the amount of the oxygen species available at the surface. The OC method corresponds to a fraction of the previous quantity which could be defined as the easily available oxygen species, or "easy oxygen" storage capacity. The OT method makes it possible to quantify these available oxygen species

in contact with the precious metals. This distinction is relative and the limits between each population of oxygen species are determined by the experimental conditions and the catalysts. The three methods were in agreement in the case of pure ceria as support, because the three populations were identical. The same is not true for the catalysts prepared on ceria–alumina. The analysis of the TPR profile makes it possible to deduce the total oxygen storage capacity and the amount of oxygen in contact with the metal. As is clear in Table 5, the values obtained by TPR for these two quantities are very different from those calculated by OC and OT. This difference can be explained by the different working temperature in each technique (room temperature instead of 300–900 K) and by the nonreversibility of the redox processes at room temperature. The TPR concerns the reduction of a fully oxidised sample which has been pre-treated in oxygen at 673 K. The OC and OT methods are related to samples reduced at 573 K under hydrogen but reoxidised only at 294 K.

In principle, one of the advantages of the OC and OT methods compared to TPR is that the OC and OT methods easily take into account the contribution of the precious metals in the calculations, since the accessible metallic area can be directly measured by hydrogen chemisorption. This was verified in the present study, but we noticed also that this type of measurement is not free from uncertainty and, depending on the type of catalyst and the experimental conditions, the results may be erroneous. For the TPR method, the same problem of correction due to the metals also exists, and the calculations must take into account the oxidation state of the metals after the oxidising treatment at 673 K. The oxidation states of the catalysts, in the fresh or aged state, were estimated from a parallel study developed on catalysts that were similar but deposited on alumina. This method can be considered as valid if we look at the good agreement of the results, mainly for the aged catalysts, for which the contribution of the precious metals may induce large differences in the results, depending on the oxidation state. However, it must be mentioned that these oxidation states measured on alumina are not at all warranted on other supports or in commercial catalysts, where peculiar interactions may occur between the metals and the support components.

Despite these limitations, the use of these three methods to measure the various types of oxygen species present on the surface appears very complementary, and the diversity of results obtained on these catalysts, far from being inconsistent, has allowed us to give a more precise description of their characteristics. In particular, the results have clarified some features of these solids: (i) the nature of the ceria–alumina interface and its evolution during ageing treatments, (ii) the influence of the metallic precursor on the redox processes, (iii) the impregnation, uniform or not, of the metals on the support, and (iv) the eventual phases

of segregation during the ageing. It is clear that these different characteristics influence directly the oxygen storage capacity of catalysts.

5. CONCLUSION

The objective of this study was to use successive $O_2/H_2/O_2$ chemisorption measurements in order to quantify, in model three-way catalysts, the ceria surface area, either alone or in interaction with the precious metals. A specific method was validated with Pt/CeO₂ catalysts of different BET surface areas. In this case, the ceria surface areas obtained by oxygen chemisorption after reduction at 573 K are in agreement with the values deduced from the TPR profiles. In addition, the measurement by O_2 titration of the hydrogen spilled over the reoxidised ceria surface leads to the same surface areas, which shows that platinum has been impregnated on the whole ceria surface.

The application of this methodology to the case of fresh and aged Pt and Pt–Rh/CeO₂–Al₂O₃ model three-way catalysts leads to a set of ceria surface areas, deduced from O_2 chemisorption and O_2 titration, much lower than those obtained by TPR. The different values have been interpreted as due to specific interactions of various components and phases of catalysts during the successive treatments.

This study illustrates how TPR and successive chemisorption measurements used as complementary methods may increase what is known about the three-way catalysts. Each method makes it possible to quantify one type of active oxygen species of the ceria. The TPR method is related to the reduction of the whole ceria surface. The oxygen chemisorption at room temperature (OC method) corresponds to the oxygen species which are easily available in the catalyst and which represent only a fraction of the surface. Finally, the titration of hydrogen by oxygen (OT method) quantifies only the part of these available oxygen species which are in direct interaction with the metallic particles. It remains to study how these distinct oxygen species play a specific role in the catalytic activity.

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