

# Titration by Oxygen of the Spill-over Hydrogen Adsorbed on Ceria–Zirconia Supported Palladium–Rhodium Catalysts

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Received July 4, 2001; revised September 14, 2001; accepted November 14, 2001

To find a method for estimating the surface area of ceria–zirconia in composite three-way catalysts, successive O<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> chemisorption measurements were performed at room temperature on model Pd and/or Rh/Ce<sub>0.63</sub>Zr<sub>0.37</sub>O<sub>2</sub> catalysts previously reduced at 573 K by hydrogen, according to a methodology developed for ceria or ceria–alumina supported metal catalysts. The quantity adsorbed during the first oxygen chemisorption was found to correspond to the reoxidation of several layers of the support. The number of layers increases when the catalysts are aged at 1323 or 1423 K, which clearly indicates the great mobility of bulk oxygen in CeO<sub>2</sub>–ZrO<sub>2</sub> supports, as already shown in the literature. After a subsequent H<sub>2</sub> chemisorption, the titration by oxygen of the hydrogen adsorbed on metal particles and on the support leads to a lower quantity of chemisorbed oxygen which is closely related to the surface area of ceria–zirconia. This relationship was observed in fresh and aged catalysts and was used to calculate a mean calibration coefficient of 5.1 μatom O m<sup>-2</sup>. Thus, contrary to temperature-programmed reduction measurements, this method of quantification by oxygen of the spill-over hydrogen can be used to estimate the surface area of ceria–zirconia in composite catalysts in which CeO<sub>2</sub>–ZrO<sub>2</sub> is one of the components of the support. This latter point is illustrated with model Pd and PdRh catalysts deposited on a 'ceria–zirconia + alumina' support. © 2002 Elsevier Science (USA)

**Key Words:** O<sub>2</sub>/H<sub>2</sub> titration; O<sub>2</sub> chemisorption; Pd/CeO<sub>2</sub>–ZrO<sub>2</sub>; Rh/CeO<sub>2</sub>–ZrO<sub>2</sub>; PdRh/CeO<sub>2</sub>–ZrO<sub>2</sub>; spill-over hydrogen; ceria–zirconia; three-way catalysts.

## 1. INTRODUCTION

In the actual formulations of three-way catalysts, ceria was replaced by ceria–zirconia (CeZr) mixed oxides to increase the thermal stability of the catalyst (1) and to improve the activity of the Ce<sup>3+</sup>/Ce<sup>4+</sup> redox couple. This redox improvement is indicated by a higher mobility of the bulk oxygen, which increases the oxygen storage capacity (OSC) of the catalysts (1–6) and results in better catalytic properties (2, 7, 8). Even after sintering, ceria–zirconia solid

solutions present high OSC properties, and it shown that their OSC could be improved after aging under redox cycling conditions (9–11).

In the last few years, a partial or total substitution of palladium for platinum and/or rhodium has also occurred in the formulations, and research has been concentrated on the preparation of Pd/Rh and high Pd containing catalysts (12, 13). To prevent the formation of bimetallic Pd–Rh particles which is deleterious for activity, techniques were improved to segregate Pd and Rh in separate washcoat layers. Moreover, for optimum performance, Pd was promoted with various rare earth metal oxides and oxygen storage materials. Consequently, together with improvements in fuel quality (reduction in Pb and S levels which are severe poisons for Pd) and engine control, these Pd-based catalysts present lower light-off temperatures and good resistance to aging at high temperature under oxidizing conditions and can be used to meet tighter future emission regulations at higher operating temperatures (12, 13).

To better understand the properties of these catalytic formulations, complementary characterization techniques need to be developed. Among the numerous characteristics of these systems, the surface area of the CeZr support seems to be an important parameter to be compared to OSC data. Indeed, for ceria–zirconia mixed oxides alone, it was observed that the BET surface area does not control OSC (9). However, in more complex systems such as industrial catalysts, the accessible surface area of the CeZr support could be more determining for OSC because of its interactions with other components. Pd itself, which is used at a higher concentration than Pt and Rh, also contributes to OSC by its ability to undergo redox cycling under exhaust conditions (13). This property presents a new difficulty in characterizing the last generation of active catalysts in automotive converters. Ceria–zirconia is present in the system with several nonreducible oxide components used as supports or stabilizers (Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, BaO, ...) (12). Therefore, during aging, the evolution of the CeZr surface area may be very different from that of the BET surface area. Thus, the aim of this work is to develop a method for

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estimating the surface area of such a CeZr support during the aging of model PdRh/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts. The basic idea was to apply a methodology, established previously with Pt-Rh catalysts deposited on ceria or ceria-alumina supports, which discriminated between the surface and bulk oxygen ions of the support (14). The method consists of successive O<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> chemisorption measurements performed at room temperature after reduction at 573 K. In fresh Pt-Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (noted as PtRh/CeAl), the ceria surface in contact with precious metals was quantified. After aging, the same calculation was not so conclusive for these catalysts. However, from the chemisorption data, interesting information could be inferred from the chlorine influence and the formation of stabilized Ce<sup>3+</sup> ions at the CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> interface (14). Although it is well known that the mobility of bulk oxygen is much higher in ceria-zirconia solid solutions, the same methodology can be tentatively applied to CeZr supported catalysts. This idea is supported by recent dynamic OSC measurements with hydrogen and oxygen pulses performed at room temperature on similar noble metal supported on Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalysts (15, 16). The results showed a linear relationship between the H<sub>2</sub> (or O<sub>2</sub>) consumed and the surface area of the catalyst, suggesting that the titration mechanisms on the surface are similar. However, if in ceria and ceria-alumina only one surface layer is involved during the titration by O<sub>2</sub> of the spill-over hydrogen (14), for ceria-zirconia, things are not so well established and could even depend on the nature of the noble metal, since Rh/CeZr leads to smaller H<sub>2</sub>-OSC values than those for Pt or Pd/CeZr (16). Therefore, it is logical to examine in detail whether the methodology and the protocol we used for ceria and ceria-alumina could lead to distinct and clearly defined results in the case of the ceria-zirconia support. Hopefully, a calibration coefficient could be derived which can be used to determine the surface area of ceria-zirconia in more complex catalysts than the actual industrial three-way catalysts. In this work, successive O<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> chemisorption measurements were performed on model PdRh/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts, in either the fresh state or after aging at 1323 or 1423 K. The results are presented, discussed in comparison to those obtained on ceria or ceria-alumina supported catalysts, and applied to the case of model Pd and PdRh/CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> multi-component catalysts.

## 2. EXPERIMENTAL

### 2.1. Materials

The catalysts were previously described (17). The ceria-zirconia support from Rhodia was a solid solution with a mass composition of CeO<sub>2</sub>/ZrO<sub>2</sub> = 70/30. On a molar basis, this composition corresponds to the Ce<sub>0.63</sub>Zr<sub>0.37</sub>O<sub>2</sub> formula, which is close to that determined by X-ray diffraction analysis, i.e., Ce<sub>0.66</sub>Zr<sub>0.34</sub>O<sub>2</sub>. The BET surface area was

122 m<sup>2</sup> g<sup>-1</sup>. The N<sub>2</sub> adsorption isotherm indicated the absence of micropores and a narrow pore size distribution centered around 3–3.5 nm.

The catalysts Pd and/or Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> (denoted as Pd/CeZr, Rh/CeZr, and PdRh/CeZr) were prepared by impregnating or co-impregnating 15 g of the support with ~70 ml of 0.01 or 0.02 N nitrate solutions [Pd(NO<sub>3</sub>)<sub>2</sub> and Rh(NO<sub>3</sub>)<sub>3</sub>]. After water elimination under vacuum at 340 K and drying at 380 K for 1 night, the solids were calcined for 2 h at 773 K under flowing nitrogen (5 L h<sup>-1</sup>). The Pd and Rh concentrations were 0.43 and 0.51 wt%, respectively, for the monometallic catalysts. For the bimetallic catalyst, they were 0.8 and 0.135 wt%, percentages representative of industrial catalysts.

The fresh catalysts had almost the same BET surface areas as that of the support (Table 1) and were aged for 5 h at 1323 K or 1423 K under a nitrogen flow containing 10% water. As shown in Table 1, these treatments strongly decrease the specific surface area, which remains at approximately only 13% of the initial BET surface (16 m<sup>2</sup> g<sup>-1</sup>) after aging at 1323 K and at 6–7% after aging at 1423 K. The presence of precious metal has no noticeable influence on the sintering of the support.

Two Pd and PdRh/CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (series CeZrAl) were prepared under the same conditions as those for the CeZr support. As shown in Table 1, the metal contents were 1.86 wt% Pd content for the monometallic catalyst and 0.92 wt% Pd and 0.09 wt% Rh for the bimetallic catalyst. The latter resulted from the mechanical mixture of two monometallic systems. The CeZrAl support was prepared by mechanically mixing 30 wt% of the ceria-zirconia support with 70 wt% alumina (SCM129, from Rhodia) for 1 h in a suspension of water (70%) and by drying under vacuum at 330 K. After 1 night at 380 K, the support was calcined for 2 h under oxygen at 773 K.

### 2.2. Characterization methods

*2.2.1. Measurement of the accessible metallic area by hydrogen chemisorption (HC).* The accessible metallic area was measured by chemisorption of H<sub>2</sub> in a static

TABLE 1  
Metal Contents and BET Surface Areas of the Catalysts

Catalysts	Metal (wt%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )		
		Fresh state	Aged at 1323 K	Aged at 1423 K
CeZr		122	16	7
Pd/CeZr	0.43	121	16	8
Rh/CeZr	0.51	119	19	7
PdRh/CeZr	0.8/0.135	120	16	8
Pd/CeZrAl	1.86	107		
PdRh/CeZrAl	0.92/0.09	110		

volumetric apparatus. The measurement was performed at room temperature after three reduction steps (total time >12 h) at 573 K, under 2.7 kPa H<sub>2</sub> and 2 h desorption under vacuum at the same temperature (18). Following the double isotherm method initially proposed by Benson *et al.* (19), two isothermal adsorptions were performed, with 15-min intermediary treatment under vacuum at 298 K, to determine the irreversibly bound chemisorbed hydrogen (HC) corresponding to hydrogen adsorbed on the metal surface. The two isothermal curves were drawn with five to six experimental points in the 0.4- to 1.3-kPa pressure domain, with each equilibrium point being obtained after a 10-min contact with the catalyst according to the protocol previously described (14). The formation of palladium hydride should not occur when limiting the adsorption pressure to 1.3 kPa. The adsorption stoichiometry was determined as one hydrogen atom for one precious metal surface atom to calculate the accessible metallic area ( $H/M$ ).

To confirm the validity of the results, some of the runs were also performed with a dynamic flow apparatus as described in the following.

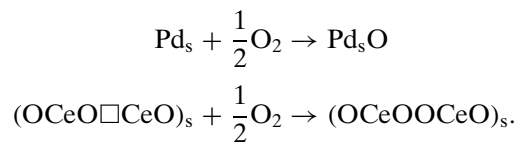
It must be also noted that 573 K had been established as the optimum reduction temperature for CeAl supported catalysts (18) and that this was also the case for ceria-zirconia as a support. Moreover, we wanted to determine whether chemisorption measurements at room temperature would lead to reliable results under our conditions. Therefore, as described under Results, a preliminary study was performed on a 0.58 wt% Pt–Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst obtained from Rhodia and studied in the CEZIRENCAT network (20). This solid was chosen to compare the data to those obtained by Hickey *et al.* (15, 16).

**2.2.2. Chemisorption of oxygen and H<sub>2</sub>/O<sub>2</sub> titration at room temperature: recall of the method and experimental protocols (14).** The method was developed previously for the study of the ceria or ceria–alumina/precious metal interface. After a standard reduction at 573 K, the oxygen chemisorption (OC) at room temperature fills the oxygen vacancies of the reduced ceria and oxidizes the surface metals atoms. Hydrogen is then added to the sample, and in the next step the irreversibly adsorbed hydrogen is titrated by oxygen. In fact, the oxygen titration (OT) not only corresponds to the titration of the hydrogen chemisorbed on the metallic particles but also includes the titration of the hydrogen atoms which have migrated on the ceria surface via the precious metals (hydrogen spill-over); thus, it is possible to estimate the surface area of the ceria which actually supports the metallic particles.

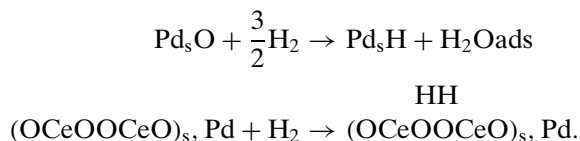
The successive reactions involved in these H<sub>2</sub>/O<sub>2</sub> chemisorption cycles are summarized in the following for a palladium catalyst. The subscript “s” refers to surface atoms. Similar equations can be used for rhodium. All the experiments were carried out at 298 K after the initial

reduction at 573 K. The hydrogen and oxygen uptakes in the initial chemisorption and the subsequent titration steps are denoted as OC, HT, and OT.

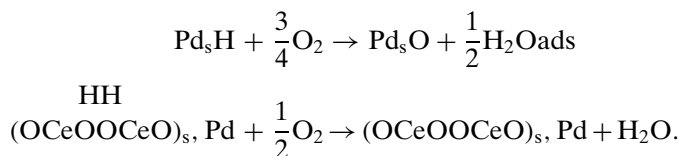
1. Oxygen chemisorption (OC). Oxygen is fixed on the Pd surface and fills the vacancies of reduced CeO<sub>2</sub>:



2. Titration of adsorbed oxygen by hydrogen (HT). H titrates O fixed on Pd and migrates over CeO<sub>2</sub> (spill-over):



3. Titration of adsorbed hydrogen by oxygen (OT). O titrates H fixed on Pd and doses the H spilled over CeO<sub>2</sub>:



The stoichiometry of the reactions was verified for the PtRh/Ce and PtRh/CeAl systems (14).

In the experiment, the successive chemisorption of hydrogen and oxygen was measured with a dynamic volumetry apparatus using a thermal conductivity detector (21). The gases introduced in the reactor were 1% H<sub>2</sub>/Ar with argon as reference or 1% O<sub>2</sub>/He with He as reference for hydrogen and oxygen chemisorption, respectively. As for hydrogen chemisorption with static equipment, the measurement of the irreversible adsorption required the succession of two chemisorption steps, with an intermediary desorption always at 298 K, under inert gas (Ar or He).

The experimental protocol already described (14) can be summarized as follows. After 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 for 2 h at the same temperature, and cooled to 298 K. Then the catalyst was contacted with 1% O<sub>2</sub>/He to measure the irreversible chemisorbed oxygen (OC). The quantity OT was obtained in the same way by the subsequent adsorption with 1% H<sub>2</sub>/Ar (or even pure hydrogen in some experiments) and then with 1% O<sub>2</sub>/He mixtures, after an intermediary desorption step under pure helium at room temperature, to desorb the reversibly chemisorbed hydrogen. This desorption step was considered as terminated when the baseline of the detector was recovered. Each value was obtained at equilibrium.

Similarly, by adsorbing hydrogen (1% H<sub>2</sub>/Ar) directly after reduction and evacuation pretreatment at 573 K, it was possible to measure HC, as defined in Section 2.2.1.

### 3. RESULTS

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

**3.1.1. Influence of the reduction temperature on the accessible metallic area.** The protocol established for CeAl supported catalysts was based on a reduction temperature of 573 K (18). However, the reduction process may be quite different for a CeZr supported system. Thus, before measuring the accessible metallic area by hydrogen chemisorption, a preliminary study was necessary to optimize the reduction temperature. This study was carried out with a 0.58 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst used as a reference. The protocol remained the same, the reduction temperature varied between 473 and 773 K, and the evacuation was performed at the reduction temperature. The static volumetric method was used to determine the irreversible chemisorption HC<sub>irr</sub>. Table 2 gives the changes in the apparent metallic dispersion ( $H/M$ ) observed after these treatments. As mentioned under Experimental, this dispersion was calculated from HC<sub>irr</sub> measured at 193 and 298 K, the former temperature being recommended to suppress the hydrogen spill-over (22–25). At 193 K, a constant dispersion of  $0.64 \pm 0.03$  is obtained for a reduction temperature between 473 and 673 K. At 298 K, and after reduction at 473 K, the measured dispersion is much higher ( $H/M = 9.50$ ) which evidently must be attributed to hydrogen spill-over on the support. After reduction at 573 and 673 K, this value decreased to 0.94. It must be noted that the value is the same for both temperatures, suggesting that under these conditions the spill-over, if any, is very limited. It can be deduced that the surface properties are similar after reduction treatment at 573 or 673 K. A constant dispersion is obtained together with a similar reduced state of the ceria-zirconia surface. Thus the 573 K

temperature which was established for CeAl supported catalysts appears to also be appropriate when CeZr is used as support. The temperature of 673 K was not chosen to avoid the possible strong metal support interaction (SMSI) effects (18, 26). For example, recent FTIR and H-NMR results obtained from Rh/CeO<sub>2</sub> catalysts have shown that SMSI can be generated when the samples are reduced at  $T \geq 573$  K (27).

Hickey *et al.* obtained, after reduction at 500 K,  $H/M$  values of 0.94 and 20.3 for the same catalyst when the adsorption was performed at 193 and 298 K, respectively (16). Their measurements correspond to the total hydrogen adsorption HC<sub>tot</sub>, without correction for reversible adsorption, and in comparison, we obtained the equivalent measurements. As shown in Table 2, the inclusion of the reversible part modifies the measured dispersion. However, for comparable experimental conditions (reduction at 473 and 500 K), the dispersion values based on HC<sub>tot</sub> are similar in the absence of spill-over, i.e., when the adsorption is performed at 193 K ( $H/M$  values of 0.91 compared to 0.94, in Hickey *et al.*).

The results demonstrate that dispersion values may be different, depending on the pretreatment or measurement conditions, which raises uncertainty over the real value of the dispersion ( $H/M = 0.9, 0.6$ , or another value?). From our data, a dispersion of 0.64 obtained at 193 K appears reasonable. However, to validate these data, it would be necessary to measure the dispersion with a methodology different from hydrogen chemisorption, such as the FTIR of adsorbed CO, which was successfully done in the case of a 0.64 wt% Pd/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst, a similar CEZIRECAT catalyst with the same support (28). After reduction at 473 K, the measured dispersion was 51%, which suggests that dispersion values close to 0.6 are also probable in our case and that some limited hydrogen spill-over occurs on the support at room temperature.

In conclusion, hydrogen chemisorption gives reproducible values for metal dispersion provided that the reduction and evacuation treatments are performed in the 573–673 K domain. Thus, the protocol established for the PtRh/CeAl system can also be applied to the PdRh/CeZr system. As deduced from the data obtained at 193 K, a very small contribution of hydrogen spill-over on the support is likely when the adsorption measurement is performed at 298 K. However, it is shown in the following that the quantities involved in this process can be considered as negligible in comparison to those obtained with the OT determination protocol.

**3.1.2. Hydrogen chemisorption measurements at 298 K.** According to the protocol previously established and validated, H<sub>2</sub> volumetric adsorption was performed under static or dynamic conditions after reduction at 573 K. For the three fresh CeZr catalysts in the static method, the adsorption curves were not strictly parallel for H<sub>2</sub> pressure

TABLE 2

Influence of the Reduction Temperature on the Accessible Metallic Area ( $H/M$ ) of 0.58 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub><sup>a</sup>

$T$ reduction (K)	$T$ measurement = 193 K		$T$ measurement = 298 K	
	HC <sub>total</sub>	HC <sub>irr</sub>	HC <sub>total</sub>	HC <sub>irr</sub>
473	0.91	0.61	12.4	9.5
573	1.18	0.67	1.61	0.94
673	0.92	0.62	1.65	0.94
773	0.69	0.35	0.63	0.24
500 <sup>b</sup>	0.94 <sup>b</sup>		20.3 <sup>a</sup>	

<sup>a</sup> H<sub>2</sub> adsorption, total and irreversible, measured at 193 and 298 K by extrapolation to zero pressure.

<sup>b</sup> Data from Ref. (16).

TABLE 3

Accessible Metallic Fraction ( $H/M$  in %) Measured at Room Temperature by Static or Dynamic  $H_2$  Volumetry

Catalysts	Fresh		Aged at 1323 K	
	Static	Dynamic	Static	Dynamic
Pd/CeZr	46	43	$\approx 1.5$	3
Rh/CeZr	80	90	$\approx 1$	
PdRh/CeZr	61	60	$< 1$	$< 1$
Pd/CeZrAl	23	17		
PdRh/CeZrAl	30			

higher than 0.6 kPa, with a slight positive deviation observed in the reversible adsorption curve, which can be explained by an incidental defective tightness of the volumetric apparatus resulting in a small drift in the equilibrium pressure. Indeed, in the series of measurements performed on the Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst, such a drift was not observed. Consequently, to calculate the irreversible chemisorbed hydrogen, only the initial part of the isotherms was used and extrapolated to zero pressure. In the dynamic method, the partial pressure used to measure the irreversible chemisorption was 1 kPa H<sub>2</sub>. The accessible metallic fraction values, expressed as  $H/M$ , are given in Table 3 for both conditions.

An agreement is obtained between both static and dynamic methods. Since for Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, the dynamic method sometimes gives results higher than those in the static method (for example, 25% in (29)) and since the dynamic method requires a longer duration for equilibrium, this seems to indicate the near absence of hydrogen spill-over on the support under our experimental conditions. This is in agreement with the results, presented earlier for the Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst, which show that to estimate the metal dispersion, the room temperature volumetric technique associated with a preliminary reduction at 573 K, methodology which was tested first for ceria–alumina supported catalysts (18, 30) seems to be valid when the metals are supported on ceria–zirconia.

As shown in Table 3, the fresh monometallic rhodium catalyst exhibits the highest dispersion, whereas the bimetallic catalyst has an intermediate accessibility between that of Pd and that of Rh. After aging at 1323 K, there is a large drop in the chemisorption, and the values for accessible metallic areas become very low (between 1 and 3%). These values are close to the sensitivity limit of both methods. Consequently, the metallic accessible area, considered to be in the range below 1%, was not measured for the catalysts aged at 1423 K.

The relatively low dispersion of about 20% obtained in the case of the fresh Pd/CeZrAl has to be attributed to the higher metal loading compared to that on the CeZr support (1.86 instead of 0.43 wt%, respectively). The metal acces-

sibility of the bimetallic PdRh/CeZrAl catalyst is slightly higher, which is demonstrated by a higher dispersion of the monometallic rhodium catalyst due to a low metal loading (0.18 wt% Rh).

### 3.2. Oxygen Chemisorption and H<sub>2</sub>/O<sub>2</sub> Titration at 298 K

**3.2.1. Case of the ceria–zirconia supported catalysts.** In ceria or ceria–alumina, after reduction at 573 K, it was discovered that the oxygen chemisorption at room temperature fills the oxygen vacancies of the reduced ceria, and the ceria surface area was calculated from the quantity OC (14). A new hydrogen/oxygen cycle leads to the titration oxygen OT which determines the ceria surface supporting particles of precious metals. The same methodology was used with ceria–zirconia supported catalysts. The obtained OC and OT values are given in Table 4. For all the catalysts, OT values are lower than the corresponding OC values. Moreover, in the aged catalysts, there is a sharp decrease in the values, about one order of magnitude lower after aging at 1423 K, compared to those for the fresh catalysts.

We calculated the equivalent ceria–zirconia surface areas from the following quantities. Let us recall that for ceria, in average 4  $\mu$ atom O of OC or OT corresponds to 1 m<sup>2</sup> of ceria (14), a value almost equal to that obtained from TPR experiments, i.e., 3.9  $\mu$ atom O for 1 m<sup>2</sup> of ceria (31). In the present case, the oxygen atoms which are eliminated during the reduction at 573 K must be linked to the reducible cerium ions. Consequently, during the OC step, since there is only 63 mol% ceria in the solid solution, we can assume that 1 m<sup>2</sup> of CeO<sub>2</sub>–ZrO<sub>2</sub> would require only 2.5 instead of 4  $\mu$ atom O.

During the OT step, on the other hand, the chemisorbed oxygen titrates the hydrogen irreversibly adsorbed on the precious metal particles and on the ceria–zirconia support surface. Previous TPR results, including hydrogen chemisorption at room temperature, showed that a better agreement between the calculated surface areas was obtained for the fresh catalysts using the 4  $\mu$ atom O m<sup>-2</sup> basis which suggests that the hydroxyls groups could be formed on the surface, without distinction among the neighboring cations between the cerium and zirconium atoms (17). Thus,

TABLE 4

Oxygen Chemisorbed on the PdRh/CeO<sub>2</sub>–ZrO<sub>2</sub> Catalysts During the OC and OT Steps

Catalysts	Chemisorbed oxygen ( $\mu$ mol O <sub>2</sub> g <sup>-1</sup> )					
	Fresh		Aged at 1323 K		Aged at 1423 K	
	OC	OT	OC	OT	OC	OT
Pd/CeZr	443	293	63	36	55	17
Rh/CeZr	498	340	81	48	61	22
Pd–Rh/CeZr	473	344	135	46	53	22

TABLE 5

Ceria-Zirconia Surface Area of PdRh/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalysts Calculated from the OC and OT Methods in Comparison to those Obtained by TPR and BET Measurements

Catalysts	CeO <sub>2</sub> -ZrO <sub>2</sub> surfaces (m <sup>2</sup> g <sup>-1</sup> ) calculated from				
	OC	OT	TPR	BET	S <sub>OT</sub> /S <sub>BET</sub>
	2.5 μatom/m <sup>2</sup>	4 μatom/m <sup>2</sup>			
Pd/CeZr	347	140	134 <sup>a</sup>	121	1.16
Rh/CeZr	383	155	125 <sup>a</sup>	119	1.30
Pd-Rh/CeZr	357	152	151 <sup>a</sup>	120	1.27
Pd/CeZr-1323 K	50	17	24 <sup>b</sup>	16	1.06
Rh/CeZr-1323 K	65	24	4 <sup>b</sup>	19	1.26
Pd-Rh/CeZr-1323K	108	23	71 <sup>b</sup>	16	1.44
Pd/CeZr-1423 K	44	8.7	15 <sup>b</sup>	8	1.09
Rh/CeZr-1423 K	49	10.8	27 <sup>b</sup>	7.5	1.44
Pd-Rh/CeZr-1423 K	43	11.2	75 <sup>b</sup>	8	1.40

<sup>a</sup> From Ref. (17).

<sup>b</sup> Calculated from data in Ref. (17), using the hydrogen uptake measured at room temperature and during the first peak at ≈450–500 K (35).

for OT, we used the same coefficient of 4 μatom O m<sup>-2</sup> to calculate the ceria-zirconia surface which supports the metal particles.

Consequently, the surfaces areas were calculated from OC and OT using the assumption of 2.5 or 4 μatom O for 1 m<sup>2</sup>, respectively. The contributions of the precious metals had been subtracted on the basis of the equations given in Section 2.2.2 using the HC<sub>irr</sub> values obtained at 298 K for the *H/M* dispersions. The results are given in Table 5 and are compared to the values estimated from the BET surface areas and TPR results (17). The surface areas calculated from OC are approximately three times higher than those of BET for the fresh catalysts. For the aged catalysts, the average factor is even higher, about 5–6. In other words, OC values are much higher than the quantities necessary to fill the oxygen vacancies of the surface as evidenced in the case of ceria or ceria-alumina supported catalysts for which the reduction pretreatment at 573 K eliminated only surface oxygen atoms (14, 32). For ceria-zirconia supported systems, the chemisorption of oxygen on the reduced catalysts concerns several layers because part of the bulk oxygen ions have been eliminated by the reduction treatment at 573 K as a consequence of their high mobility. This confirms the great reducibility of this type of support in agreement with well-documented literature (9–11, 33, 34).

The surface areas from OT and BET are similar. As shown in Table 5, the ratio S<sub>OT</sub>/S<sub>BET</sub> is close to 1.3 and independent from that for aging catalysts. The ratio is, however, a little lower in the presence of palladium than in the presence of rhodium. One can conclude that the titration by oxygen of the spill-over hydrogen is in close relationship with the surface area of the ceria-zirconia support. Therefore, assuming that OT concerns only the CeZr surface, we can deduce an experimental calibration coefficient to be

applied for OT which is equal to 5.1 ± 0.7 μatom O m<sup>-2</sup>. This coefficient is valid, whatever the state of the catalyst, in the fresh state or after severe aging.

The ceria-zirconia surface areas calculated from TPR are similar to the BET values only for the fresh catalysts. For the aged solids, the values are rather scattered, although the contribution of the precious metals in the TPR profiles were precisely evaluated. This evaluation was made by studying a Pd or Rh on alumina catalyst aged at 1323 K under the same conditions as those used in the present study, and it was found that only one-third of Rh<sup>3+</sup> and one-half of Pd<sup>2+</sup> were reduced during TPR (35). Thus the discrepancy observed in Table 5 for the aged samples between the BET and TPR values must be attributed to the change in TPR profiles after aging. As described previously (17), the TPR peak at 450–500 K is amplified for the aged as compared to the fresh catalysts, and there is no clear boundary between surface and bulk reduction.

*3.2.2. Application in the case of PdRh/CeZrAl catalysts.* The OT method was applied to the two catalysts supported on CeZrAl. The results are summarized in Table 6. The OT values are 107 and 123 μmol O<sub>2</sub> g<sup>-1</sup> for the monometallic and the bimetallic catalysts, respectively. After correction for the contribution of the precious metals and using the experimental calibration coefficient determined earlier (5.1 μatom O m<sup>-2</sup>), it is possible to calculate a ceria-zirconia surface area of 33 and 40 m<sup>2</sup> g<sup>-1</sup> for the Pd and PdRh catalysts, respectively. These values are not very different from those of the BET surface area calculated for CeZr if we assume that the addition of alumina has no influence on the ceria-zirconia surface area, i.e., 36 m<sup>2</sup> g<sup>-1</sup>. Conversely, starting from the calculated value, of 36 m<sup>2</sup> g<sup>-1</sup>, the coefficients which would be derived from the OT values would not be very different from those determined for the

TABLE 6

Catalysts	CeO <sub>2</sub> -ZrO <sub>2</sub> surfaces (m <sup>2</sup> g <sup>-1</sup> ) calculated from			
	OT	OT <sup>a</sup> using	BET <sup>b</sup>	Calculated coefficient (μatom O m <sup>-2</sup> )
	(μmol O <sub>2</sub> g <sup>-1</sup> )	5.1 μatom O m <sup>-2</sup>		
Pd/CeZrAl	107	33	36	4.7
Pd-Rh/CeZrAl	123	40	36	5.6

<sup>a</sup> After subtraction of the precious metals contribution.

<sup>b</sup> Assuming that alumina has no influence on the ceria-zirconia surface area.

CeZr series (4.7 and 5.6 instead of 5.1 μatom O m<sup>-2</sup>). This observation supports the validity of the method.

#### 4. DISCUSSION

The objective of this study was to apply oxygen chemisorption and O<sub>2</sub>/H<sub>2</sub> titration techniques to determine the surface area of the ceria-zirconia support from OC and OT, according to a methodology previously developed with CeAl supported catalysts. These chemisorption methods are based on the preliminary reduction of the cerium ions by hydrogen at 573 K for 12 h. This temperature was defined using precious metal catalysts supported on CeO<sub>2</sub> or CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. In this work, we observed that, for a Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst, the hydrogen chemisorption values at 298 K were the same after reduction at 573 or 673 K. Thus the temperature of 573 K was considered as an optimum for the ceria-zirconia supported catalysts.

With the CeZr supported catalysts of the present study, the application of the same methodology leads to significant differences between the surface areas calculated from OC, and those calculated from OT. Indeed, the results obtained by measuring OC show that the reducibility of the support at 573 K occurs on not only the surface but also the bulk of the solid solution. Even after the aging treatment at 1323 or 1423 K which considerably decreases the BET surface area, the catalysts exhibit a high reducibility at 573 K and finally a relatively high OSC. From the OC measurements and by comparison to the BET surface area, we calculated the number of layers involved in the reduction at 573 K at about three for the fresh catalysts reaching five to six for the catalysts aged at 1423 K. These numbers of layers are calculated on the basis of a homogeneous solid solution with 63 mol% of cerium on not only the surface but also the bulk. Even if we assume a total cerium enrichment at the surface, it is clear that much more than one layer is reduced after the treatment at 573 K. These observations are in agreement with the literature (9, 16, 36, 37) and are particularly demonstrated by the results obtained by Hickey *et al.* in the measurement of OSC by H<sub>2</sub> at increasing temperature on noble metal catalysts supported on Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> in comparison to catalysts supported on ceria

(16). The H<sub>2</sub>-OSC values measured at 373-773 K confirmed that reduction is a surface-related process over Pt/CeO<sub>2</sub>, whereas for ceria-zirconia supported samples, deeper reduction/vacancy creation occurs as the temperature is increased. We can conclude from this study that, since the number of reduced layers varies with the aging temperature, OC is not reliable for determining the ceria-zirconia surface area. The same conclusion can be reached from the TPR results (17). The discrimination between the surface and the bulk was possible only for the fresh catalysts as shown in Table 5. For the aged catalysts, the low temperature peak on the TPR profiles becomes broader toward higher temperature, and the deconvolution of the profile in distinct peaks becomes impossible, which indicates that the oxygen atoms of the first layers of the CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution have a reactivity close to that of the surface oxygen atoms. Under these conditions, the TPR technique is unable to quantify the ceria-zirconia surface area in every case.

On the other hand, quantification at room temperature of the spill-over hydrogen by oxygen (OT) appears to be an interesting method for estimating the CeO<sub>2</sub>-ZrO<sub>2</sub> surface. A relationship exists between the BET surface area and the amount of oxygen adsorbed OT. A calibration coefficient of 5.1 μatom O m<sup>-2</sup> was calculated with a limited relative error (±15%). The main point is that the coefficient remains the same, whatever the aging pre-treatment, even after aging at 1423 K. It can be seen that without correcting OT from the contribution of the precious metal (HC<sub>irr</sub>), this coefficient would not be very different (5.3 μatom O m<sup>-2</sup>). This small variation indicates that the error, eventually introduced in the calculation when using HC<sub>irr</sub> measured at 298 K because it may have included some hydrogen spill-over on the support, is negligible. For example, the dispersion measured at 298 K for Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> is 0.94 instead of 0.67 when HC<sub>irr</sub> is measured at 193 K. This difference would correspond to ~0.8 m<sup>2</sup> g<sup>-1</sup> of CeZr support. This near absence of hydrogen spill-over can be obtained only on a well-reduced ceria-zirconia surface, i.e., after reduction at  $T \geq 573$  K, and is not the case when the reduction is performed at a lower temperature. For example, after reduction at 500 K and even after evacuation at 673 K, the ceria-zirconia remains

partly oxidized and favors the migration of hydrogen on the support surface with a consumption of 2.8  $\mu\text{mol m}^{-2}$  as observed by Hickey *et al.* (16).

However, the same authors have performed dynamic OSC measurements with hydrogen and oxygen pulses at room temperature on similar catalysts. As in our study, this measurement corresponds approximately to the titration by oxygen of the hydrogen stored on the surface, although it probably includes the reversible fraction of the adsorbed hydrogen, which is not the case in our measurements. From the H<sub>2</sub> (or O<sub>2</sub>) consumed, the values calculated for Pt/CeO<sub>2</sub> catalysts, 3.8  $\mu\text{mol}$  of H<sub>2</sub> spilled over a ceria surface area of 1 m<sup>2</sup> are in agreement with those observed in our previous work (14, 31), 3.9–4  $\mu\text{mol m}^{-2}$ . For Pt or Pd/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalysts, a higher value was calculated, 6.2  $\mu\text{mol}$  of H<sub>2</sub> for 1 m<sup>2</sup>, whereas for the Rh/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> system (16) the value is only 2.4. This discrepancy was not elucidated. To compare our protocol to those data, we determined the corresponding coefficients on the same catalysts by applying the OT method according to the experimental conditions defined previously, which resulted in finding the value of 4  $\mu\text{atom O m}^{-2}$  in good agreement with the 3.8  $\mu\text{mol H}_2 \text{ m}^{-2}$  value for 0.54Pt/CeO<sub>2</sub>. The OT method gives a coefficient of 5.8  $\mu\text{atom O m}^{-2}$  for 0.58Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (5.6  $\mu\text{atom O m}^{-2}$  by using 104 m<sup>2</sup> g<sup>-1</sup> for the BET surface area according to Ref. (38)). This value is rather similar to that of Hickey *et al.* which is in the range of the values, between 4.3 and 5.8  $\mu\text{atom O m}^{-2}$  with a mean value of 5.1  $\mu\text{atom O m}^{-2}$ , calculated in the present study for the Pd and PrRh series. Thus, we obtain nearly the same coefficient for Pt, Pd, or Rh catalysts supported on CeZr supports, and this coefficient does not appear to be modified after aging of the catalysts. This type of measurement was valid for composite supports such as “ceria-zirconia + alumina” and illustrates the fact that, under our conditions, it is possible, by successive H<sub>2</sub>/O<sub>2</sub> adsorption cycles performed at room temperature, to quantitatively oxidize the hydrogen spilled over the support. Compared to ceria, the excess hydrogen uptake measured at 1 m<sup>2</sup> (5.1 instead of 4  $\mu\text{mol}$ ) suggests that the presence of zirconium ions in the ceria fluorite structure favors the adsorption of hydrogen on the surface. It is not possible to correlate this value to a precise surface geometry. It can be only determined that this coefficient is approximately twice that calculated with 63–68 mol% Ce<sup>4+</sup> ions at the surface of a model ceria (2.5–2.7  $\mu\text{atom O m}^{-2}$ , see Section 3.2). Further work is necessary to study this in more detail and to determine the eventual variation of this coefficient with the composition of the solid solution.

Finally, it may be emphasized that in our initial assumptions, it was supposed that the surface titrated by OT corresponded to the ceria surface supporting metallic particles. In fact, Hickey *et al.* (16) showed that by mechanically mixing a platinum/alumina catalyst with a ceria-zirconia support, it was possible to observe some hydrogen spill-over

already at room temperature, provided that platinum was in a reduced state. Based on this observation, we infer that the values of the surface area from OT lead to the values of the total ceria-zirconia surface area without discrimination, whether or not the ceria-zirconia particles support some reduced noble metal atoms.

## 5. CONCLUSION

The data obtained on Pd and/or Rh deposited on CeO<sub>2</sub>-ZrO<sub>2</sub> demonstrated the existence of highly mobile bulk oxygen atoms, in agreement with the better OSC evidenced on these catalysts when compared to the ceria or ceria-alumina supports. As a result, reduction of these catalysts at 573 K concerns not only the surface of the solids but also a part of the bulk oxygen atoms. Consequently, unlike the case for ceria and ceria-alumina supports, the subsequent oxygen chemisorption at room temperature cannot be used to estimate the ceria-zirconia surface area. This holds true for fresh and aged catalysts and confirms previous TPR results on these solids which were unable to discriminate between the surface and bulk reduction steps.

On the other hand, the method of titration of hydrogen by oxygen at room temperature (OT) seems suitable for determining the ceria-zirconia surface of a series of catalysts prepared with the same base ceria-zirconia support. Since the same calibration coefficient can be used for fresh and aged catalysts, it would be very useful to study catalysts after aging. The possibility of using this method to estimate the surface area of the ceria-zirconia support in composite catalysts was examined with two Pd and PdRh catalysts deposited on a support containing both alumina and ceria-zirconia.

## ACKNOWLEDGMENTS

Rhodia is gratefully acknowledged for supplying the ceria-zirconia and alumina supports and the Pt catalysts (CEZIRENCAT project). The technical assistance of Mrs. L. Retailleau for the chemisorption measurements on Pt/CeO<sub>2</sub> and Pt/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> is gratefully acknowledged.

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