

Preparation of Alumina-Supported Ceria. II. Measurement of Ceria Surface Area after Impregnation with Platinum or Rhodium

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The surface area of cerium oxide was tentatively determined in model three-way catalysts using (i) a methodology based on the exploitation of the hydrogen temperature-programmed reduction (TPR) profiles and (ii) the adsorption of CO₂ on the hydroxyl groups of alumina followed by FTIR spectroscopy. These two methods were performed on a ceria–alumina support after impregnation with RhCl₃ and H₂PtCl₆ and calcination under nitrogen at 773 K. Whereas the two methods gave agreeing results on the initial support, the results were not so straightforward for catalysts. In this case, the TPR profiles are deeply modified with respect to the support. Due to the presence of platinum and rhodium, the reduction peak corresponding to the ceria surface reduction is shifted toward lower temperatures. It also includes the quantity of hydrogen necessary for the reduction of the precious metal oxide. After examining the metal mean oxidation degree, it has been possible to calculate the ceria surface area in the catalyst. A 20–30% decrease was found compared to the initial support. On the contrary, with the CO₂-FTIR method, the calculated ceria surface area increases after impregnation. It can be attributed to the fact that the density of OH species responsible for CO₂ adsorption is modified by the presence of chlorine introduced during the preparation. These results are discussed and compared to those for the support alone. A reexamination of the TPR curves has permitted the extent of ceria surface not in contact with precious metal to be taken into account. It appears that 10 to 30% of the initial ceria surface would remain uncovered by the precious metals after impregnation. Finally, the TPR method can be considered as the most reliable and potentially rich source of informations on the catalyst surface state. © 1997 Academic Press

1. INTRODUCTION

It is admitted that, among the different promoters utilized in three-way catalysts, the cerium dioxide, or ceria, makes the characterization of these systems highly diffi-

cult. It is however important to know the extent of the ceria surface area, since it plays a key role in the oxygen storage capacity, and hence in the catalytic properties of the system. A large set of techniques has been used in order to study the support of the ceria–alumina-based catalysts. Among them, the temperature-programmed reduction (TPR), Raman and XPS spectroscopies, and X-ray diffraction (XRD) are very often found in the literature (1–5). In a preceding work (6), we have described two methods for measuring the surface area of cerium oxide in a mixed ceria–alumina support. The first one is based on the exploitation of the first hydrogen uptake peak observed during TPR tests which could be attributed to the reduction of the ceria surface. The second has to do with the specific adsorption of CO₂ on the hydroxyl groups of alumina to form hydrogenocarbonate species having an absorption band at 1235 cm⁻¹ which can be easily followed by FTIR spectroscopy. By determining the accessible alumina area and knowing the total BET surface area, it is easy to deduce the ceria surface area. In the case of model ceria–alumina supports in the absence of precious metals, the latter was found identical to that obtained with the TPR method (6). In the present work, we studied the application of these two methods to the case of catalysts, i.e., the same supports, including pure alumina and ceria, after impregnation with platinum and rhodium metals. This paper is a part of a more general study of three-way catalysts devoted to better understand the origin and the evolution of this type of catalysts from the preparation to an aged state. In addition to the surface area of ceria and alumina, the other parameters under investigation were the metallic area and the metal surface composition but they are not considered here.

2. EXPERIMENTAL

2.1. Materials

The ceria–alumina support was prepared by grafting Ce(AcAc)₃ on the hydroxyl groups of a SCM129

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Rhône-Poulenc alumina support (107 m² g⁻¹) as described before (6). The final calcination temperature was 673 K. Two different support samples originating from two preparations were used, with, respectively, 18.9 and 17.3 wt% cerium content, and 110 and 97 m² g⁻¹ BET surface area.

Five cerium dioxide samples were used as well. The first one, from Rhône-Poulenc, was calcined under air at 673 K. Its BET surface area was 127 m² g⁻¹ after desorption under vacuum at 673 K. The others were prepared by calcination of the same oxide between 900 and 1120 K. In the following, they are referenced according to their specific area put in parentheses, i.e., Ce₍₁₂₇₎, Ce₍₈₀₎, Ce₍₆₀₎, Ce₍₃₀₎, and Ce₍₅₎.

These supports were impregnated with aqueous solutions of H₂PtCl₆ and/or RhCl₃ in order to prepare monometallic or bimetallic catalysts with metal loading between 0.5 and 2 wt%. The bimetallic catalysts were prepared by coimpregnation. After drying overnight under vacuum at 383 K, the solids were treated 2 h at 773 K under nitrogen flow. The obtained catalysts are presented in Table 1 with the corresponding chemical analyses. After calcination at 773 K, the chlorine content was almost the same as that introduced with the chlorinated precursor.

A chlorine-free platinum catalyst was prepared by impregnating the support at 343 K with a solution of platinum acetylacetonate in toluene. After drying overnight under vacuum at 373 K, the solid was calcined 2 h at 673 K in air in order to eliminate the organic moiety. The corresponding solid is referenced 0.5Pt/CeAl-Ac.

2.2. Characterization Methods

The BET method was used to measure the specific area of the samples. The nitrogen adsorption was done at 77 K in

an automated volumetric setup built in the laboratory, after a vacuum desorption at 773 K. All the BET measurements were referred to the initial mass of the sample, as in the case of TPR and FTIR experiments.

The ceria surface area was determined according to our previous results (6, 7) by using the first hydrogen uptake composite peak on the TPR profiles. The experiments were performed on 0.1 g of catalyst, pretreated under air at 673 K for 1 h, and then outgassed under argon flow for 1.5 h at 773 K. After cooling to room temperature, a flux of 20 ml min⁻¹ of 1 vol% hydrogen in argon was introduced to the sample and the TPR experiment was performed using a 20 K/min heating rate up to 1073 K, with this temperature kept constant for 45 min. More details on the experimental setup can be found in Ref. (8). By supposing that the hydrogen consumption is not disturbed by desorption or reaction products, the error on the actual hydrogen measurements can be estimated less than 0.5 μmol H₂.

The alumina surface area was estimated by FTIR spectroscopy of CO₂ adsorbed specifically on the alumina surface hydroxyls. More precisely, the band at 1235 cm⁻¹ (δ C-O-H bending mode), characteristic of the hydrogenocarbonates formed by adsorption, was discriminated from the bands displayed by ceria and its optical density could be directly related to the free alumina surface (6). Accordingly, using the total BET surface area value, a ceria surface could be deduced. The measurements were obtained with a BRUKER IFS 110 on self-supported wafer samples (0.01 to 0.03 g/cm²). They were pretreated 1 h at 673 K under 26.6 kPa oxygen and then 3 h at 773 K under high vacuum, before adsorption of CO₂ at room temperature (2 kPa). The catalysts were finally evacuated at 295 K for 30 min.

Finally the monometallic catalysts surfaces were examined by X-ray photoelectron spectroscopy in order to determine the oxidation state of the precious metal. A Fisons Escalab 200 spectrometer was used for this purpose.

TABLE 1

Chemical Analysis of the Catalysts (wt%)

Support	Catalyst	Pt	Rh	Ce	Cl
Alumina	0.5Pt/Al	0.57			0.47
	0.5Rh/Al		0.46		
	1Pt-0.2Rh/Al	1.0	0.15		
Ceria	0.5Pt/Ce ₍₁₂₇₎	0.43			0.44
	0.5Pt/Ce ₍₈₀₎	0.45			
	0.5Pt/Ce ₍₆₀₎	0.40			
	0.5Pt/Ce ₍₃₀₎	0.48			0.45
	0.5Pt/Ce ₍₅₎	0.46			
	0.5Rh/Ce ₍₁₂₇₎		0.51		
	1Pt-0.2Rh/Ce ₍₁₂₇₎	0.95	0.23		1.32
Ceria-alumina	0.5Pt/CeAl	0.59		18.9	
	2Pt/CeAl	2.09		19.2	
	0.5Pt/CeAl	0.42		16.6	0.44
	0.5Pt/CeAl-Ac	0.49		18.9	
	0.5Rh/CeAl		0.45	19.4	
		1Pt-0.2Rh/CeAl	1.13	0.19	19.3

3. RESULTS

First, we will describe the effects of the impregnation on the ceria reduction temperatures by comparing the TPR profiles of the platinum and/or rhodium precursors deposited on alumina, ceria, or ceria-alumina support. Then, in order to calculate the ceria surface area of the ceria or ceria-alumina catalysts, we will discuss the contribution of the oxidized precious metals reduction to the total hydrogen consumption. As indicated in Section 2.2, before each TPR experiment, the solids were heated under air at 673 K and then under argon at 773 K. Under these conditions, the precise oxidation state is debatable and will be considered in detail. Finally, we will present the results obtained by FTIR spectroscopy of CO₂ adsorbed on the system.

3.1. Reduction Processes Observed by TPR on the Different Catalysts

3.1.1. Pt and/or Rh/Al₂O₃ catalysts. Figure 1 gives the TPR profiles of the three catalysts supported on alumina: 0.5Pt/Al, 0.5Rh/Al, and 1Pt-0.2Rh/Al. A hydrogen uptake peak is observed with a maximum temperature at 593, 423, and 521 K, respectively, for platinum, rhodium, and bimetallic samples. The position of these reduction peaks is in agreement with those given in Ref. (9), which confirms the easier reducibility of rhodium. Moreover, the reduction of alumina supported rhodium at relatively low temperatures was also observed by Vis *et al.* (10) and McCabe *et al.* (11).

For the bimetallic catalyst, there is only one peak ascribable to the precious metal reduction and centered at 521 K, a temperature just between those of platinum and rhodium. Consequently, the two precursors seem to be reduced simultaneously, in agreement with the observations of Kacimi and Duprez (9). This could mean that there exists an intimate interaction between the two metals, with Rh⁰ speeding up the platinum reduction. However, this observation does not prove that the two metals interact inside the

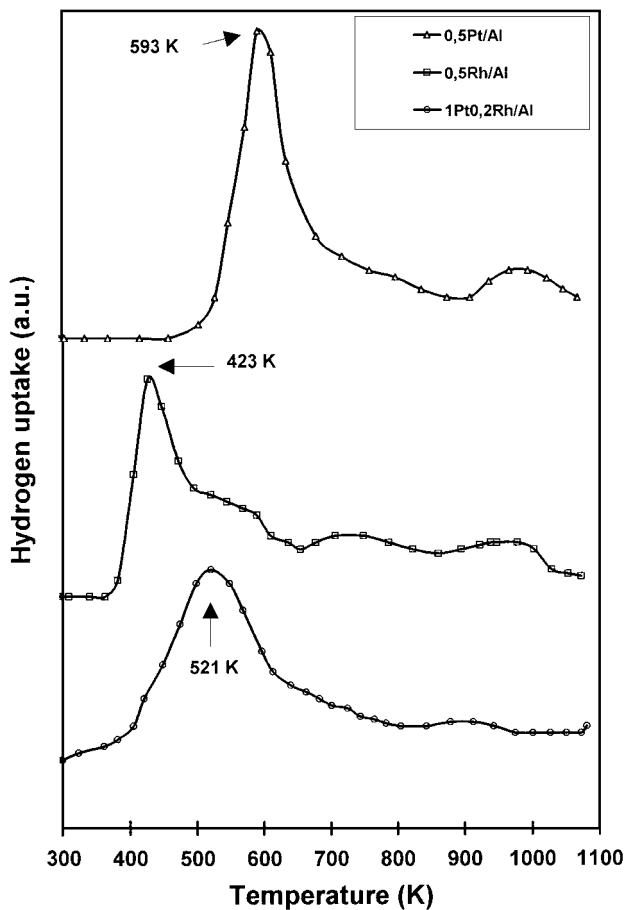


FIG. 1. Hydrogen TPR profiles of alumina supported Pt and/or Rh catalysts.

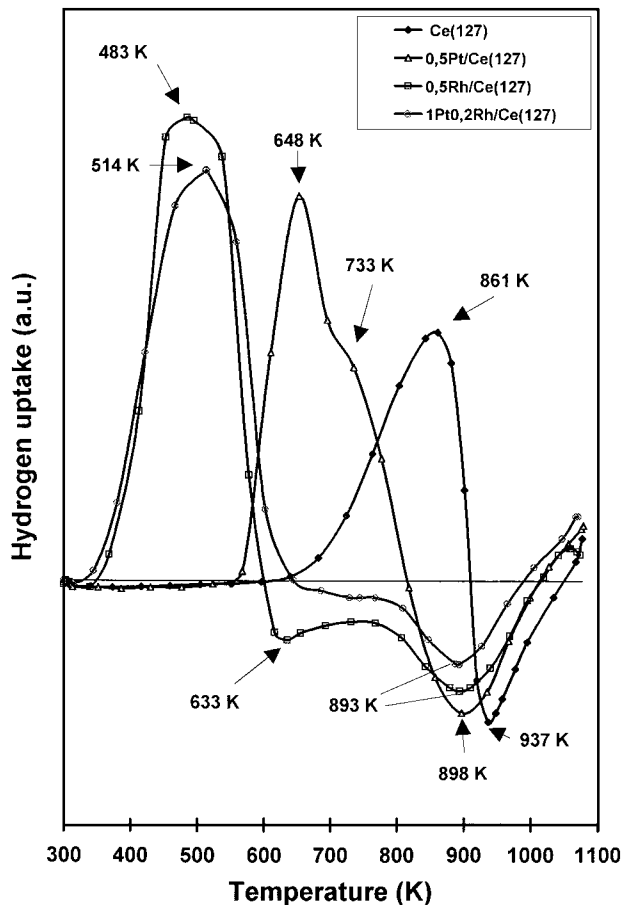


FIG. 2. H₂ TPR profiles of ceria-supported Pt and/or Rh catalysts.

same metallic particle. Indeed, it can be also supposed that hydrogen, after dissociation on metallic rhodium, is able to spill over to the separated Pt-containing particles and then be reduced at a lower temperature than in the absence of rhodium.

3.1.2. Pt and/or Rh/CeO₂ catalysts. In Fig. 2 are given the TPR curves for the monometallic and bimetallic catalysts prepared on the ceria support with a BET surface area of 127 m² g⁻¹. The curve for the support alone is given for comparison. The profiles are rather complicated but the general appearance is almost the same. When the temperature increases, there is successively a composite hydrogen uptake, a negative peak at about 900 K (double in the case of Rh/CeO₂ with first a minimum at 633 K) and again a small positive peak or drift which is not finished at 1073 K.

The main peak of interest for this study is the first maximum which corresponds to the reduction of the ceria surface in the case of the support. For metallized samples, it includes, as will be shown below, both the oxidized metal reduction and the ceria surface reduction. The origin of the negative peak at 900 K was already discussed for the support Ce₍₁₂₇₎ (7, 8). From separate experiments using gas chromatography analysis (12) or mass spectrometry analysis (8),

it could be attributed to the evolution of H₂, CO, and some CO₂ in the gas phase, resulting from the desorption of hydrogen stored by the solid (metal and reduced ceria) and from the reduction or decomposition of carbonate species present in the ceria bulk and not eliminated during the pre-treatment. Thus, the negative peaks in the TPR profiles must be attributed to the desorption of both H₂ and CO, the latter having a higher thermal conductivity than argon. This peak, very intense for the support Ce₍₁₂₇₎, was found less intense for cerias of lower surface area (<80 m² g⁻¹). To limit the error caused by this negative peak on the calculation of the ceria surface area from the first peak of the TPR profile, a procedure using the first ascending part of the peak and its mirror image was tried. Although TPR peaks are not necessarily symmetric, this method was found to be accurate enough and the most suitable for a series of ceria samples (7), and a linear relation between the surface area and the H₂ consumption during the first peak was obtained. The reduction occurring at higher temperature, after the negative peak, corresponds to the reduction of bulk ceria as already shown in Refs. (3, 7, 12).

For the 0.5Pt/Ce₍₁₂₇₎ catalyst, the temperature of the first peak is lowered from 861 K for pure ceria to 648 K, with a shoulder at 733 K. The lower temperature compared to the support alone indicates that the precious metal in the metallic state facilitates the ceria surface reduction. This phenomenon is well documented in the literature (5, 13–17). It includes the dissociative hydrogen adsorption on the metallic sites and the migration of this hydrogen or spillover on the whole ceria surface, thus facilitating the reduction of this surface at low temperature (15, 17–19).

In the case of the rhodium catalyst, the reduction temperature is even lower: 483 K. This result supports the idea of a higher reducibility of rhodium compared to platinum, as observed before when supported on alumina.

The curve for the bimetallic catalyst looks like that of 0.5Rh/Ce, with a maximum at 514 K. As for alumina, this maximum is located between those corresponding to platinum and rhodium.

3.1.3. Pt and/or Rh/CeO₂-Al₂O₃ catalysts. Figure 3 gives the TPR curves corresponding to the ceria-alumina support and to the Pt or Rh monometallic and Pt-Rh bimetallic catalysts deposited on the same support. The catalysts profiles are simpler than on pure CeO₂. They present a well-resolved peak at low temperatures (490–690 K) followed by a smaller wave of hydrogen consumption at higher temperatures (700–990 K). The latter is broad and seems to be composed of at least two different peaks. Compared to the CeO₂-Al₂O₃ support, the temperature of the first peak is lowered by 200–300 K. This observation illustrates the participation of the precious metals in the reduction of the cerium dioxide, as for the ceria-supported catalysts. Moreover, as noted for ceria catalysts, the first peak includes both the reduction of

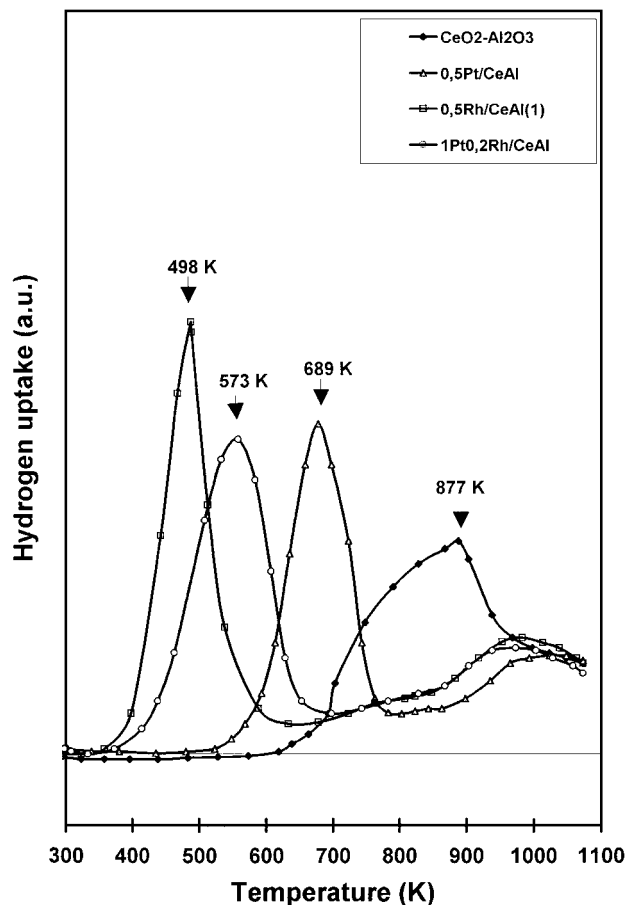


FIG. 3. H₂ TPR profiles of ceria-alumina support and ceria-alumina-supported Pt and/or Rh catalysts.

the oxidized metals and that of the cerium oxide surface (2, 5, 13–17).

No “negative peak” is observed as it was for catalysts supported on Ce₍₁₂₇₎, which suggests that bulk carbonates in this ceria-alumina support are present at low or even zero concentration. However, to check the validity of the TCD signal and verify that it is not changed by a possible desorption of products, a similar TPR test was performed on the 0.5 Pt/CeO₂-Al₂O₃ sample using a mass spectrometer analysis. There was no evidence of hydrogen or CO desorption at 900 K. However, traces of methane were observed below 750 K, and a small desorption of CO₂ was noted at around 1000 K. Since the thermal conductivity of CO₂ is not very different from that of argon (42×10^{-6} cal. cm cm⁻² s⁻¹ °C⁻¹ instead of 44×10^{-6} cal. cm cm⁻² s⁻¹ °C⁻¹), the influence of this desorption on the profile must be limited. Effectively, the quantitative measurement of the MS hydrogen uptake has been found identical to that obtained by TCD (275 μmol g⁻¹ instead of 272 for the TCD low-temperature peak, and 637 instead of 647 μmol g⁻¹ for the total consumption). Thus, for this type of ceria-alumina-supported catalysts, the TCD signal can be considered as reliable.

TABLE 2

Maximum of the Low-Temperature Peak (K) Observed for the Pt and/or Rh/Support Systems

Support	0.5Pt	0.5Rh	1Pt 0.2Rh
Al ₂ O ₃	593	423	521
CeO ₂	648	483	514
CeO ₂ -Al ₂ O ₃	689	498	573

3.1.4. Comparison of the results on the three supports.

Table 2 gives the temperature of the maximum of the first peak for each of the catalysts studied. Whatever the support, the maximum for the bimetallic catalyst is always between those observed for the platinum or rhodium monometallic catalysts. Thus, this peak corresponds to the concerted reduction of the two metals and the ceria surface. This result is in agreement with the work of Marecot *et al.* (16) on the influence of the preparation mode of PtRh/CeO₂-Al₂O₃ solids on their catalytic properties. When the two metals are coimpregnated, they show that the TPR curves have only one hydrogen consumption peak situated at a temperature between those of the monometallic catalysts. However, in the case of successive impregnation, they observe two distinct peaks corresponding to the successive reduction of Rh-CeO₂ and Pt-CeO₂.

A general temperature increase is observed from alumina to ceria and then to ceria-alumina. It can be interpreted by the fact that in presence of ceria, in addition to the reduction of the metals (occurring also on alumina), the reduction of the support surface requires additional hydrogen, which may apparently shift the maximum on the TPR curve to higher temperatures. The highest temperatures, however, are noted for the ceria-alumina support. Two interpretations can be proposed to explain this observation. The first, based on the same reasoning as for ceria, would indicate a higher hydrogen consumption and then a higher ceria surface. This interpretation does not hold, if one considers the BET surfaces. The second explanation may be related to the preparation of the ceria-alumina support. By grafting cerium acetylacetonate on alumina and then calcining under oxygen, it is clear that a certain degree of interaction is established between ceria and alumina, which probably lowers the reducibility of the cerium oxide in the mixed support. However, it must be noted that XRD analysis did not detect the formation of a mixed phase such as CeAlO₃ phase. In addition, magnetic measurements on the support or the Pt/CeO₂-Al₂O₃ did not evidence a significant amount of Ce³⁺ in the initial solids before reduction.

3.2. Determination of Ceria Surface Area (TPR)

In the case of metal catalysts, the first peak, which is shifted to lower temperatures than for the support alone, includes the quantity of hydrogen necessary to reduce the

oxidized precious metal and the one corresponding to the ceria surface reduction. In the experimental conditions used in this work, it was established on ceria samples that the reduction of 1 m² of surface area required 3.9 μmol of hydrogen. We keep the same factor in the following. However, to calculate the ceria surface area by the TPR method, we must first estimate the mean oxidation state of the metals at the beginning of the TPR test, i.e., after the pretreatment at 673 K under air and then at 773 K under argon. In this section, we start to compare the possible oxidation degrees found in the literature to those we have determined for alumina-supported catalysts. Then we apply the calculation method to the other catalysts supported on ceria and ceria-alumina.

3.2.1. Oxidation degree for platinum: Case of Pt/Al₂O₃.

The oxidation state of platinum in oxidizing atmosphere depends on the catalytic systems and the experimental conditions (20). The known oxidation degrees for platinum are 0, +2, and +4, corresponding, respectively, to Pt⁰, PtO, and PtO₂. When a reduced supported metal platinum is exposed to ambient air, a Pt₅O surface layer is formed which can be reduced by hydrogen at room temperature (20). By treating a Pt/γ-Al₂O₃ catalyst at various temperatures under oxygen atmosphere, Lieske *et al.* (22) have shown that the mean platinum oxidation state increases from 1.5 to 4.0 when the temperature varies from 300 to about 870 K. At a higher temperature, a sintering of the metallic particles is obtained in parallel with a fast decrease of the oxidation degree.

Similar observations were made at the laboratory on a 2%Pt/Al₂O₃ sample which was prereduced by H₂ at 773 K (23). Using temperature-programmed oxidation (TPO), the profile indicated an oxygen uptake peak up to 800 K, with a maximum at 735 K. For higher temperatures, the oxidized platinum was decomposed. The total oxygen consumption at 800 K corresponded to a O/Pt ratio close to 1. At this temperature, it can be supposed that the platinum particles are constituted of a metallic platinum core covered by PtO₂. This model is in agreement with Lietz *et al.* (24) who show on the same type of catalyst that platinum oxidation is limited to the surface layers.

In our case, there was no prereduction, and the platinum is probably in the initial oxidation state of the impregnating salt, i.e., Pt⁴⁺. The hydrogen consumption during the TPR on the 0.5Pt/Al₂O₃ sample gives a ratio of 1 Pt atom for 2.5 oxygen atoms. This ratio is superior to the value of 2 corresponding to the stoichiometry of the PtO₂ reduction. The excess of hydrogen uptake cannot be attributed to hydrogen adsorption on the metallic surface, since it is certainly desorbed during the TPR at high temperature. It may correspond to the fixation of hydrogen on the oxygen atoms of alumina situated in the vicinity of the metallic particles to form hydroxyl groups.

To support this hypothesis, we have followed, by FTIR spectroscopy, the eventual formation of hydroxyl groups

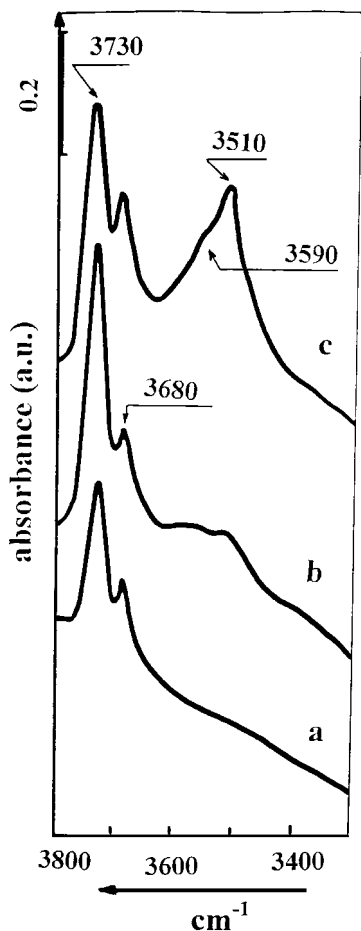


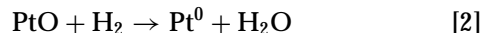
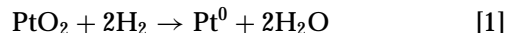
FIG. 4. FTIR spectra recorded at room temperature in the hydroxyl groups range for a 2%Pt/Al₂O₃ catalyst: (a) spectra after treatment at 773 K [vacuum + reduction under hydrogen (13.3 kPa) + evacuation]; (b) oxidation under 26.6 kPa O₂ at 573 K and evacuation at 673 K; (c) reduction under 26.6 kPa H₂ at 473 K and evacuation at 473 K.

(3800–3300 cm⁻¹ range) during the reduction of the 2%Pt/Al₂O₃ sample. Figure 4 gives the spectra recorded at room temperature after the three following series of treatments: (i) treatment under vacuum 1 h at 773 K and then 13 h reduction under hydrogen (13.3 kPa) and 2 h evacuation always at 773 K; (ii) oxidation for 5 h under 26.6 kPa O₂ at 573 K, followed by 2 h evacuation at 673 K; (iii) 4 h reduction under 26.6 kPa H₂ at 473 K and then 2 h evacuation at the same temperature. The initial spectra (curve a) presents two bands at 3730 and 3680 cm⁻¹ characteristics of the OH groups on alumina surface and stable at 773 K. After oxidation, there is a small increase of the absorbance of the 3730 cm⁻¹ band but no significant modification of the spectra (curve b). However, after reduction and evacuation at 473 K, an intense vibration is evidenced at 3510 cm⁻¹, with a small shoulder at 3590 cm⁻¹ (curve c). Since no absorption has appeared simultaneously in the 1600 cm⁻¹ region, this band cannot be assigned to some water introduced as impurities in hydrogen. Moreover, at 473 K, this water would

have been desorbed. We can deduce that this 3510 cm⁻¹ bands correspond to the formation of hydroxyl groups on the alumina surface through the reduction of platinum. It was no more observed after a new reduction and evacuation at 573 K, showing the relatively low stability of these hydroxyls groups.

To check the 4+ oxidation state of platinum in this solid after the standardization treatment, an XPS analysis was also performed. The presence of a peak at 315.2 eV was ascribed to Pt²⁺ (PtO) in agreement with the conclusions of Shyu (25) and Schwartz (26), although other authors (27) attribute this peak to chlorinated compounds, the chlorine originating in the H₂PtCl₆ precursor.

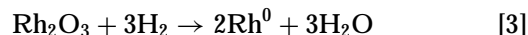
As a result, we have opposite arguments to choose between the Pt²⁺ and Pt⁴⁺ states. Consequently, in a first approach, we still continue to consider the two possibilities for the fresh catalysts, and the hydrogen quantities necessary for the complete platinum reduction will be calculated according to the reactions



3.2.2. Oxidation degrees of rhodium: Case of Rh/Al₂O₃. Unlike platinum oxides, there is only one stable form of rhodium oxide, Rh₂O₃, corresponding to a Rh oxidation degree of +3. A TPO study on a 2%Rh/Al₂O₃ reduced at 773 K by hydrogen has shown only one oxygen uptake peak at 448 K (23). The O₂ consumption, including the room temperature adsorption, corresponds to an O/Rh ratio equal to 1.5, which means a total oxidation of rhodium into the Rh₂O₃ sesquioxide form, in agreement with Refs. (26, 28).

The TPR calibration performed on the same sample leads to a total H₂ quantity corresponding to a ratio O/Rh = 1.85. This value is slightly higher than the 1.5 needed for the reduction of Rh₂O₃. As it was shown above for Pt/Al₂O₃, we can suppose that some hydrogen adsorption occurs on the alumina oxygen atoms close to the metal.

In agreement with the TPR calibration, the XPS analysis of the 0.5Rh/Al₂O₃ catalyst also shows that rhodium is in a +3 state. In conclusion, in the case of rhodium, the reaction to be considered is



3.2.3. Case of Pt or Rh/CeO₂ catalysts. In these samples, the ceria surface area can be assimilated to the BET area of the catalyst, which allows to check the validity of the TPR method. We consider that the first TPR peak before the negative peaks corresponds to the reduction of the metals and that of the ceria surface. The reduction of the ceria surface at lower temperatures than for pure ceria originates from the spillover of hydrogen, which occurs on metallized ceria and favors this process. Indeed, magnetic measurements have shown a complete surface reduction of the oxide at room

temperature for a Rh/CeO₂ solid prepared from a rhodium nitrate precursor (19).

However, the presence of metal and the resulting spillover should not influence the bulk reduction of ceria below roughly 800 K, because it probably requires higher temperatures to remove the oxygen of the lattice. This statement is supported by the fact that the reduction percentage of ceria, in Rh/CeO₂ catalysts, was practically unchanged when reduction temperature increased from 623 to 773 K and corresponded approximatively to that expected for a fully surface reduced ceria (29). To confirm this point, we have checked that surface reduction of CeO₂ is nearly the same when reducing pure CeO₂ or when reducing Pt/CeO₂ or Rh/CeO₂. For this purpose, we prepared four other Pt/CeO₂ starting from cerias with BET area between 80 and 5 m² g⁻¹.

The results are given in Table 3. The ceria surface areas were calculated from the first TPR peak, after subtraction of the theoretical hydrogen quantities according to reactions [1], [2], or [3]. The obtained values are very close to the BET values. A better, though imperfect, agreement is found between the two series of values, starting with the PtO hypothesis. This is especially shown in the case of 0.5Pt/Ce₍₅₎. Consequently, the PtO hypothesis appears to be the most appropriate for fresh catalysts in presence of ceria. For the Rh/CeO₂ and PtRh/CeO₂ samples, the comparison between the two values of the ceria surface areas also shows a good agreement.

In conclusion, the equality observed between the BET area and the TPR ceria surface establishes clearly that, if the spillover of hydrogen facilitates the reduction of the ceria surface at lower temperature, the surface and bulk reduction processes still remain well separated and distin-

guishable on the TPR profiles. Thus, the TPR method can give a correct estimate of the ceria surface area.

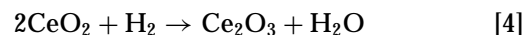
3.2.4. Application to the catalysts supported on CeO₂-Al₂O₃. The XPS results on the Pt/CeO₂-Al₂O₃ sample after calcination at 673 K show that platinum is under the PtO form, as was observed for the ceria support. Similarly, for the 0.5Rh/CeO₂-Al₂O₃ sample, the rhodium oxidation state evidenced by XPS is Rh³⁺. The same conclusion is found in the literature for Rh/CeO₂-Al₂O₃ or SiO₂ (26) and Rh/CeO₂ catalysts (15, 28).

The ceria surface areas were calculated as for M/CeO₂ using the first TPR peak. However, considering the absence of a negative peak in ceria-alumina-supported catalysts, the calculation was done with the experimental hydrogen consumption during the first peak, and not using the symmetrical procedure. This is fully justified, since, as mentioned in Section 3.1.3, the quantitative measurement of the MS hydrogen uptake has been found identical to that obtained by TCD.

The results are given in Table 4. Insofar as the mean oxidation state of platinum is different on alumina or ceria and since it is not possible to know *a priori* the location of platinum, we have again assumed for platinum the reduction of PtO or PtO₂. The quantities of hydrogen used in the calculation are included in Table 4.

For the CeAl support alone, the value of S_{CeO₂} determined by TPR is 84 m² g⁻¹ cat, or 363 m² g⁻¹ CeO₂, considering the 23.2 wt% CeO₂ content. It means that the ceria is highly dispersed on alumina, and it can be calculated that around two-thirds of the cerium ions are on the surface. For the catalysts, it is not possible from the results to determine the initial oxidation state of platinum. From the preceding observations, however, the PtO hypothesis seems the most reasonable. Under these conditions, the calculated ceria surface for the catalysts is between 62 and 52 m² g⁻¹.

For the M/CeO₂-Al₂O₃ samples, we have also determined the hydrogen consumption during the complete TPR, including the isothermal part at 1073 K. In this case, after the reduction of ceria surface, the hydrogen uptake corresponds to the reduction of the bulk. For ceria samples (7), it was observed that, for a given temperature, the bulk reduction percentage was the highest for the most dispersed. Therefore, we have calculated the reduction extent for the present samples. It corresponds to the ratio between the total hydrogen uptake and the theoretical hydrogen quantities necessary to the reduction of all the Ce⁴⁺ ions into Ce³⁺ according to the equation



and to the reduction of the metals, following the preceding hypothesis, PtO → Pt⁰, Rh₂O₃ → Rh⁰.

In the case of M/CeO₂, the reduction extent varied between 8% for the 0.5 Pt/Ce₍₅₎ sample and 24–27% for the

TABLE 3

Ceria Surface Areas Measured by the BET or TPR Methods on Model Pt and/or Rh/CeO₂

Solid	S _{BET} (m ² g ⁻¹ cat)	S _{CeO₂TPR} (m ² g ⁻¹ cat)	Reduction extent (%)
0.5Rh/Ce ₍₁₂₇₎	124	131	25
0.5Pt/Ce ₍₁₂₇₎	117	110 ^a -105 ^b	24 ^a
0.5Pt/Ce ₍₈₀₎	78	80 ^a -74 ^b	18 ^a
0.5Pt/Ce ₍₆₀₎	59	59 ^a -54 ^b	19 ^a
0.5Pt/Ce ₍₃₀₎	27	36 ^a -30 ^b	14 ^a
0.5Pt/Ce ₍₅₎	4.9	6.4 ^a -0.4 ^b	8 ^a
1Pt-0.2Rh/Ce ₍₁₂₇₎	117	122 ^a -107 ^b	27 ^a

Note. S_{CeO₂} is [H₂ exp. - H₂ th. Pt - H₂ th. Rh]/3.9 (in m² g⁻¹), where H₂ exp. and H₂ th. are, respectively, the experimental low-temperature peak hydrogen uptake and the theoretical hydrogen quantity necessary for the metal reduction starting from PtO, PtO₂, and Rh₂O₃. Reduction extent is the ratio between experimental total hydrogen consumption and the maximum theoretical hydrogen consumption (CeO₂ → Ce₂O₃; PtO or PtO₂ → Pt⁰; Rh₂O₃ → Rh⁰).

^a With PtO hypothesis.

^b With PtO₂ hypothesis.

TABLE 4
Ceria Surface Areas Measured by TPR on Model Pt and/or Rh/CeO₂-Al₂O₃

Solid	S_{BET} (m ² g ⁻¹ cat)	H ₂ exp. (μmol g ⁻¹)	H ₂ th./Pt (μmol g ⁻¹)	H ₂ th./Rh (μmol g ⁻¹)	$S_{\text{CeO}_2\text{TPR}}$ (m ² g ⁻¹ cat)	Reduction extent (%)
CeAl	110	329	—	—	84	91
0.5Pt/CeAl	107	272	30 ^a -61 ^b	—	62 ^a -54 ^b	92 ^a
0.5Rh/CeAl	109	273	—	66	53	99
1Pt0.2Rh/CeAl	104	288	58 ^a -116 ^b	28	52 ^a -37 ^b	92 ^a
2Pt/CeAl	104	382	107 ^a -214 ^b	—	71 ^a -43 ^b	97 ^a

Note. H₂ exp., experimental low-temperature peak hydrogen uptake. H₂ th., theoretical hydrogen quantity necessary for the metal reduction starting from PtO, PtO₂, and Rh₂O₃. S_{CeO_2} , [H₂ exp. - H₂ th. Pt - H₂ th. Rh]/3.9 (m² g⁻¹). Reduction extent, ratio between experimental total hydrogen consumption and the maximum theoretical hydrogen consumption (CeO₂ → Ce₂O₃; PtO or PtO₂ → Pt⁰; Rh₂O₃ → Rh⁰).

^a With PtO hypothesis.

^b With PtO₂ hypothesis.

M/Ce₍₁₂₇₎ (see Table 3). For the Ce-Al support alone, the reduction extent of 91% indicates an almost complete reduction. Similarly, for the M/CeO₂-Al₂O₃ catalysts, the reduction extents are also close to 100%. It probably means that the bulk ceria content is very low in the mixed support; i.e., the ceria is highly dispersed on the alumina surface. This is in good agreement with the value of S_{CeO_2} in ceria-alumina determined by TPR (363 m² g⁻¹ CeO₂).

3.3. Generalization of the TPR Method for the Calculation of the Ceria Surface Area in Mixed Ceria-Alumina-Supported Catalysts

To ascertain the validity of the TPR method, we have verified that it could be applied to more highly loaded catalysts. Consequently, we prepared a 2 wt% Pt catalyst on the same ceria-alumina support. We have also checked that the presence of chlorine in the catalyst which is known to modify the hydrogen adsorption and spillover on the ceria surface (10, 29-30) was not a determining factor in the application of the TPR method. For this purpose, we prepared a new 0.5 wt% platinum catalyst starting from platinum acetylacetonate. However, in this case, due to the lack of availability of the initial ceria-alumina support, it was necessary to prepare a new ceria-alumina sample, which required, for a better comparison, the preparation of a new 0.5 wt% platinum catalyst with hexachloroplatinic acid.

3.3.1. Influence of the platinum loading. The TPR curve for 2Pt/CeAl is compared in Fig. 5 to that of 0.5Pt/CeAl. They present the same type of evolution, but when the platinum concentration increases, the temperature of the first maximum is decreased from 678 to 573 K. This shift can be interpreted by considering that a higher Pt loading tends to decrease the PtO dispersion. Since bulk platinum oxide reduces at a much lower temperature than dispersed oxide (20), it seems normal to observe a lower reduction temperature for the highly Pt loaded solid. The accessible metallic areas measured by hydrogen chemisorption after reduction

at 573 K, respectively, 59 and 36% for the 0.5 and 2% Pt (31, 32), are in good keeping with this hypothesis.

The surfaces of CeO₂ calculated from the integration of the first TPR peak are given in Table 4. Those obtained with the PtO hypothesis are close (62 and 71 m² g⁻¹). With the

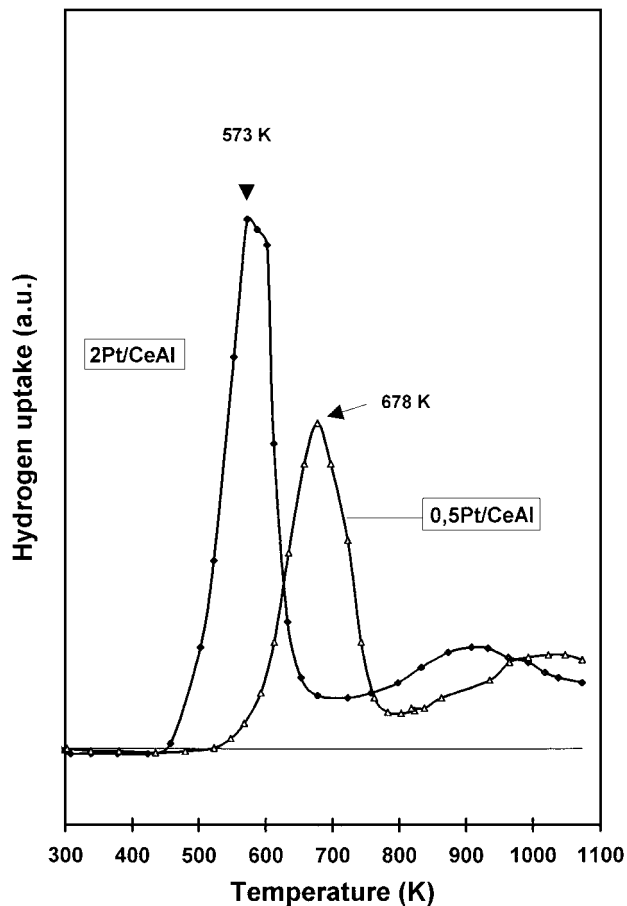


FIG. 5. Influence of platinum loading: H₂ TPR curve for 2Pt/CeAl and 0.5Pt/CeAl.

PtO₂ hypothesis, the difference between the two catalysts would be a little higher (54 and 43).

3.3.2. Influence of the platinum precursor. The TPR curves for the platinum catalysts prepared from acetylacetonate or H₂PtCl₆ are presented in Fig. 6. The main difference between the two TPR profiles is the position of the first reduction peak, 588 K for the solid from acetylacetonate instead of 676 K (with a small shoulder at 638 K) for the solid prepared from the chlorinated precursor. This difference can result from the presence of chlorine in the second case which inhibits the hydrogen spillover on the ceria surface (29–30) and consequently decreases the reduction rate. This inhibiting effect has also been evidenced by magnetic measurements which show that the hydrogen spillover phenomenon is less intense on the 0.5Pt/CeAl catalyst prepared with the chlorinated precursor than it is with acetylacetonate (33).

However, the calculated TPR surface areas (Table 5) are the same in the presence or absence of chlorine (54 and 53 m² g⁻¹, with the PtO hypothesis). This results shows that the TPR method for the calculation of the ceria surface area can be applied whatever the precursor, chlorinated or not.

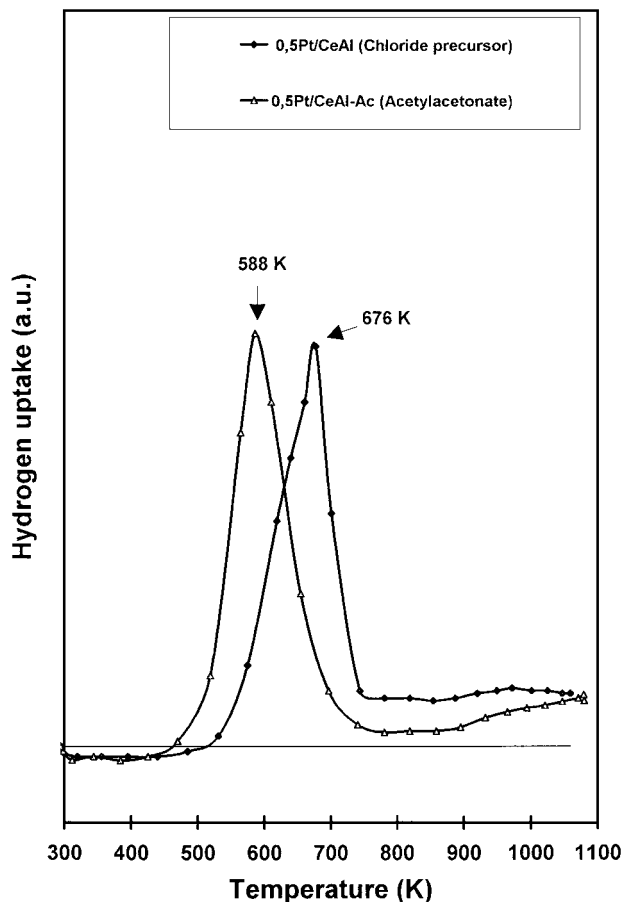


FIG. 6. Hydrogen TPR curve corresponding to 0.5Pt/CeO₂-Al₂O₃ prepared from chloride or acetylacetonate precursor.

TABLE 5

Influence of Chlorine on the Ceria Surface Areas Measured by TPR

Catalyst	Cl (wt%)	S _{BET} (m ² g ⁻¹ cat)	S _{CeO₂TPR} (m ² g ⁻¹ cat)
0.5Pt/CeAl ^a	0.44	97	54
0.5Pt/CeAl ^a -Ac	—	96	53

^a Refers to a new sample of the ceria-alumina support.

It must be noted that the two different 0.5Pt/CeAl samples prepared from chlorinated precursor present a small variation in the ceria surface (54 instead of 62 before) which has to be attributed to the different support preparations, with different BET surface areas (97 instead of 107 m² g⁻¹).

In conclusion, the presence of chlorine in the catalyst may modify the TPR profile but does not change the value of the ceria surface area calculated from the integration of the low-temperature peak. This is in agreement with the fact that, for the platinum or rhodium catalysts supported on bulk CeO₂ and prepared from chlorinated precursors, the ceria TPR surfaces were found nearly identical to the BET surface areas.

3.4. Determination of the Specific Surface Area of Alumina (FTIR/CO₂)

The adsorption of CO₂ on bulk alumina or ceria supports leads to different infrared spectra. In a preceding paper, it has been shown that these differences could be utilized to estimate the uncovered surface of alumina in mixed ceria-alumina supports through the measurement of the optical density of the hydrogenocarbonate band at 1235 cm⁻¹. This band is ascribable to the adsorption of CO₂ on the alumina surface hydroxyls (6). Thus, by determining the BET surface area, it was possible to obtain indirectly the CeO₂ surface area. We have applied this method to the present study on CeO₂-Al₂O₃ catalysts, in order to confirm the results obtained by TPR.

Nevertheless, the presence of metals and chlorine after impregnation may modify the OH density on the alumina surface. Since the measurement of the free alumina surface is based on the CO₂ adsorption on these hydroxyls, any decrease in the number of hydroxyls will result in a lower measured alumina surface, and consequently in an overestimate of the ceria surface area. Indeed, it is known that chloride ions substitute OH groups on the surface of several oxides (34). Accordingly, we have verified this point by determining the perturbations brought by the presence of chlorine on the intensity of the hydrogenocarbonate band at 1235 cm⁻¹ in order to determine the calibration coefficient on a chlorinated alumina having the same amount of chlorine as 0.5Pt/CeAl. We also tested the platinum catalyst prepared from platinum acetylacetonate to check if the method could be applied to a free chlorine catalyst.

TABLE 6

Measurement of Ceria Surface Areas by FTIR Spectroscopy of CO₂ Adsorbed Specifically on Alumina at Room Temperature: Comparison with TPR Results

Solid	Cl (wt%)	S _{BET} (m ² g ⁻¹ cat)	OD _{1235 cm⁻¹} (g ⁻¹ cat)	S _{Al₂O₃/IR} (m ² g ⁻¹ cat)	S _{CeO₂/IR} (m ² g ⁻¹ cat)	S _{CeO₂/TPR} (m ² g ⁻¹ cat)
Al	0	107	2.04	107		
CeAl ^a	0	110	0.614	32	78	84
CeAl ^b	0	97	0.513	27	70	67
0.5Pt/CeAl ^b -Ac	0	96	0.773	41	55	53
Al-Cl	0.44	107	1.63	107		
0.5Pt/CeAl ^b	0.44	97	0.397	26	71	54
2Pt/CeAl ^a		104	0.062	4.1	100	71
0.5Rh/CeAl ^a		109	0.130	8.7	100	53
1Pt0.2Rh/CeAl ^a		104	0.089	5.9	98	52

Note. The calculation of Al₂O₃ surface is based on the OD calibration coefficient determined in the absence or in the presence of chlorine.

^a and ^b Refer to two different preparations of the support.

Table 6 presents the results obtained for the two alumina supports. It shows that the presence of chlorine on the alumina surface decreases the hydroxyl population (second part of the Table 6). The resulting calibration coefficient for the optical density (OD = 0.015 m⁻² instead of 0.019 m⁻²) is decreased by almost one-fourth.

Figure 7 presents the IR spectra of CO₂, in the 1100–1800 cm⁻¹ range, for the catalysts 2Pt/CeAl, 0.5Rh/CeAl, and 1Pt0.2Rh/CeAl prepared from chlorinated precursors. After adsorption of CO₂ at room temperature, the infrared spectra show mainly the characteristic bands of carbonate type species adsorbed on the ceria surface (two wide bands at around 1590 and 1350 cm⁻¹, with more specific bands at 1615, 1580, 1460, 1350, and 1275 cm⁻¹), some frequency shifts being observed compared to bulk CeO₂ (6). Concerning the 1235 cm⁻¹ band, it appears as a shoulder with a very low intensity. The results obtained with the OD calibration coefficient of 0.015 m⁻² (presence of chlorine) are given in Table 6. It appears that the ceria surface deduced from the IR method is higher than that of the initial ceria-alumina support. It is also much higher than that calculated by the TPR method. This result would mean that ceria is more dispersed when platinum or rhodium is deposited on the support. However, compared to the support alone, these catalysts were submitted only to an impregnation followed by a treatment under nitrogen at 773 K, and, *a priori*, there is no reason to suppose a deep modification of the support surface which would have increased the coverage of alumina by ceria.

This is not observed for the catalyst prepared with the acetylacetonate precursor, 0.5Pt/CeAl-Ac. In this case, by using the OD calibration coefficient of 0.019 m⁻² (absence of chlorine) for the 1235 cm⁻¹ band, the deduced alumina surface area is 41 m² g⁻¹. Consequently, the ceria surface area obtained by the infrared method (55 m² g⁻¹) is the same as that given by TPR (53 m² g⁻¹), showing the validity of

the IR method in these conditions. Moreover, this measurement on 0.5Pt/CeAl-Ac seems to indicate that the deposit of platinum on the surface decreases the ceria accessibility, since S_{CeO₂} is lowered, from 70 m² g⁻¹ for the support to 55 m² g⁻¹ for the catalyst.

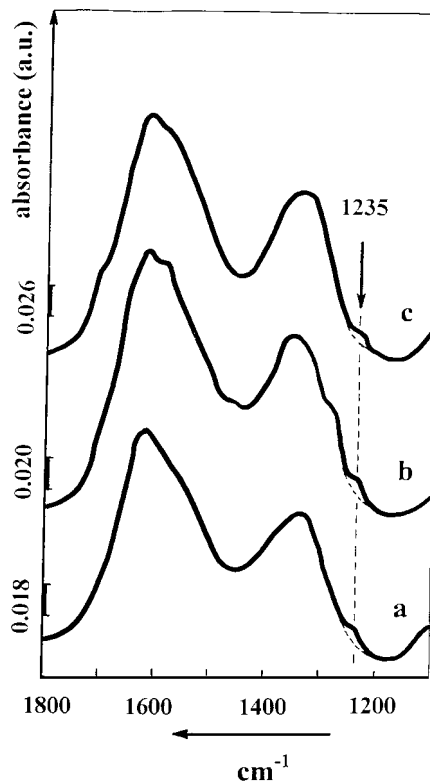


FIG. 7. FTIR spectra of CO₂ adsorption onto 2Pt/CeAl (spectrum a), 0.5Rh/CeAl (spectrum b), and 1Pt0.2Rh/CeAl (spectrum c). After the pretreatment, CO₂ (2 kPa) was introduced at 295 K for 1 h and evacuated for 30 min at 295 K.

It can be concluded that the IR method can be considered valid if the systems examined are free of chlorine. In the case of the catalysts prepared with chlorinated precursors, the OH number is decreased by the chlorine ions and it appears difficult or even impossible to modelize the resulting "precious metal–chlorine–ceria–alumina" surface in order to determine the corresponding calibration coefficient.

4. DISCUSSION

The validity of the results presented in Table 6 needs further discussion. Concerning the first part of the table related to solids without chlorine, both techniques, although completely independent, give identical results. On the contrary, in the case of the catalysts containing chlorine (second part of the table), the results are not so consistent.

For TPR, an error could result from the estimation of the hydrogen quantity required for reducing the oxidized precious metal. However, if we exclude the case of 2Pt/CeAl, the obtained ceria surface is practically constant for all the catalysts, whether based on rhodium which has a well-defined oxidation degree or on platinum, for which the mean oxidation state is more questionable. Thus, we can consider that this method gives reliable and reproducible results.

The IR method suggests an apparent increase in the ceria surface area, whereas there is no evidence of such an effect. We have interpreted this increase by a perturbation of the infrared measurement due to the presence of chlorine on the support surface which modifies the alumina hydroxyl population. This interpretation was supported by the measurements made on a platinum catalyst prepared from an acetylacetonate which show that the ceria surface area was the same with the two methods: 55 m² g⁻¹ by TPR and 53 m² g⁻¹ by IR.

Assuming that the TPR method gives valid results, it remains to be understood why the measured ceria surface

is lower after impregnation. Compared to the initial support, for which S_{CeO_2} is almost 70–80 m² g⁻¹, the ceria surface area is close to 50–55 m² g⁻¹ in the impregnated catalysts. In the absence of an absolute measurement, it is difficult to ascertain the precise value of this surface. An approximate calculation of the area occupied by the precious metal atoms indicates that the metallic area is only 1 or 2 m² g⁻¹ catalyst. Thus, a coverage of ceria by the metal cannot explain this difference. Besides, it can be remarked that for the highly loaded 2 wt% platinum solid, the ceria surface is 71 m² g⁻¹, a value closer to the initial value of 84 m² g⁻¹.

A closer examination of the results can lead to a more interesting explanation. The TPR calculation was based on the integration of the first peak, corresponding to the reduction of both the precious metal and the ceria surface. By this scheme, it was implicitly assumed that the precious metal is in contact with ceria, so that the hydrogen spillover can occur from the metal onto the ceria and facilitates the reduction of the ceria surface at low temperature. If the impregnation has left some ceria zones free of metals, we can easily deduce that the corresponding ceria will not be reduced at a low temperature simultaneously to the metal but only at a higher temperature, i.e., at around 870 K as it is for the support alone. Indeed, we have reexamined on the TPR profiles the drift observed after the first peak and before the bulk reduction. For all the catalysts prepared on ceria–alumina, it is constituted by a small curvature or a flat zone in the region 750–850 K followed by an increase in the slope of the trace (Fig. 3). The corresponding hydrogen uptake could be considered as due to the reduction of the ceria surface not in contact with precious metals. Although the deconvolution is very imprecise and sometimes a little arbitrary, we have calculated for each system this contribution to the total ceria surface area. The results are given in Table 7 where $S_{\text{CeO}_2\text{TPR}^1}$ refers to the ceria surface zones in contact with a precious metal and $S_{\text{CeO}_2\text{TPR}^2}$ corresponds

TABLE 7

Measurement of the Different Ceria Surface Areas Obtained by TPR: Comparison with IR Results

Solid	S_{BET} (m ² g ⁻¹ cat)	$S_{\text{CeO}_2\text{TPR}^1}$ (m ² g ⁻¹ cat)	$S_{\text{CeO}_2\text{TPR}^2}$ (m ² g ⁻¹ cat)	$S_{\text{CeO}_2\text{TPR}^3}$ (m ² g ⁻¹ cat)	$S_{\text{CeO}_2\text{IR}}$ (m ² g ⁻¹ cat)
CeAl ^a	110		84	84	78
0.5Pt/CeAl ^a	107	62	6	68	
0.5Rh/CeAl ^a	109	53	23	76	100
1Pt0.2Rh/CeAl ^a	104	52	31	83	98
2Pt/CeAl ^a	104	71	18	89	100
CeAl ^b	97		67	67	70
0.5Pt/CeAl ^b	97	54	11	65	71
0.5Pt/CeAl ^b -Ac	96	53	7	60	55

Note. TPR¹ refers to the ceria surface zones in contact with a precious metal. TPR² refers to the ceria surface zones without precious metal. TPR³ is the sum of $S_{\text{CeO}_2\text{TPR}^1} + S_{\text{CeO}_2\text{TPR}^2}$.

^a and ^b Refer to two different preparations of the ceria–alumina support.

to the ceria surface zones without precious metal. Thus, $S_{\text{CeO}_2\text{TPR}^3}$ is the sum of $S_{\text{CeO}_2\text{TPR}^1} + S_{\text{CeO}_2\text{TPR}^2}$.

It becomes clear from Table 7 that the values are now much closer to that of the support alone. In other words, by taking into account all the ceria surfaces, whether or not in contact with a precious metal, the initial ceria surface of the support is recovered. We can conclude that the impregnation process was not uniform and that some parts of the support were not covered by the metal precursor.

5. CONCLUSION

The measurement of ceria surface areas of model platinum and/or rhodium catalysts supported on a ceria-alumina support has been realized by two independent methods: the exploitation of the hydrogen TPR curves and that of the 1235 cm⁻¹ infrared band resulting from the adsorption of CO₂ on the alumina surface hydroxyls.

The IR method can be considered to give reliable results for systems free of chlorine, which allows to use the calibration coefficient determined previously on the alumina support. When the catalysts are prepared with chlorinated precursors, which is the case of most of the three-way catalysts, the OH population is decreased by the chlorine ions adsorbed on the alumina surface. Under these conditions, the number of hydrogenocarbonate species created by CO₂ adsorption is also decreased which prevents a correct measurement of the free alumina surface, and then of the ceria surface area.

On the other hand, the TPR method gives more reliable results independent of the preparation conditions, in particular the nature of the precursor. A careful quantitative study of the TPR profiles can provide the total accessible ceria surface area and determine the ceria surface in contact or not with precious metal. For the catalysts of this study, the results show a rather good agreement between the initial ceria surface area of the support and that calculated after impregnation. It is deduced that TPR methods can constitute an excellent tool for studying the surface chemical state of three-way catalysts. The FTIR spectroscopy can also contribute to the understanding of that surface provided that the OH population is not too modified by the preparation and the following treatments. In a later paper, these two methods will be applied to the case of the same systems submitted to high-temperature treatments, in order to follow the evolution of the ceria surface and to better understand the catalysts aging processes.

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