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Magnetic study of the interaction of hydrogen with a $Pt/CeO_2–Al_2O_3$ catalyst: influence of the presence of chlorine

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Abstract

The influence of a chlorinated precursor on the redox properties of ceria was studied by comparing two $Pt/CeO_2–Al_2O_3$ catalysts prepared from hexachloroplatinic acid and platinum acetylacetonate. In absence of chlorine, a dispersion value higher than 100% has been measured by irreversible hydrogen chemisorption. To interpret this result, the interaction of H_2 with the support and the two catalysts were studied by magnetic measurements. The variations of the Ce^{3+} content have given evidence that different redox processes may occur. The hydrogen spillover is clearly observed in presence of platinum with the phenomenon being more pronounced for the ex-acetylacetonate catalyst. The limited amount of hydrogen irreversibly adsorbed at 294 K on the support for this free chlorine reduced catalyst is sufficient to explain the excessive value obtained for the platinum dispersion. The results show a fixation of chlorine on the supported ceria phase which inhibits the mobility of hydroxyl species responsible for the hydrogen spillover. Moreover, independently to the presence of chlorine, a reduction at 573 K seems to stabilise a significant fraction of Ce^{3+} ions against reoxidation under air at room temperature. This was not the case for bulk ceria and probably originates from ceria/alumina interactions occurring after reduction.

Keywords: Ceria–alumina; Platinum catalyst; Reduction by H_2; Magnetic study; Ceria redox properties; Influence of chlorine; Cerium aluminate

1. Introduction

In the case of metallic catalysts supported on silica or alumina, the dispersion of the metallic phase is classically measured by hydrogen chemisorption. Usually, the stoichiometry of the adsorption is assumed to be one hydrogen atom for one surface metallic atom. However, in the case of metal supported on ceria, it has been observed that the support is able to chemisorb large amounts of hydrogen via a spillover phenomenon. For example, Bernal et al. [1] have found that adsorption of H_2 at 294 K on a 2.9 wt%Rh/CeO_2 corresponds to a H/M_{total} ratio of 4. Similarly, Bensalem et al. [2] found a value of 3 for H/M_{total} after H_2 adsorption at 373 K on a 1.6 wt%Pd/CeO_2. Such H/M_{total} values must be associated with the migration of hydrogen from the metal on the support surface [3,4]. It is accompanied by a change of a part of the cerium ions from the 4+ to the 3+

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state, this reduction process being easily monitored by magnetic measurements [2,5–7].

With Rh/CeO_2 catalysts, we have previously shown that the ceria redox behaviour could be modified by the presence of residual chlorine ions at the surface. This was interpreted as due to the substitution of lattice oxygen ions by chlorine coming from the precursor, which limits the migration of the hydrogen species on the support [8]. This effect is certainly favourable when measuring the dispersion of the metallic phase by hydrogen adsorption. Indeed, in the case of platinum supported on ceria–alumina and prepared from chlorinated precursors, the dispersion has been found the same as that obtained from FTIR spectroscopy of CO adsorbed on metallic platinum [9]. However, we have also shown for these $Pt/CeO_2–Al_2O_3$ catalysts that, during a TPR/H_2, the reduction of the ceria surface starts at lower temperature in absence than in presence of residual chlorine [10]. Again, this is probably due to higher mobility of hydrogen in absence of chlorine. If it is the case, it may be important to determine to what extent the intervention of hydrogen spillover may modify the determination of the metallic accessible area in chlorine free catalysts. In this respect, the use of magnetic measurements to monitor the Ce^{4+} content changes during hydrogen adsorption is highly valuable. Therefore, the purpose of this work is to extend the results obtained on metal ceria catalysts to a platinum catalyst deposited on a ceria–alumina support. By the way, we want to examine the modifications brought in the redox processes by the presence of alumina and the influence of chlorinated precursor on the hydrogen chemisorption in such systems.

2. Experimental

The ceria–alumina support was prepared by three successive graftings of cerium acetylacetonate on the hydroxyl groups of an alumina (Rhône-Poulenc-SCM 129) and further calcination at 673 K. The final content in CeO_2 was 23.2%. The specific surface area (SSA) was 97 $m^2\,g^{-1}$ and the ceria surface area measured from TPR/H_2 results was 67 $m^2\,g^{-1}$ [10].

Two $Pt/CeO_2–Al_2O_3$ catalysts were prepared. The first one, referenced Pt/CeAl–Cl was obtained by impregnating alumina during 30 min with an aqueous solution of H_2PtCl_6 and drying, first under vacuum at 320 K in a rotary evaporator and then under air at 380 K for one night. The solid was then calcined under a flow of nitrogen at 773 K for 2 h. After this treatment, it contains 0.42 wt% Pt and 0.44 wt% Cl. The corresponding Cl/Pt atomic ratio is 5.76 instead of 6 for H_2PtCl_6, meaning that practically all the chlorine ions are still present in the catalyst after calcination at 773 K. For the second solid, prepared in absence of chlorine, Pt/CeAl–acac, the impregnation was realised with a solution of platinum acetylacetonate in toluene at 343 K. After two successive dryings under vacuum at 310 and 370 K, the solid was calcined under air at 673 K for 2 h. The platinum content was 0.49 wt%. The SSA of the two catalysts remained unchanged for both solids compared to the support.

The platinum accessible area was measured by hydrogen chemisorption in static conditions, at room temperature in a volumetric apparatus. The total and reversible hydrogen adsorption isotherms were determined in order to determine HC_{irr}, the irreversible hydrogen uptake. Before the adsorption measurements, the sample was first evacuated for 1 h at 723 K (heating ramp=7 K min^{-1}), then reduced for 1 h at 573 K under 2.7 kPa H_2 static pressure and evacuated again, always at 573 K. This protocol was repeated once more in order to eliminate the water produced by the reduction and finally a third reduction was performed for one night and followed by an evacuation at the same temperature for 2 h.

The platinum dispersion was also measured by FTIR spectroscopy using CO as a probe molecule, according to a method already described [11]. The IR spectra were recorded on self supported wafers using a Nicolet spectrometer (MAGNA 550). The pretreatment was identical to that applied for H_2 chemisorption, except the final evacuation temperature set at 723 K. The CO adsorption was carried out at room temperature under 2.7 kPa CO. The spectra under consideration were obtained after evacuation for 1 h at 298 K.

In order to determine the Ce^{3+} content, magnetic susceptibility measurements were carried out with a Faraday microbalance. The paramagnetic susceptibility was determined at room temperature and calculated by extrapolation at infinite field [12]. The corresponding reduction percentages were calculated assuming a 100% reduction for the Ce_2O_3 phase and

using the Curie–Weiss law determined for this solid by Sata and Yoshimura [13], i.e. $\chi=4.44\times10^{-3}/(T+90)$, expressed in e.m.u. CGS g^{-1} (to be multiplied by 12.56×10^{-3} to obtain the SI units). The reduction experiments were performed with 200 mg under a flow of hydrogen (30 cm^3 min^{-1}). After introduction of H_2 at 298 K, the sample was heated to 573 K for 2 h, then left for 12 h at this temperature, evacuated for 2 h always at 573 K before cooling to room temperature.

3. Results

3.1. Accessible metallic area by hydrogen chemisorption and FTIR spectroscopy of adsorbed CO

The accessible metallic area H/M was measured by hydrogen chemisorption for the two catalysts, by extrapolation to zero pressure of the two linear portions of the isotherm in the 0–1.5 kPa pressure. From HC_{irr} and assuming a stoichiometry of one hydrogen atom per platinum surface metal atom, the obtained H/M values for Pt/CeAl–Cl and Pt/CeAl–acac are 0.73 and 1.20, respectively. Though the metal dispersion of the first solid is quite reasonable for a 0.5% Pt loading, that measured for the catalyst prepared from the acac precursor is problematic if one assumes that there is no reason to change the stoichiometry adopted for platinum.

We have verified these dispersion values by measuring with FTIR spectroscopy the absorbance of the νCO band corresponding to CO linearly adsorbed on the platinum surface atoms. It is situated at 2071 and 2058 cm^{-1} for Pt/CeAl–Cl and Pt/CeAl–acac, respectively. The position given in literature for platinum on alumina or silica is usually in the range of 2075–2067 [11,14–16]. In the presence of a basic support as magnesia, the band shifts down to about 2060 cm^{-1} [11] and in the case of platinum on ceria, it was observed at a much lower wave number at 2030 cm^{-1} [17]. In line with these observations, the wave number observed for Pt/CeAl–acac (2058 cm^{-1}) appears a little low compared to Pt/alumina and can be attributed to a donor effect of the basic sites of ceria. However, in presence of chlorine which is an electroacceptor ligand and is known to decrease the back donation of the metal d electrons towards the $2\pi^*$ orbitals of CO bound to platinum, the effect of the support seems to be compensated and the band is shifted to a higher wave number at 2071 cm^{-1}. The bridged CO band observed at about 1850 cm^{-1} is not considered in the method but may account for a few percents of the total adsorbed CO. The metal accessible area values calculated by this method are given in Table 1. The dispersion value is confirmed for Pt/CeAl–Cl, although a little lower, in agreement with previous observations [18]. However, the dispersion measured for Pt/CeAl–acac is now 52%, value which can be considered as more reasonable. It can be concluded that the higher dispersion obtained from hydrogen adsorption must originate from a participation of the ceria to the chemisorption process. To precise this phenomenon, we have carried out the same type of measurements in a Faraday microbalance and have followed the parallel Ce^{3+} content variations.

Table 1
Accessible metallic area expressed as H/M dispersion (%)

	Dispersion	
	Pt/CeAl–Cl	Pt/CeAl–acac
HC_{irr} static volumetry	73	>100 (120)
FTIR of adsorbed CO	62	52

3.2. Magnetic study of the interactions of the reduced catalysts with hydrogen

The variations of the oxidation state of ceria were followed by magnetism on the two catalysts and the support alone during the different steps of the chemisorption process. In the initial state, there was practically no measurable Ce^{3+} content in the samples. After treatment under vacuum at 723 K and reduction under hydrogen flow at 573 K for 12 h, the magnetic susceptibility was measured at 573 K, first under hydrogen pressure and then after 2 h treatment under vacuum. The calculated reduction percentages, expressed as the fraction of the cerium ions under Ce^{3+} state $[Ce^{3+}/(Ce^{3+}+Ce^{4+})]$ are given in Table 2.

The first observation is the high reduction extent observed after reduction at 573 K in the case of the ceria–alumina support, 50%, compared to about 9% in

Table 2
Reduction percentages expressed as $[Ce^{3+}/(Ce^{3+}+Ce^{4+})]$ of Pt/CeAl–Cl and Pt/CeAl–acac catalysts and CeAl support after reduction under H_2 and evacuation at 573 K

	H_2, 573 K	Vacuum, 573 K
CeAl	48 (47)	50 (48)
Pt/CeAl–Cl	72 (75)	56 (52)
Pt/CeAl–acac	53 (54)	37 (37)

The values between parenthesis were obtained after reoxidation at room temperature and a second treatment under hydrogen at 573 K.

Table 3
Reduction percentages expressed as $[Ce^{3+}/(Ce^{3+}+Ce^{4+})]$ of Pt/CeAl–Cl and Pt/CeAl–acac catalysts and CeAl support (adsorption of 2.7 kPa H_2 at 294 K after reduction under H_2 and evacuation at 573 K)

	Vacuum, 294 K	H_2, 294 K	Vacuum, 294 K
CeAl	52	51	53
Pt/CeAl–Cl	51	51	51
Pt/CeAl–acac	39.5	42	42

the case of pure ceria sample having a SSA of 49 $m^2\,g^{-1}$ [8]. In this latter case, the percentage corresponded approximately to the reduction of the cerium ions on the surface. The high reduction value for the CeAl support indicates that the ceria is well dispersed on alumina. Following the theoretical model of Johnson and Mooi [19,20] or the experimental results obtained by magnetism on various ceria samples [6], the corresponding SSA would be 269 or 309 $m^2\,g^{-1}$ of ceria, respectively. These values are in agreement with the TPR results obtained with this support, which gave a ceria surface of 67 $m^2\,g^{-1}$ of catalyst, i.e. 289 $m^2\,g^{-1}$ of ceria [10]. Thus, both magnetic and TPR results agree on the idea that as for ceria alone, a complete reduction of the ceria surface occurs in the ceria–alumina support, before that of the bulk.

The reduction percentage is not very different for Pt/CeAl–acac, 53% instead of 50% for the support alone. Thus, the presence of metallic platinum does not significantly increase the reduction percentage, which seems normal, if one considers that, at 573 K, the reduction remains limited to the surface. However, the reduction extent is much higher for Pt/CeAl–Cl, 72%, compared to 53% Pt/CeAl–acac, i.e. a 19% Ce^{3+} difference. A similar increase was observed in Rh/CeO_2 catalysts, for which a reduction treatment at 623 K induced 22.1% and 11.4% reduction for the solids prepared with chloride or nitrate precursor, respectively [8]. It was attributed to the substitution of lattice oxygen ions by chlorine. The same explanation can be proposed in the present study.

For the two Pt/CeAl solids, part of the Ce^{3+} is reoxidised by evacuation under vacuum. This is due to the hydrogen back spillover from the support through the platinum metallic particles, as previously established with ceria as support. The important facts to be noted here are that: (i) the spillover occurs at 573 K with almost the same extent in presence or in absence of chlorine and that: (ii) it is perfectly reversible as evidenced by the second series of measurements (Table 2, values between parenthesis). In the case of rhodium ceria catalysts, there was no hydrogen spillover at 623 K in presence of chlorine, whereas it was observed for the catalyst prepared with a nitrate precursor, i.e. in absence of chlorine.

We have studied the influence of temperature and performed the same measurements at 294 K on the samples pretreated at 573 K under hydrogen. As shown in Table 3, the sequence ''vacuum–hydrogen (2.7 kPa)–vacuum'' induces no change in the reduction percentage of ceria on Pt/CeAl–Cl, meaning that there is no hydrogen spillover at room temperature on this catalyst. The 2–3% increase observed in the Ce^{3+} content for the catalyst prepared from $Pt(acac)_2$ is close to the error limit but the increase is significant. Although there is almost no spillover onto the support, the dispersion measurement method through hydrogen chemisorption is not validated for all that. Indeed, it must be noticed that a 2% variation in the Ce^{3+} content is equivalent to 13.5 μmol H_2 per g of catalyst, which corresponds to 107% dispersion for a 0.49 wt% Pt loading. Thus, this slight excess of hydrogen adsorbed on the support may explain alone the dispersion value of 120% observed for Pt/CeAl–acac. The fact that after desorption at room temperature, there is no variation in the Ce^{3+} content (42%) indicates the irreversible character of this adsorption on the support. Consequently, the metal dispersion measured by volumetry includes evidently some quantity of hydrogen adsorbed on the support. In these conditions, the platinum dispersion measured by the infrared method of adsorbed CO must be considered as a more reliable measurement.

In conclusion, the platinum catalysts prepared on a ceria–alumina support behave similarly to those prepared on ceria. However, a high reversibility of hydrogen adsorption is observed at 573 K which corresponds to the hydrogen spillover on the ceria support. This spillover at 573 K appears independent on the chlorine content but is a function of temperature. At room temperature, on a catalyst reduced and evacuated at 573 K, there is no spillover observed when chlorine is present on the surface. On the other hand, hydrogen adsorption on the support is evidenced on a free chlorine reduced catalyst, with a very limited extent which however is sufficient to induce an important error on the measured value of the metal dispersion.

3.3. Magnetic study of the interactions of the reoxidised catalysts with hydrogen

The reversibility of the hydrogen adsorbed on the support is the best evidenced on oxidised ceria surface [1–3]. Therefore, to study more deeply the influence of chlorine, we have investigated the reversibility of the hydrogen chemisorption on the same sample after a new reduction at 573 K under hydrogen and a reoxidation at room temperature under 2.7 kPa of oxygen. Then, after evacuation at room temperature, hydrogen was adsorbed (2.7 kPa) and the sample was evacuated again as above. The results are given in Table 4.

Contrary to the case of ceria–metal catalysts, the complete reoxidation of the ceria was not observed in the present study. After introduction of oxygen at 294 K, the ceria reduction percentage in the catalyst ex-chlorinated precursor is still 32%, and that of the ex-acac catalyst is about 21%, value which is almost that of the support. Thus, the reduction at 573 K has created a high percentage (≈20%) of Ce^{3+} ions which are stable against reoxidation at room temperature.

Table 4
Reduction percentages expressed as $[Ce^{3+}/(Ce^{3+}+Ce^{4+})]$ of Pt/CeAl–Cl and Pt/CeAl–acac catalysts and CeAl support (adsorption of H_2 (2.7 kPa) was performed at 294 K on the catalysts reoxidised at room temperature)

	Vacuum	O_2	Vacuum	H_2	Vacuum
CeAl	50	20	22	21	22
Pt/CeAl–Cl	51	32	31	35	36
Pt/CeAl–acac	39	21	20.5	35	34.5

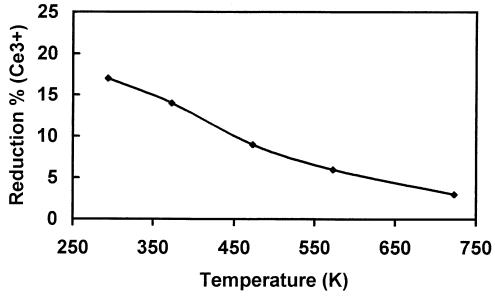

Fig. 1. Evolution of the reduction percentage of the ceria–alumina during reoxidation. The support was prereduced for 12 h at 573 K under hydrogen. It was then heated for 15 min under 2.7 kPa O_2 at each temperature.

Moreover, the Ce^{3+} ions associated with chlorine are also stable, since there remains always a 10% difference between the two catalysts, as it was observed for the first hydrogen adsorption at room temperature.

As discussed below, these 20% Ce^{3+} ions, stable towards oxygen, could be located at the interface between alumina and ceria. To precise if they can be reoxidised at higher temperature, the support reoxidised at room temperature was heated under 2.7 kPa oxygen for 15 min at different temperatures up to 723 K. The results are given in Fig. 1. The reoxidation is activated. At 473 K, the residual Ce^{3+} percentage in the support is still 9%. The reoxidation is not fully complete at 723 K (3% Ce^{3+}).

On the catalysts reoxidised at 294 K, the subsequent hydrogen adsorption, always at 294 K, shows no variation of the reduction percentage for the support alone, whereas the presence of platinum induces the expected spillover phenomenon. Indeed, for Pt/CeAl–acac, the reduction extent increases from 20.5% to 35% when it is put in contact with hydrogen. For Pt/CeAl–Cl, the variation is more limited, from 31% to 35%. For the two catalysts, there is no change in the reduction extent after evacuation at room temperature, which means that there is no reversibility of the hydrogen adsorbed in those conditions.

4. Discussion

4.1. Reliability of the platinum dispersion measurements

The magnetic results have shown that a limited amount of hydrogen can be irreversibly adsorbed at

294 K on the supported ceria phase in the case of the free chlorine catalyst. This amount is sufficient to explain the excessive values obtained for the platinum dispersion. Therefore, it was stated that the FTIR method based on CO chemisorption could be considered as more reliable for determining the metal dispersion. This point needs some further discussion. Indeed, it must be remarked that after reduction and evacuation at 573 K, the ceria is highly reduced (37% for Pt/CeAl–acac and 56% for Pt/CeAl–Cl). One may ask if such a high reduction percentage can modify the chemisorption capability of the metal, and hence the measurement of the metal dispersion, through the occurrence of strong interactions between platinum and the reduced CeO_{2-x} phase. For example, in the case of Pt/CeO_2 catalysts, it was shown that increasing the reduction temperature from 473 to 973 K disturbed their chemical properties in a progressive way and that, in addition, the reduction at 973 K induced a covering of the metal by the reduced support [21]. In the present study, the hypothesis of a metal decoration effect can be rejected because the reduction temperature is much too low and also because not more than one layer of the ceria phase has been reduced. Concerning the possible electronic effects occurring between the platinum and the reduced ceria surface, they are certainly involved in the surface chemistry. However, their influence on the platinum chemisorption behaviour is probably limited if we consider, from the FTIR data, that the wave numbers observed for the linearly adsorbed CO band are nearly those observed usually when platinum is supported on alumina or silica. Consequently, in absence of other proved method, the use of FTIR for measuring the CO chemisorbed on platinum remains very convenient for determining the metal dispersion.

4.2. *Influence of residual chlorine*

Chemical analysis has shown that almost all the chlorine introduced during the preparation of Pt/CeAl–Cl catalyst remains fixed on the support. Bernal et al. [8] have reported that chlorine remained trapped even if a Rh/CeO_2 catalyst was heated at 1173 K under hydrogen. However, most of chlorine ions were eliminated by heating the catalyst under oxygen at 773 K. It results that, in our conditions, the calcination carried out on the chlorinated catalyst and the pretreatment before reduction at 573 K appear insufficient to remove the chlorine species from the solid.

One of the consequences of the residual chlorine is the decrease of the hydrogen chemisorption by ceria of the support. This inhibiting effect has already been observed on pure ceria. It is found again in this study, since the hydrogen spillover is much less important at room temperature on the reoxidised surface of Pt/CeAl–Cl than on Pt/CeAl–acac. In fact, chloride may substitute to oxygen ions in the ceria lattice during the reduction under H_2. By the way, there are less sites able to chemisorb hydrogen leading to the formation of hydroxyl species on the surface and the hydrogen spillover is strongly inhibited. This process being activated, when the temperature of the adsorption is increased, spillover is again observed, which explains that the same variation in the Ce^{3+} percentage occurs at 573 K when evacuating both catalysts. It must be also noted that, probably due to the high dispersion of ceria in the present case, the chlorine ions cannot substitute all the surface oxygen ions and consequently are unable to suppress totally the hydrogen spillover.

The formation of CeOCl species to explain these results is quite reasonable. Le Normand et al. [22] have shown by XRD and XPS studies that ceria surface can react with chlorine to form CeOCl or $Ce(OH)_2Cl$ phases in Pd/CeAl catalysts prepared from a $Pd(NH_3)_4Cl_2$ precursor. Similarly, the CeOCl phase was evidenced by XRD by Kepinski et al. [23] in Pd/CeO_2 catalysts. However, in our case, XRD analysis did not detect traces of this phase. This is probably due to the poorly crystallised state and the low content of this supposed phase. Indeed, after reduction at 573 K and cooling to room temperature, the difference in the Ce^{3+} percentage between the two platinum catalysts which could be related to CeOCl content is about 10%, which represents only 2–3% of CeOCl per g of catalyst, hardly detectable by XRD analysis, specially when they are present as a thin bidimensional surface layer. It is noteworthy that chemical analysis gives a Cl/Ce atomic ratio of 9.2% which is of the same order as the value of 10% Ce^{3+} associated with CeOCl. This would mean that each chlorine ion initially present in the catalyst is associated with one cerium ion after reduction, supporting the model of a complete substitution of lattice O^{2-} by Cl^-. However, the mechanisms are probably more complex insofar as they have

to take into account the difference observed at 573 K in the Ce^{3+} content between the Pt/CeAl–Cl and Pt/CeAl–acac. Indeed, this difference is almost two times higher than at 294 K (19% instead of about 10% as seen in Tables 2 and 3) and has no clear interpretation.

4.3. Role of alumina in the redox processes

In addition to the existence of stabilised Ce^{3+} species in the form of CeOCl, the magnetic results support the formation during the reduction process of other Ce^{3+} ions, stable at room temperature against reoxidation by oxygen. They are not ascribable to the presence of either platinum or chloride since the support behaves similarly. In fact, when the latter is put, after reduction at 573 K, into contact with O_2 at 294 K, about 20% of Ce^{3+} are still present. This percentage is similar for the catalyst prepared from $Pt(acac)_2$ and slightly higher (∼30%) when the platinum precursor is chlorinated, this increase being ascribed to the presence of CeOCl. Since these stable Ce^{3+} ions are not observed with pure ceria, their formation must be related to the presence of alumina. Several authors have deduced by XPS or XRD analysis the formation of the $CeAlO_3$ phase after reducing treatments on ceria–alumina supports in presence or not of Pt or Pd [24–27]. As suggested by Humbert et al. [28], the nucleation of $CeAlO_3$ occurs by the diffusion of Al^{3+} ions in the partially reduced CeO_2 lattice. The small size of Al^{3+} compared to Ce^{3+} (ionic radius=51 and 128 pm, respectively [29]) makes the diffusion easy. However, the incorporation of Ce^{3+} ions in the vacant positions of alumina lattice is also quite possible. Moreover, according to a model proposed by Humbert et al. [28] the geometrical arrangement between the three structures of CeO_2, $CeAlO_3$ and transition Al_2O_3 favours the formation of cerium aluminate at the interface. In this study, since the ceria is well dispersed on Al_2O_3, the reduction presumably creates a great number of Ce^{3+} ions at the interface with alumina. However, we have no direct evidence of the formation of this $CeAlO_3$ phase. In fact, the XRD analysis can hardly give a clear answer due to the poor crystallisation of the solids and the low concentration of this hypothetical phase. Moreover, the observation of $CeAlO_3$ seems to require much higher temperature, if one considers that Humbert et al. [28] could detect it in a Pt–Rh/CeO_2–Al_2O_3 catalyst submitted to different redox cycles at 1223 and 1323 K, but not after the same cycles at 1123 K. Shyu et al. [24] also mention that, due to diffusional limitations, prolonged heating in H_2 at 870 K or higher temperature are necessary to lead to a solid solution which eventually forms $CeAlO_3$. Thus, it is logical that after reduction at only 573 K this phase could not be observed. However, it is clear from the magnetic results that this mild reducing treatment is sufficient to stabilise a significant fraction of the Ce^{3+} ions at the interface between reduced ceria and alumina. These new entities show a good stability against reoxidation at room temperature.

4.4. Reactions occurring during the interaction of H_2 with the Pt/CeO_2–Al_2O_3 catalysts

Thus it appears that the description of the redox properties of ceria in these platinum catalysts is rather complex. To summarise, there are four different types of Ce^{3+} species which can be deduced from the magnetic study. Their formation and their reactivity may be described according to the following set of reactions:

$$2Ce^{4+} + 2O^{2-} + H_2 \Leftrightarrow 2Ce^{3+} + 2OH^- \quad (1)$$

$$2Ce^{3+} + 2OH^- \Rightarrow 2Ce^{3+} + V_O + H_2O + O^{2-} \quad (2)$$

$$2Ce^{4+} + 2O^{2-} + (Cl^-)_{Pt} + H_2 \Rightarrow 2Ce^{3+} + (Cl^-)_{Ce} + H_2O + O^{2-} \quad (3)$$

$$(Ce^{3+})_{Ce} + (Al^{3+})_{Al} \Rightarrow [(Ce^{3+})_{Al} + (Al^{3+})_{Ce}] \quad (4)$$

where V_O is an oxygen vacancy, $(Cl^-)_{Pt}$ and $(Cl^-)_{Ce}$ are chlorine ions associated with platinum and cerium and $(Ce^{3+})_{Al}$, $(Ce^{3+})_{Ce}$, $(Al^{3+})_{Al}$ and $(Al^{3+})_{Ce}$ are cerium or aluminium ions in interaction with aluminium or cerium.

Reaction (1) occurs at low and moderate temperature in presence of platinum and is reversible. This means that upon evacuation, hydrogen can be desorbed which leads to the reoxidation of the Ce^{3+} ions. For this reaction, the presence of platinum is necessary as it is shown by comparing the variations of the reduction percentages obtained for CeAl and Pt/CeAl. Thus, for the support and the Pt/CeAl–acac catalyst, under hydrogen at 573 K, the reduction percentages are close (48% and 53%) and correspond approximately to the reduction of all the surface cerium ions.

However, they differ notably after evacuation at the same temperature, 50% instead of 48% for the support, but only 37% instead of 53% for Pt/CeAl–acac. For the CeAl support, the hydrogen chemisorbed under the form of hydroxyl groups has been desorbed according to reaction (2). This process is irreversible and corresponds to the elimination of oxygen ions through water formation. This is the main reaction path for the support alone. For the Pt/CeAl–acac catalyst, the reversibility of reaction (1) partly restores, on the surface, the association of Ce^{4+} and O^{2-} species which are susceptible to adsorb again some hydrogen. The extent of this reversibility is large at 573 K, even for the Pt/CeAl–Cl catalyst, for which the reduction percentage decreases from 72% to 56% by evacuation. This means that chlorine ions do not constitute impassable barriers for the hydrogen spillover on a well reduced surface provided that the temperature is high enough to allow hopping of the adsorbed hydrogen.

At room temperature, the spillover is very limited or even non-existent on these catalysts prereduced at 573 K. In the case of Pt/CeAl–acac, some hydrogen adsorbed on platinum can be transferred at 294 K on the reduced support but not desorbed. This slight adsorption explains the excessive dispersion measurement determined in this case. It is not observed, when the reduced surface contains chlorine ions. It can be thought, that chlorine ions remain localised in the vicinity of the platinum particles which stops totally the migration of hydrogen on the reduced ceria surface.

After reoxidation at room temperature, there is again a great number of oxygen sites available and the hydrogen chemisorption occurs very easily according to reaction (1).

The initial oxidation state of ceria can be restored by oxygen chemisorption which has been found to occur at room temperature according to the following reaction:

$$2Ce^{3+} + V_O + O^{2-} + 1/2\,O_2 \Rightarrow 2Ce^{4+} + 2O^{2-} \quad (5)$$

In competition with reaction (2) and the reverse of reaction (1), the reaction (3) is specific of the presence of chlorine in the catalyst. In spite of a lack of experimental evidences, it is proposed to account for the substitution of lattice oxygen by chlorine. This reaction seems to require the presence of hydrogen, since no Ce^{3+} was evidenced after the initial calcination at 773 K under nitrogen. The existence of chlorine ions in the ceria surface modifies all the surface equilibrium, and in particular, the reversible reduction (1), because it inhibits the formation of hydroxyl species. Moreover, the reoxidation of the Ce species associated with chlorine (reaction (6)) is not effective at room temperature. This is deduced from the higher residual Ce^{3+} percentage in the Pt/CeAl–Cl put in contact with oxygen at 294 K (30%), compared to those obtained with Pt/CeAl–acac and the support alone (20%). As shown previously with a Rh/CeO_2 solid [8], a treatment under oxygen at 773 K is necessary to eliminate most of the chlorine trapped initially.

$$2Ce^{3+} + (Cl^-)_{Ce} + O^{2-} + 1/2\,O_2 \Rightarrow 2Ce^{4+} + 2O^{2-} + Cl^- \quad (6)$$

When introducing hydrogen on a sample reoxidised at room temperature, there is a great increase of the Ce^{3+} percentage for Pt/CeAl–acac (from 20.5% to 35%) whereas for Pt/CeAl-Cl, the increase is low (from 31% to 35%). The fact that the variation of the reduction extent is higher for the solid free of chlorine illustrates very well that the chlorine ions on the surface inhibit the hydrogen spillover onto the ceria surface.

Finally, the formation of Ce^{3+} ions stabilised at the interface between ceria and alumina according to reaction (4) deeply modifies the previous redox processes in the sense that these ions are very stable and can be fully reoxidised in Ce^{4+} ions only at temperature close to 773 K instead of room temperature for reaction (5).

5. Conclusions

The redox behaviour of ceria in Pt/CeO_2–Al_2O_3 catalysts is strongly influenced by the presence of the alumina support. The very high reduction percentages obtained after reduction by H_2 at 573 K, much higher than those expected for bulk ceria supported catalysts treated in the same way, show that the preparation method has resulted in a highly dispersed CeO_2 on alumina. When using a chlorinated platinum precursor, the chlorine is almost quantitatively retained by

the catalyst, as indicated by chemical analysis, and magnetic results show that it remains fixed on the supported ceria phase after reduction. As for catalysts prepared on pure ceria, the presence of chlorine deeply modifies the redox properties of the ceria phase and the kinetics of the hydrogen spillover. However, the presence of alumina makes the processes more complex. A high reversibility of hydrogen adsorbed on the supported ceria phase is observed at 573 K. It appears independent on the presence of chlorine but is function of temperature. This may be attributed to the fact that the ceria surface is very high in the ceria–alumina of this study and chlorine is unable to substitute all the surface oxygen ions and thus cannot inhibit totally the hydrogen spillover. At room temperature, on a catalyst reduced and evacuated at 573 K, there is no spillover observed when chlorine is present on the surface. On the other hand, the limited amount of hydrogen which is irreversibly adsorbed on the support on a free chlorine reduced catalyst is sufficient to explain the excessive value obtained in the platinum dispersion measured by hydrogen volumetry.

On the same catalysts reoxidised at room temperature, the hydrogen spillover is fully obtained with the catalyst free of chlorine, whereas it is still observed but with a limited extent for a catalyst containing chlorine.

Finally, the ceria/alumina interactions occurring after reduction at moderate temperature (573 K) seem to stabilise a relatively large fraction of Ce^{3+} ions against reoxidation at low temperature. Consequently, this stabilisation could decrease the oxygen storage capacity by inhibiting the redox behaviour of a significant part of the ceria.

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