



Interaction of molecular hydrogen with three-way catalyst model of Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ type

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

The interaction of H₂ with a composite Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ system and its redox properties are investigated by means of H₂ and O₂ chemisorption, temperature programmed reduction (TPR) and desorption techniques. It is shown that the high H₂ spillover capabilities of Pt/CeO₂-ZrO₂ are maintained even after supporting the system on Al₂O₃. The re-oxidation experiments performed on the reduced moieties show that the stability of Ce(III) species is increased by Al₂O₃, while the presence of Pt favours the re-oxidation.

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1. Introduction

CeO₂ and more recently Ce_xZr_{1-x}O₂ mixed oxides are a key component in three-way catalysts due to their redox Ce⁴⁺/Ce³⁺ activity responsible for the oxygen storage/release capacity (OSC) [1]. Ce_xZr_{1-x}O₂ also promote processes related to H₂ production such as hydrocarbon reforming and partial oxidation, etc. [2,3]. The favourable effects of Ce_xZr_{1-x}O₂ are related to both the ability to provide mobile oxygen species and the great affinity of the M/CeO₂ (M = metal) systems towards H₂ [4]. The adsorption of H₂ over NM/CeO₂ (NM = noble metal) is reversible at room temperature (RT), leading to generation of Ce³⁺ species which are

re-oxidised by simple evacuation [5]. Increasing the temperature of H₂ adsorption leads to the so-called irreversible reduction, i.e. generation of oxygen vacancies and water [5]. While the beneficial effects of Al₂O₃ on thermal stability of the CeO₂-ZrO₂ system are known [6], H₂ adsorption and reactivity with the NM/CeO₂-ZrO₂/Al₂O₃ system has received scarce attention, despite their correlation to the catalytic properties [7,8].

2. Experimental

Ce_{0.6}Zr_{0.4}O₂ (13 wt.%) / γ-Al₂O₃ (indicated as CZ60/Al₂O₃) was prepared using a citrate method [6]. CZ60/Al₂O₃ and Al₂O₃ were impregnated to incipient wetness with Pt(NH₃)₂(NO₃)₂ and calcined at 500 °C

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for 5 h. Pt content (1.5 and 0.87 wt.%, respectively for Pt/CZ60/Al₂O₃ and Pt/Al₂O₃) was determined by atomic emission spectroscopy (ICP-AES) on a Jobin Yvon (series JY24) instrument after extraction of Pt with aqua regia.

Temperature programmed reduction (TPR) was carried out as previously reported using, however, 200 mg of sample to enhance the sensitivity [9]. H₂ chemisorption and BET surface area were measured on a Micromeritics ASAP 2000 analyser. The samples (ca. 0.5 g) were first cleaned in flow of O₂ (5%)/He for 1 h at 500 °C and then reduced in a flow of H₂ (5%)/Ar (25 ml min⁻¹) at a heating rate of 10 °C min⁻¹ up to the selected temperature (350, 500 and 800 °C). After 2 h at this temperature, the samples were evacuated at 400 °C for 4 h and cooled under vacuum to the adsorption temperature (−80 or 25 °C). A pressure change of less than 0.01% for 11 consecutive readings taken at 30 s intervals was used as an equi-

librium criterion. TPD experiments were conducted on a Micromeritics Pulse Chemisorb 2700 apparatus. Samples were calcined in O₂ flow (50 ml min⁻¹) at 400 °C for 1 h, purged in Ar flow (50 ml min⁻¹) for 1 h at 350 °C, cooled down to −70 °C and then reduced (H₂ (8%)/Ar at 15 ml min⁻¹, heating rate 8 °C min⁻¹ to 500 °C). After cooling down in pure H₂ (50 ml min⁻¹) to −70 °C, TPD was performed in Ar flow (12 ml min⁻¹), heating rate 16 °C min⁻¹ to 500 °C.

3. Results and discussion

3.1. Volumetric H₂ chemisorption

The results of the H₂ chemisorption on the Pt/CZ60/Al₂O₃ and Pt/Al₂O₃ are reported in Table 1. The comparison of the data obtained at −80 and

Table 1
H₂ chemisorption and BET surface areas measured over Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ and Pt/Al₂O₃

| Run | Sample | T_{ox}^{a} (°C) | $T_{\text{red}}^{\text{b}}$ (°C) | BET (m ² g ⁻¹) | H/Pt ^c | | Adsorbed volume ^d (time) ^e (ml g ⁻¹ (min)) | | | |
|-----|--|------------------------------------|-------------------------------------|--|-------------------|-------|---|----------|----------------|----------|
| | | | | | −80 °C | 25 °C | −80 °C | | 25 °C | |
| | | | | | | | 0 Torr ^h | 400 Torr | 0 Torr | 400 Torr |
| 1 | 1.5% Pt/Ce _{0.6} Zr _{0.4} O ₂ (13%)/Al ₂ O ₃ | – | 350 | 150 | 0.57 | 0.99 | 0.49 (37 min) | 0.92 | 0.85 (146 min) | 1.01 |
| 2 | | – | 500 | 150 | 0.49 | 0.58 | 0.42 (23 min) | 0.78 | 0.50 (57 min) | 0.66 |
| 3 | | 350 ^f | 350 | 150 | 0.57 | 0.77 | 0.49 (35 min) | 0.94 | 0.66 (85 min) | 0.80 |
| 4 | | – | 800 | 145 | 0.16 | 0.23 | 0.14 (12 min) | 0.20 | 0.20 (14 min) | 0.54 |
| 5 | | 75 ^f | – | 145 | 0.48 | 1.67 | 0.41 (31 min) | 0.84 | 1.44 (198 min) | 1.61 |
| 6 | | 300 ^f | – | 145 | 0.29 | 2.61 | 0.25 (223 min) | 0.89 | 2.25 (671 min) | 2.50 |
| 7 | | 150 ^f | 350 | 145 | 0.27 | 0.27 | 0.23 (14 min) | 0.75 | 0.23 (24 min) | 0.47 |
| 8 | | 350 ^g | 350 | 144 | 0.34 | 0.40 | 0.29 (18 min) | 0.75 | 0.35 (23 min) | 0.55 |
| 9 | | 500 ^g | 350 | 145 | 0.43 | 0.49 | 0.37 (19 min) | 0.65 | 0.42 (43 min) | 0.53 |
| 10 | | 600 ^g | 350 | 144 | 0.39 | 0.55 | 0.34 (22 min) | 0.66 | 0.47 (61 min) | 0.60 |
| | 0.87% Pt/Al ₂ O ₃ | | 350 | 186 | 0.68 | 0.69 | 0.34 (22 min) | 0.57 | 0.35 (42 min) | 0.52 |
| 11 | | | 500 | 185 | 0.69 | 0.69 | 0.35 (17 min) | 0.60 | 0.35 (35 min) | 0.40 |
| 12 | | 350 ^f | 350 | 185 | 0.69 | 0.69 | 0.35 (23 min) | 0.60 | 0.35 (37 min) | 0.42 |
| 13 | | – | 800 | 171 | 0.54 | 0.50 | 0.27 (17 min) | 0.60 | 0.25 (28 min) | 0.30 |
| 14 | | 350 ^f | 350 | 170 | 0.58 | 0.54 | 0.29 (15 min) | 0.33 | 0.27 (26 min) | 0.31 |

^a T_{ox} : temperature at which the sample has been re-oxidised after the previous run for 2 h in flow of 5% O₂ in He.

^b T_{red} : temperature at which the sample has been pre-reduced for 2 h in flow of 5% H₂ in He. The sample has been evacuated at 400 °C for 4 h before H₂ chemisorption experiments.

^c H₂ chemisorption experiments carried out at the reported temperature.

^d Adsorption of H₂ obtained by back extrapolating the linear part of the adsorption isotherm in the region 2–20 Torr (0 Torr) and cumulative adsorption value at 400 Torr.

^e Time required for reaching the equilibrium at 2 Torr of pressure.

^f Sample from previous run.

^g Sample previously reduced at 800 °C.

^h 1 Torr = 133.332 Pa.

25 °C reveals the presence of H₂ spillover effects. Spilling of H₂ over the support is an activated process, accordingly by lowering the adsorption temperature this process can be effectively arrested [10]. The time to reach the equilibrium (equilibrium time) is an independent criterion for discriminating the presence/absence of spillover phenomena, since H₂ adsorption on the metal was equilibrated within approx. 20 min at an equilibrium pressure of 2 Torr [11]. Most of the equilibrium times at –80 °C were around this value, runs 1 and 3 (Table 1) being somewhat higher (35–37 min), and quite high in run 6 (223 min). Therefore, the contribution of H₂ spilt over the support appears minimal in all the experiments conducted at –80 °C, except run 6, where, however a low H/Pt was obtained. In this case, the sample was re-oxidised at 300 °C leading to metal passivation, which can easily account both for the slow H₂ uptake and low H/Pt.

The equilibrium time at 25 °C largely exceeded 20 min in all the runs except 4, 7 and 8. Accordingly, with the exception of these three runs, significant H₂ spillover occurs. Consistently, the equilibrium is always attained within 20–30 min over the Pt/Al₂O₃, where significant spillover should not be expected due to the lack of the acceptor phase.

In Pt/Ce_xZr_{1-x}O₂ systems, H/Pt ratios as high as 12–20 are observed after reduction at moderate temperatures (≈200 °C), that decrease to 1.6–1.7 when the reduction temperature is increased to 300–400 °C [12]. The H/Pt ≈1 observed at 25 °C on freshly reduced Pt/CZ60/Al₂O₃ might appear somewhat low given the high surface area of the present material. The presence of exposed Al₂O₃ that could have blocked spilling of the adsorbed species cannot be invoked since H₂ can spill over the Ce_xZr_{1-x}O₂ phase at RT even when physically mixed with Pt/Al₂O₃ [13]. At RT, spilled H₂ is suggested to be adsorbed exclusively at the surface of CeO₂. However, due to the low amount of Ce_{0.6}Zr_{0.4}O₂ (13 wt.%), we calculate that 36 m² g⁻¹ of Al₂O₃ are covered by Ce_{0.6}Zr_{0.4}O₂, if we assume that the (100) plane of the mixed oxide grows as a monolayer (with cell parameter of 0.5307 nm). H₂ chemisorption on platinum can be evaluated by back extrapolating to 0 Torr the linear part of the H₂ adsorption isotherm measured at –80 °C to avoid contribution from physisorption. By back extrapolating the linear part of the H₂ adsorption isotherm measured at 25 °C it is possible to estimate the amount of hydro-

gen chemisorbed both on the metal phase and stored on/in the ceria-zirconia system. Therefore, the amount of spilled H can be calculated by the difference between the amount of H₂ adsorbed at 25 and –80 °C, leading to a surface density of 4.1 adsorbed H nm⁻² of Ce_{0.6}Zr_{0.4}O₂. This value is in line with the values of 3.5 and 6.2 H atoms nm⁻² previously found for Pt/Ce_{0.68}Zr_{0.32}O₂ [8,12]. Evidence for crystalline Ce_{0.6}Zr_{0.4}O₂-supported phase could not be detected from the XRD pattern which suggests either the presence of an amorphous phase dispersed on the Al₂O₃ surface or an upper limit of 2 nm for the Ce_{0.6}Zr_{0.4}O₂ particles. By considering a spherical geometry of the particles and a bulk density of 5.58 ml g⁻¹, a surface density of 4.3 adsorbed H atoms nm⁻² is calculated for such a particle size, which is very close to the above value. Both values indicate that extensive H₂ spillover does occur in our system and that the presence of Al₂O₃ does not depress this property to any appreciable extent.

Fig. 1 reports the effects of redox treatments on the chemisorption isotherms. All the isotherms measured at 25 °C feature comparable aspect, i.e. a flat adsorption isotherm for pH₂ >100 Torr. The overall chemisorption capability is strongly depressed by increasing the reduction temperature. The aspect of the isotherms measured at –80 °C closely resembles each other, however, no flat zone is observed above 100 Torr, the amount adsorbed still increasing with increasing the H₂ pressure. This is an indication that, in addition to the chemisorption process, physisorption of H₂ takes place at this temperature. A curious consequence of this phenomenon is that as the reduction temperature is increased up to 800 °C, the H₂ adsorption capability decreases more rapidly at 25 °C compared to –80 °C: starting from a situation where the isotherm measured after reduction at 350 °C at 25 °C is above than that obtained at –80 °C, the opposite is observed after reduction at 800 °C. Noticeably, when Pt/CZ60/Al₂O₃ is reduced at 800 °C, re-oxidised at 350 °C and then re-reduced at 350 °C, the adsorption capability starts to be recovered partially moving the isotherm obtained at 25 °C above that measured at –80 °C. These large modifications of the adsorption isotherms are related to the presence of the Ce_{0.6}Zr_{0.4}O₂ phase. Consistently, Pt/Al₂O₃ does not feature any unusual behaviour, the adsorption isotherm measured at –80 °C being always above

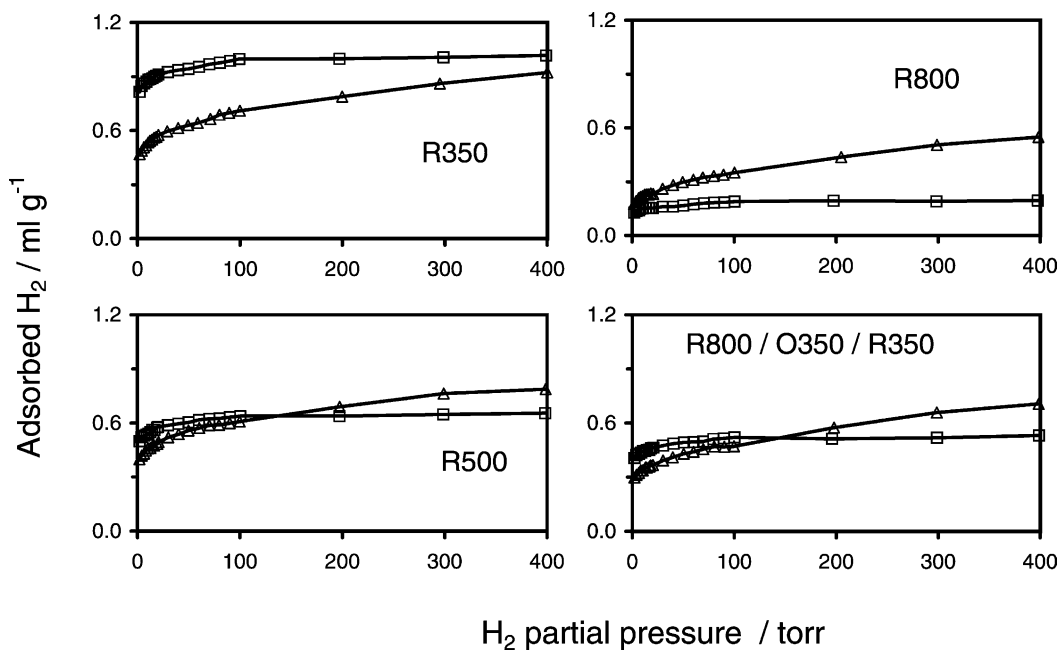


Fig. 1. H_2 chemisorption isotherms measured at -80 (Δ) and 25°C (\square) over $\text{Pt}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2/\text{Al}_2\text{O}_3$ subjected to different reducing (R) and oxidation (O) treatments at the indicated temperature ($^\circ\text{C}$).

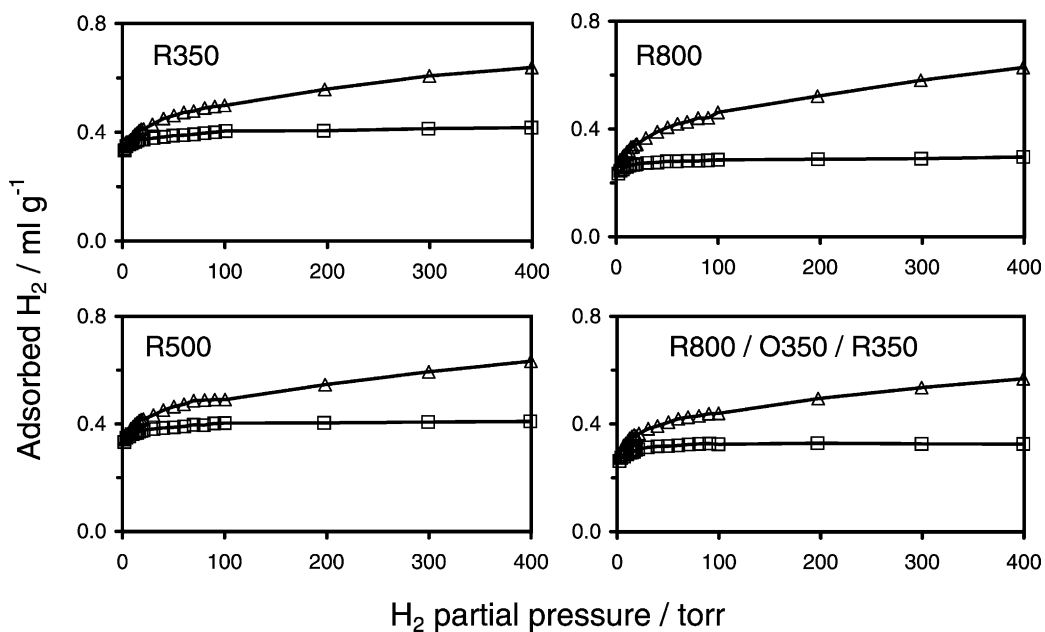


Fig. 2. H_2 chemisorption isotherms measured at -80 (Δ) and 25°C (\square) over $\text{Pt}/\text{Al}_2\text{O}_3$ subjected to different reducing (R) and oxidation (O) treatments at the indicated temperature ($^\circ\text{C}$).

that at 25 °C due to occurrence of physisorption (ca. 0.20 ml g⁻¹) at -80 °C (Fig. 2).

As the reduction temperature is increased from 350 to 800 °C (Table 1), H/Pt measured at -80 °C decreased from 0.57 to 0.16. If a spherical geometry for the Pt particles is assumed, this would account for an increase of average particle size from 2.3 to 7.1 nm, provided that other phenomena do not contribute to the decrease of the extent of H₂ chemisorption. However, this is not the case in the NM/CeO₂-containing systems: CeO₂ is a reducible oxide and susceptible to the strong metal/support interaction (SMSI) phenomena [14]. However, no evidence for metal decoration effects were observed in Rh/CeO₂ after reduction at 500 °C that typically generates the SMSI state (metal decoration effects) in Rh/TiO₂ [14]. Consistently, increasing the reduction temperature from 150 to 350 °C, the apparent H/Pt observed over Pt/Ce_{0.68}Zr_{0.32}O₂ decreased by about 500 and 30%, respectively at 25 and -80 °C without any significant particle size modification and decoration effects as checked by HREM, suggesting a deactivation of the H₂ chemisorption due to electronic effects [11]. We believe that both chemical deactivation and loss of spillover capabilities contribute to the above deactivation, as indicated by the comparable H/Pt measured at -80 and 25 °C. This is substantiated by the relatively small decrease of H/Pt experienced by Pt/Al₂O₃ and by the fact that when Pt/CZ60/Al₂O₃ was re-oxidised even at mild temperatures (75–300 °C), H₂ chemisorption was recovered to a significant extent. No Pt re-dispersion is expected to occur below 500 °C.

Noticeably, H/Pt = 1.67 is measured at 25 °C after oxidation at 75 °C which increases up to 2.61 at a re-oxidation temperature of 300 °C, indicating recover of spillover capability and favourable effects of the reduction/mild re-oxidation sequence. The equilibrium time is more than three times higher in the sample re-oxidised at 300 °C compared to that at 75 °C. In both cases, the TPR profiles (see below) revealed the presence of reducible PtO_x species on the surface. Accordingly, we attribute this phenomenon to a different rate of transport (spillover) of H₂ species over the support. This is substantiated by observation of H₂ adsorption even at -80 °C, where Pt reduction should be more difficult. We believe that the slower attainment of equilibrium observed increasing the re-oxidation temperature from 75 to 300 °C

should be associated with a more difficult reduction of PtO_x species passivated by the higher oxidation temperature, leading to a slow rate of spillover.

Significantly, almost no hydrogen spillover is observed for Pt/CZ60/Al₂O₃ after reduction at 800 °C followed by an oxidation at low temperature and a reduction at 350 ° (runs 7 and 8). For re-oxidation temperatures higher than 500 °C both H/Pt ratio and hydrogen spillover significantly increase. As suggested by a referee, the influence of effects like changes in the metal distribution on the catalyst (changing the relative amount of contacts between Pt and ceria-zirconia mixed oxide entities) or encapsulation of active Pt or Ce-Zr mixed oxide entities after the severe redox treatments could be invoked for this behaviour. Moreover, the main beneficial effect of the presence of a solid solution between Ce and Zr is related to avoiding formation of CeAlO₃. However, for high concentration of ceria and after long ageing at high temperature, formation of some CeAlO₃ was observed [15]. Re-oxidation of CeAlO₃ occurs at high temperature [16] and therefore its presence could be partially responsible for the absence of spillover observed in runs 7 and 8.

3.2. Temperature programmed reduction and oxygen uptake measurements

TPR profiles of CZ60/Al₂O₃ and Pt/CZ60/Al₂O₃ subjected to consecutive redox treatments are reported in Fig. 3. TPR profiles of CeO₂-ZrO₂ mixed oxides represent quite complex aspects due to a number of factors: phase non-homogeneity, pre-treatments, etc. [1]. Supporting Ce_xZr_{1-x}O₂ on Al₂O₃ leads to broad reduction features (Fig. 3b) that may appear even at quite low temperatures compared to unsupported mixed oxide [6,17]. Redox ageing (TPR followed by a mild oxidation) shifts the reduction to ca. 300 °C. Importantly, whereas high temperature oxidation moves the reduction peak to ca. 600 °C in the unsupported Ce_xZr_{1-x}O₂, presence of Al₂O₃ minimises this undesirable deactivation (Fig. 3b).

Pt/CZ60/Al₂O₃ features quite complex TPR profiles that approximately occur in the following temperature intervals: (i) sub-ambient/ambient reduction, (ii) 100–300 °C, (iii) 300–500 °C, and (iv) at 600–800 °C. Low temperature reduction is favoured by Pt due to its ability to activate and spill H₂ [18]. However, the reducibility depends on the nature of the surface

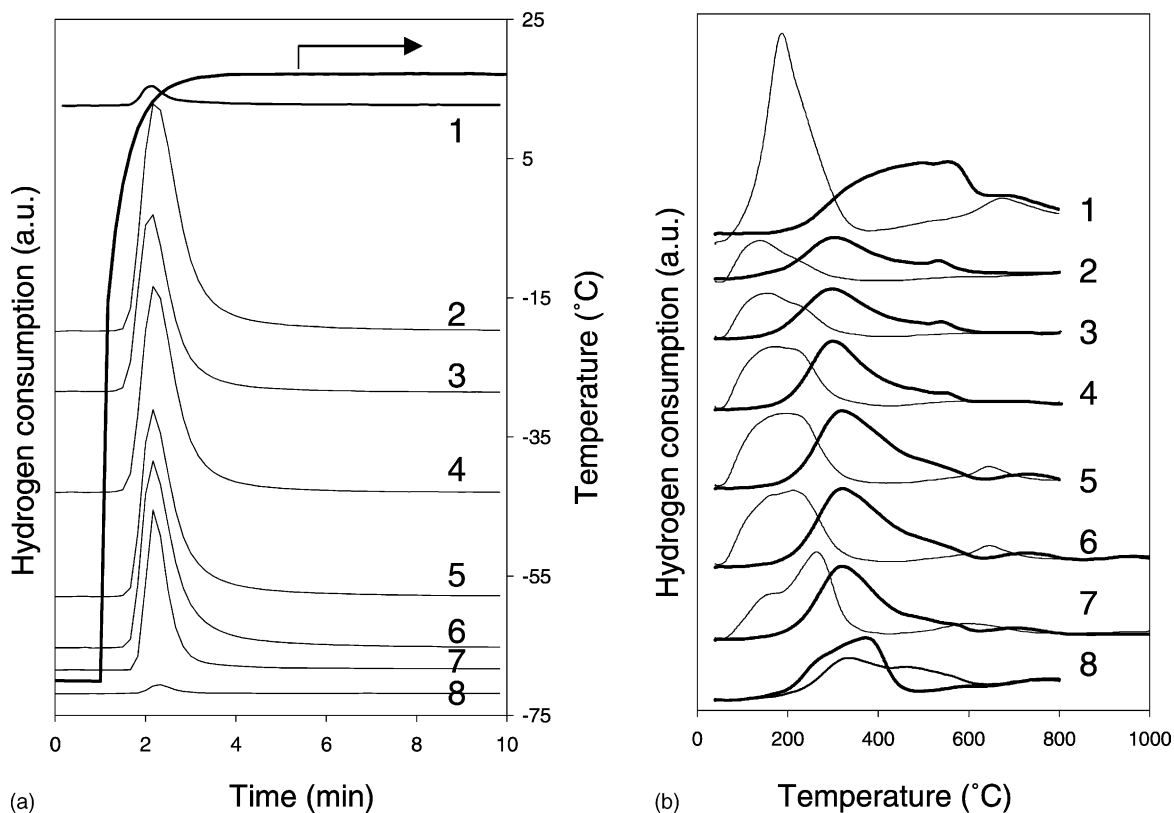


Fig. 3. Temperature programmed reduction of Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ (thin line) and Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ (bold line): (a) sub-ambient to ambient temperature; (b) ambient to 800 or 1000 °C. (1) fresh sample, (2) sample from run (1) oxidised at 75 °C, (3) sample from run (2) oxidised at 150 °C, (4) sample from run (3) oxidised at 300 °C, (5) sample from run (4) oxidised at 427 °C, (6) sample from run (5) oxidised at 427 °C, (7) sample from run (6) oxidised at 427 °C, (8) sample from run (7) oxidised at 1000 °C.

species generated by the calcination of the Pt precursor: chemisorbed oxygen can react with H₂ even at sub-ambient temperature, while PtO and PtO₂ are reduced at ca. 50 and 100 °C [19]. Notice that oxidation to give bulk PtO and PtO₂ was observed, respectively, at 100 and 300 °C in Pt/Al₂O₃ [19]. The TPR profiles of the fresh (calcined 500 °C) and oxidised at 1000 °C samples significantly differ from others as denoted by the absence of significant H₂ uptake near RT. This suggests the presence of some bulk Pt oxide—reduced with difficulty—that is generated by the deep oxidation treatment. Also an interaction between the metal particles and oxygen atoms of the CeO₂-ZrO₂ phase could have generated hardly reducible Pt-O-Ce species [1], in addition to some surface dehydroxylation, both factors leading to a less efficient reduction process.

The intense peak at 180 °C observed in the fresh sample is associated with the reduction of the Pt oxide and Ce_{0.6}Zr_{0.4}O₂ mixed oxide. Consistent with the high spillover capability of this sample, reduction occurs at a temperature close to that expected for PtO₂ reduction. The peak above 600 °C is likely associated with some CeO₂ non-incorporated in the sample, as detected previously [6].

Redox ageing consisting of TPR/oxidation (up to 427 °C) improves the reducibility of the system. In fact, the TPR profiles of all the recycled samples are characterised by an intense H₂ uptake at RT, in addition to the broad reduction at 100–240 °C. Due to the relatively mild re-oxidation conditions, passivation of the Pt particles by chemisorbed oxygen rather than deep oxidation to form a bulk Pt oxide should have occurred in these oxidation treatments. Such species

would be reduced at low temperatures, favouring extensive adsorption of H_2 at the $Ce_{0.6}Zr_{0.4}O_2$ surface. In agreement with the TPD investigation (see below) we associate the RT peak to reversible Ce(IV) reduction via a spillover mechanism [5] and the peak at 100–240 °C to reduction in the bulk of the mixed oxide. There are some modification of this reduction feature with the pre-treatment, however, no clear trend could be discerned.

3.2.1. Effect of temperature on the re-oxidation process

O_2 uptake was measured after TPR at different temperatures using a pulse method (Table 2). Re-oxidation of Pt particles in the Pt/CZ60/ Al_2O_3 cannot be easily distinguished from that of the reduced $Ce_{0.6}Zr_{0.4}O_{2-x}$ moiety. By considering the Pt dispersion of 16%, measured in the chemisorption measurements after reduction at 800 °C, passivation of Pt surface with one oxygen per exposed metal atom would require 0.15 ml of $O_2 g^{-1}$ of material. Bulk oxidation of Pt to PtO and PtO₂ requires 0.9 and 1.9 ml of $O_2 g^{-1}$ of Pt/CZ60/ Al_2O_3 , respectively. Re-oxidation of reduced $Ce_xZr_{1-x}O_2$ moieties is fast and effective even at RT: about 75% of the oxidation proceeded at RT while re-oxidation was fully accomplished by 100 °C, independently of the oxide composition [20].

Both metal-free and Pt-loaded samples do not show appreciable H_2 uptake above 800 °C suggesting comparable degree of reduction of the $Ce_{0.6}Zr_{0.4}O_2$ component to be achieved in both systems. Based on this assumption, the excess of the O_2 uptake observed in the Pt/CZ60/ Al_2O_3 compared to CZ60/ Al_2O_3 (Table 2) can be attributed to Pt-derived “redox reactions”. According to the reduction temperature (800 or 1000 °C), two sets of difference values are obtained: 0.5 and 0.8–0.9 ml $O_2 g^{-1}$, the latter value suggests oxidation of Pt particles to give bulk-like PtO, PtO₂ not being formed under our re-oxidation conditions. When the reduction temperature is increased up to 1000 °C, re-oxidation of Pt particles in the bulk becomes more difficult under the present transient conditions, which could be associated with some Pt sintering induced by the high temperature reduction. Consistently, when the sample oxidised at 75 °C is further oxidised at 427 °C (Table 2), negligible oxidation of Pt particles is observed. Curiously, the difference values slightly decrease as the oxidation temperature is increased from 75 to 427 °C on the sample reduced at 800 °C. As shown by runs 4 and 5 (Table 2), this cannot be attributed to a progressive sintering of Pt particles as these experiments were performed consecutively. Rather, it suggests that the kinetics of re-oxidation of the $Ce_{0.6}Zr_{0.4}O_{2-x}$

Table 2
Oxygen uptake measured over $Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ and Pt/ $Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ after TPR treatments

| Run ^a | Treatment | Oxygen uptake ^b | Temperature (°C) | | |
|------------------|-----------|----------------------------|--|--------------------|------------|
| | | | Amount adsorbed (ml g ⁻¹) (Ce(III) re-oxidation (%)) | | |
| | | | CZ60/ Al_2O_3 | Pt/CZ60/ Al_2O_3 | Difference |
| 1 | TPR 800 | 75 | 1.34 (52) | 1.83 | 0.51 |
| 2 | TPR 800 | 150 | 1.41 (54) | 2.35 | 0.94 |
| 3 | TPR 800 | 300 | 1.40 (54) | 2.29 | 0.89 |
| 4 | TPR 800 | 427 | 1.98 (76) | 2.77 | 0.79 |
| 5 | TPR 800 | 427 | 1.97 (76) | 2.75 | 0.78 |
| 6 | TPR 1000 | 427 | 1.63 (63) | 2.10 | 0.47 |
| 7 | TPR 1000 | 1000 | 1.92 (74) | 2.39 | 0.47 |
| 8 | TPR 800 | 75 | 1.13 (43) | 1.59 | 0.46 |
| 9 | | 427 | 0.56 (21) | 0.63 | 0.07 |

^a Consecutive runs. The fresh sample has been subjected to a cleaning procedure at 500 °C for 1 h under O_2 pulses before the TPR was performed up to indicated temperature.

^b Assuming a Pt metal dispersion of 16%, the passivation of Pt surface with one oxygen per exposed metal atom would require 0.15 ml of $O_2 g^{-1}$ of Pt (1.5%)/ $Ce_{0.6}Zr_{0.4}O_2$ (13%)/ Al_2O_3 . Bulk oxidation of Pt to PtO and PtO₂ would require, respectively, 0.9 and 1.9 ml of $O_2 g^{-1}$. Difference calculated by subtracting the values obtained for $Ce_{0.6}Zr_{0.4}O_2$ (13%)/ Al_2O_3 from those obtained for Pt (1.5%)/ $Ce_{0.6}Zr_{0.4}O_2$ (13%)/ Al_2O_3 .

moieties might be favoured by the presence of the supported Pt.

The highest O₂ uptake in the re-oxidation of the reduced Ce_{0.6}Zr_{0.4}O_{2-x}/Al₂O₃ that corresponds to 76% of Ce(III) being re-oxidised, is fully consistent with the value of 77% previously obtained on unsupported Ce_{0.6}Zr_{0.4}O_{2-x} [21]. Only about 70% of the ultimate O₂ uptake is achieved by re-oxidation at 75–300 °C, indicating that the presence of Al₂O₃ stabilises reduced Ce(III) moieties at the surface as in case of CeO₂-Al₂O₃ [1]. CeO₂ and CeO₂-ZrO₂ mixed oxides tend to form bidimensional patches at the Al₂O₃ surface whose redox activity differs from that of the bulk oxide [17].

Redox cycles carried out up to 1000 °C decrease the ability of the system to undergo re-oxidation as denoted by a decrease of 20% of the O₂ uptake compared to reduction at 800 °C. Full re-oxidation could be achieved by increasing the oxidation temperature to 1000 °C. This suggests that the deactivation of the redox properties likely occurs through generation of reduced CeAlO₃-like moieties that can be re-oxidised only upon a high temperature oxidation. Presence of some CeAlO₃ has been detected by XRD on the redox aged sample subjected to mild oxidation as the last

treatment. The relatively high CeO₂ content favours phase segregation upon high temperature treatments, CeO₂-rich phase thus generated are expected to react more easily with the Al₂O₃ compared to ZrO₂-rich oxides [6].

3.3. Temperature programmed desorption of H₂

Fig. 4 reports the TPD profiles obtained on the investigated samples after pre-treatment in O₂ flow at 400 °C for 1 h, reduction at 500 °C and cooling down in pure H₂ to -70 °C. TPD of H₂ from Pt/CZ60/Al₂O₃ features three desorption peaks centred at 50, 190 and 370 °C (Fig. 4). The comparison with the TPD of Pt/Al₂O₃ suggests contribution from H₂ adsorbed on the metal as being responsible for the H₂ desorbed at low temperatures, even though some reverse spillover of H₂ presumably contributes to this signal as well. An interaction between Pt and Ce_{0.6}Zr_{0.4}O₂ is in fact suggested by the comparison of the desorption pattern obtained for CZ60/Al₂O₃. It is reasonable to associate the H₂ desorption that occurs above 400 °C in CZ60/Al₂O₃ (Fig. 4) with the broad peak at 370 °C in Pt/CZ60/Al₂O₃. Pt strongly promotes H₂ storage at low temperatures on the support, which is

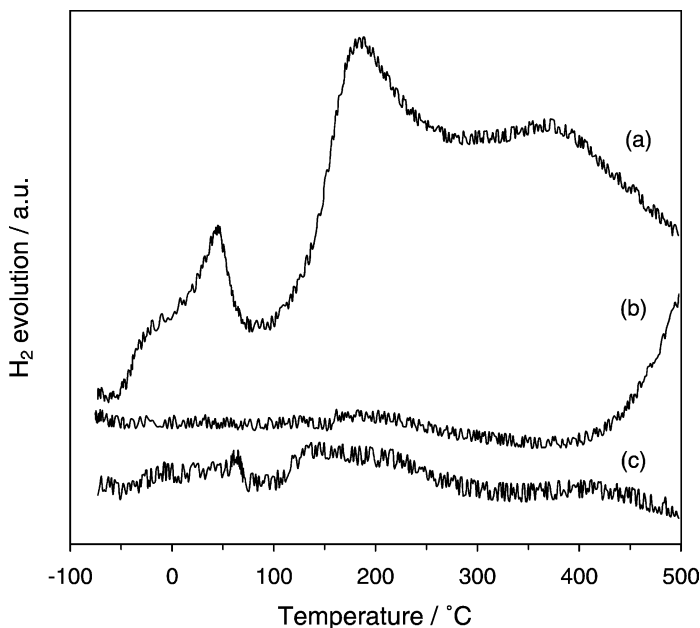


Fig. 4. Temperature programmed desorption of H₂ from Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ (a), Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ (b) and Pt/Al₂O₃ (c).

then reversibly desorbed during the TPD experiment [5]. Spillover phenomenon therefore accounts for the strong increase of the amount H_2 chemisorbed on Pt/CZ60/ Al_2O_3 compared to Pt/ Al_2O_3 . Interestingly, the desorption feature occurring near to RT suggests that the consumption of H_2 found in the TPR profiles might be related to the so-called reversible reduction rather than creation of oxygen vacancies.

4. Conclusions

The present results reveal significant effects of Al_2O_3 on the hydrogen activation capabilities and the redox properties of the Pt/ CeO_2 - ZrO_2 system: (i) the extent of the hydrogen spillover is not depressed by the presence of Al_2O_3 to any appreciable extent; (ii) low temperature reduction in terms of TPR behaviour is promoted, (iii) the re-oxidation behaviour is affected by the presence of Al_2O_3 as a support due to stabilisation of reduced Ce(III) moieties, however, the presence of ZrO_2 and Pt plays a favourable role in that the re-oxidation process is facilitated. This confirms the ability of ZrO_2 to thermally stabilise the OSC property of CeO_2 even in these composite systems.

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