Kinetics of hydrogen chemisorption on high surface area Pd/Ce$_{0.8}$Zr$_{0.2}$O$_2$

F.C. Gennari[a,b], C. Neyertz[a], G. Meyer[a], P. Fornasiero[b,*], M. Graziani[b]

[a] *Centro Atómico Bariloche (CNEA) and Instituto Balseiro (UNC), 8400 S.C. de Bariloche, Argentina*
[b] *Center of Excellence for Nanostructured Materials, INSTM – Trieste Unit and Chemistry Department, University of Trieste, Via L.Giorgieri 1, 34127 Trieste, Italy*

Abstract

The effect of pre-reduction conditions on the H$_2$ chemisorption kinetics of high surface area Pd(0.53 wt.%)/Ce$_{0.8}$Zr$_{0.2}$O$_2$ was investigated by means of temperature-programmed reduction, oxygen-storage capacity, IR spectroscopy and volumetric hydrogen measurements. In the 20–80 °C range, the pre-reduction rate was very fast and dependent on temperature, with an apparent activation energy of 58 kJ mol^{-1}. Distinction between PdO reduction and H spillover processes is only possible at low H$_2$ pressures. The total H$_2$ uptake and the chemisorption rate strongly decrease by the use of high H$_2$ pressures during the pre-reduction process. Irreversible reduction with the concomitant oxygen vacancies formation occurs at low temperature, as demonstrated by in situ IR experiments. However, H$_2$ uptake on the Pd(0.53 wt.%)/Ce$_{0.8}$Zr$_{0.2}$O$_2$ during pre-reduction and chemisorption is recovered by reoxidation at 400 °C.
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1. Introduction

The study of the interaction of H$_2$ with noble metal/Ce$_x$Zr$_{1-x}$O$_2$ systems is of great interest for its implications in industrial catalysis, particularly for catalytic converters [1]. Among the various investigated systems, Pd based Ce$_x$Zr$_{1-x}$O$_2$ materials represent the most challenging and complex ones. In fact, Pd is able to adsorb hydrogen, forming various hydrides, and to promote extensive hydrogen spillover onto the support, even at low temperature (above −90 °C) [2]. Notably, all these aspects do not allow determination of Pd dispersion by simple H$_2$ chemisorption methods [2]. Moreover, it is not clear whether hydrogen atoms enter the bulk or are only chemisorbed on the surface. Fierro et al. have suggested the formation of bulk H$_y$CeO$_{2-x}$ bronze-like species [3]. Bruce et al. indicated that the hydrogen uptake leads to both surface hydroxylation and incorporation of hydrogen into ceria lattice [4]. Sholberg et al. predicted the formation of bulk hydroxyl groups after hydrogen interaction with CeO$_2$ [5]. In contrast, Perrichon et al. suggested that hydrogen uptake on ceria is strictly a surface process [6].

In the present study, the kinetics of H$_2$ uptake on Pd supported on high surface area Ce$_{0.8}$Zr$_{0.2}$O$_2$ solid solution is investigated, with particular attention to the relation between the ability of hydrogen spillover and storing, the nature of the occluded hydrogen species and the degree of reduction.

2. Experimental

2.1. Preparation of catalyst

Ce$_{0.8}$Zr$_{0.2}$O$_2$ was prepared by co-precipitation technique [7] using Ce(NO$_3$)$_3$ · 6H$_2$O (Aldrich 99.99 %), ZrO(NO$_3$)$_2$·xH$_2$O (MEL Chemicals, 99.99 %) and NH$_3$ (Carlo Erba). After co-precipitation, the product was filtered, suspended in isopropanol and stirred under reflux for 6 h.

* Corresponding author. Tel.: +39 040 558 3973; fax: +39 040 558 3903.
E-mail address: pfornasiero@units.it (P. Fornasiero).

Finally the sample was dried overnight at 110 °C and then calcined in air for 5 h at 500 °C. The obtained product is hereafter indicated as CZ80. Pd 0.53 wt% was loaded on $Ce_{0.8}Zr_{0.2}O_2$ by incipient wetness impregnation using $Pd(NH_3)_2(NO_2)_2$ as metal precursor. After drying at 110 °C, the sample was calcined at 500 °C for 5 h. Hereafter this sample is designed as Pd/CZ80.

2.2. Characterization techniques

N$_2$ adsorption isotherms were measured at −197 °C in a Micromeritics ASAP 2000 analyzer, after degassing the sample at 350 °C for 12 h. Powder X-ray diffraction patterns were collected on a Philips PW 1710/01 instrument with Cu Kα radiation. In situ FT-IR spectra were recorded at room temperature (rt) on a Perkin-Elmer 2000 FT-IR spectrometer with MCT detector using a static quartz cell. The procedure used during cleaning, reduction studies and surface methanol adsorption has been previously reported [8].

A standard cleaning procedure under O_2/Ar flow at 500 °C [8,9] was always applied as a first step before temperature-programmed reduction (TPR) or oxygen-storage capacity (OSC) measurements, to ensure a clean sample surface and reproducible experimental conditions. TPR experiments were performed in a conventional system equipped with a TCD [9], under 5% H_2/Ar (25 ml min^{-1}, heating rate 20 °C min^{-1}). Total-OSC was measured at 427 °C after TPR by a pulse method [10]. Dynamic OSC measurements were performed by alternatively pulsing every 75 s H_2 and O_2 over the sample (20 mg, maintained in a flow of Ar of 25 ml min^{-1}) at selected temperature [9].

Hydrogen pre-reduction and chemisorption kinetics were measured using an experimental set up previously reported [11]. The sample was pre-treated in O_2 at 400 °C for 1 h. The sample was then cooled to the selected reduction temperature (25–80 °C) and kept under vacuum for 0.5 h at this temperature. After reduction, the sample was evacuated first at the reduction temperature and then at 400 °C for 4 h, cooled to the chemisorption temperature and held at that temperature for 0.5 h. After each chemisorption measurement, a regeneration procedure, consisting in the reoxidation of the sample at 400 °C for 1 h, followed by the reduction–evacuation steps, was applied.

3. Results and discussion

3.1. Surface and structural characterization

Fresh CZ80 is a mesoporous material with a BET surface area of 135 m^2 g^{-1}, BJH average pore diameter of 7.5 nm (calculated from desorption isotherm) and total pore volume of 0.25 ml g^{-1}. XRD analysis of CZ80 shows a poorly crystalline material. Structural data of the solid solution has been obtained from the XRD pattern after calcination for 5 h at 1000 °C. A good fitting was achieved assuming the presence

of a cubic phase ($Fm3m$) of composition $Ce_{0.8}Zr_{0.2}O_2$ ($a = 0.5374$ nm). The surface composition of CZ80 was determined by FT-IR technique, using information from methanol dissociation into methoxy species. The intensity of the on-top methoxy (I) species on Zr^{4+} was found to be directly proportional to the surface composition [12]. On the basis of the linear calibration curve obtained for this species [8], the surface composition of CZ80 resulted, as expected, 80% rich-cerium.

3.2. TPR and OSC measurements by O_2 uptake

Fig. 1 depicts H_2 uptake during the TPR of CZ80 and Pd/CZ80. The profile of CZ80 shows a wide reduction peak centered around 555 °C. Theoretical calculation on pure single phase $Ce_xZr_{1-x}O_2$ indicates that the surface and bulk reduction can occur at the same temperature, leading to a single reduction profile [13]. In the present case, a weak shoulder is observed above 750 °C. On the bases of the homogeneity of the present sample, this broad H_2 consumption can be mainly associated with the presence of some kind of buoyancy effect, i.e. baseline derive due to the sample sintering/compacting that can occur during the TPR and give rise to an apparent H_2 uptake. Pd/CZ80 shows a sharp peak at 140 °C, the intensity of which indicates that concomitant palladium and cerium reduction occurs. The significant shift in the reduction temperature respect to the pure support is in agreement with the well-known ability of noble metals to promote H_2 dissociation and spillover [9]. A high temperature broad peak is observed also for Pd/CZ80, which can be associated with the sintering of the sample as for the pure support.

It is well established that quantification of H_2 uptake from TPR experiments is affected by various artefacts [1], the most evident of which is the difficulty of the baseline identification.
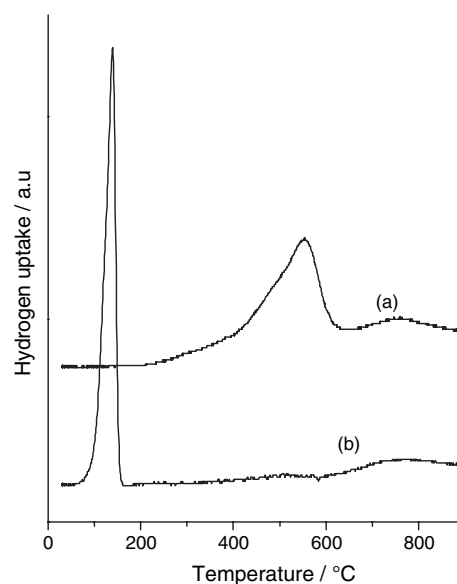

Fig. 1. Temperature-programmed reduction profiles of CZ80 (a) and Pd/CZ80 (b).

Table 1
Total and dynamic OSC for CZ80 and Pd/CZ80

Sample	Total O_2-OSC (μmol g^{-1})[a]	Dynamic OSC (μmol O_2 g^{-1})[b]			
		30 °C	60 °C	90 °C	150 °C
CZ80	826	0	0	0	0
Pd/CZ80	898	237	346	346	346
Pd/CZ80[c]	-	340	340	340	340

[a] Measured at 427 °C after TPR experiments.
[b] Standard deviation 9 μmol g^{-1}; sample pre-reduced at 200 °C.
[c] From previous run after dynamic OSC up to 150 °C.

Therefore we decided to quantify the H_2 uptake by measuring the oxygen necessary to reoxidize the reduced sample and/or titrate the hydrogen stored in the material. In principle, two types of OSC measurements may be distinguished: total and dynamic OSC. The former represents the maximum amount of transferable oxygen at a given temperature after reduction [1,9]. The latter refers to the O_2 uptake measured during continuous cycling between reducing (H_2) and oxidizing (O_2) atmospheres [1,9]. Table 1 reports the OSC data for CZ80 and Pd/CZ80. Recalling that re-oxidation of ceria–zirconia solid solutions occurs at 427 °C [10] and assuming that after reduction at 1000 °C and cooling to 427 °C under Ar, no hydrogen is retained in the support, the total OSC indicates the degree of reduction. For CZ80 the O_2 uptake corresponds to about 60% of cerium reduction. The slightly higher O_2 uptake measured on Pd/CZ80 can be mainly associated with some Pd reoxidation, even if we cannot exclude that the presence of noble metal may somehow enhance the total degree of reduction.

In the case of CZ80 no O_2 or H_2 uptake was measured during dynamic OSC up to 200 °C. Significant dynamic OSC values were measured at rt for Pd/CZ80 pre-reduced at 200 °C, in agreement with recent works [9]. This behavior is attributed to hydrogen spilled over the support followed by titration by O_2, with water evolution. It was demonstrated that this phenomenon requires the presence of a noble metal to activate H_2 [9]. It is worth noting that already at 60 °C, the O_2 uptake corresponds to 40% of the total uptake measured on the pure support after reduction at 1000 °C. The low temperatures selected for both pre-reduction and the further H_2-OSC measurements, ensure the absence of Pd sintering, metal particle decoration and encapsulation, support sintering, etc. [14]. The H_2 uptake (not reported in Table 1, since it is twice of the O_2 uptake) at 60 °C is 692 μmol g^{-1}. Hydrogen uptake of 50 and 3080 μmol g^{-1} can be estimated, respectively, for reduction of PdO to Pd, and CeO_2 to Ce_2O_3. Metallic Pd may absorb H_2 to form PdH$_x$ (α or β) [15], depending on the experimental conditions used. Assuming a Pd/H ratio equal to 1:1, an additional H_2 consumption of 25 μmol g^{-1} might be expected for Pd/CZ80. On the basis of the model proposed by Perrichon et al. [6], the complete surface reduction of our Pd/CZ80 should involve 421 μmol g^{-1} of H_2. Then, even considering the complete reduction of Pd^{2+} to Pd and the formation of bulk Pd hydrides, significant hydrogen spillover to the support occurs, involving more than the simple surface reduction.

3.3. Volumetric chemisorption of hydrogen

The effect of pre-reduction temperature on H_2 uptake of Pd/CZ80 was studied at $p(H_2) = 133$ kPa varying the reduction temperature in the range 25–80 °C. Typical pre-reduction kinetic curves are shown in Fig. 2, highlighting very fast reduction rates. The H_2 uptake saturates at a value of about 705 μmol g^{-1} of sample, independently of the temperature. Similar H_2 uptake was obtained after dynamic OSC and associated with spillover phenomena. An apparent activation energy (E_{app}) of 58 ± 7 kJ mol^{-1} can be estimated from the results reported in Fig. 2, for 50% of H_2 uptake [16]. This value is comparable with those reported by Fallah et al. [17] (67 kJ mol^{-1}) and by Sadi et al. (63 kJ mol^{-1}) [18], for the CeO_2 initial reduction and for reduction of Rh/CeO_2 catalysts, respectively, suggesting similar rate controlling process. However, we have to consider that the estimation of E_{app} depends on two main factors: (1) partial pressure of oxygen on oxide surface, which is generally unknown; (2) oxide intrinsic characteristic such as density of surface site. The information on the partial pressure of oxygen is essential for determining the equilibrium $H_2 + O_2 \Leftrightarrow H_2O$. The lack of this information precludes any direct comparison with literature.
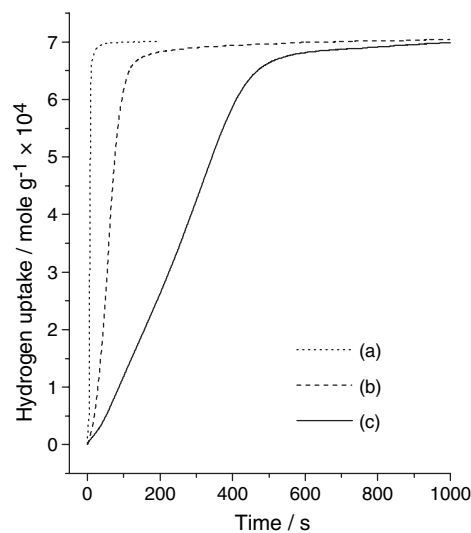

Fig. 2. Reduction kinetics of Pd/CZ80 at 80 °C (a), 50 °C (b), 25 °C (c). $p(H_2)$ 133 kPa.

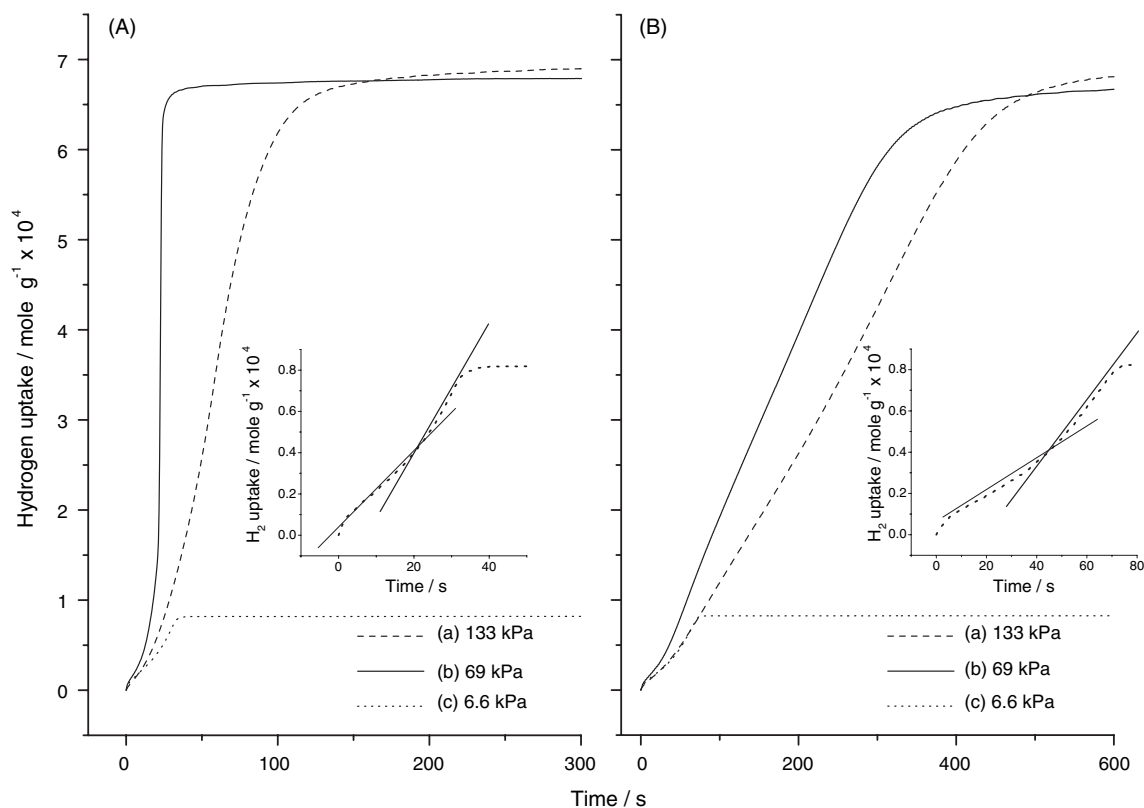Fig. 3. Effect of H$_2$ pressures on the reduction rate of Pd/CZ80 at 50 °C (A) and 25 °C (B). p(H$_2$) of 133 kPa (a), 69 kPa (b) and 6.6 kPa (c).

Fig. 3 illustrates the effect of H$_2$ pressure on the pre-reduction rate, at 50 and 25 °C. No distinction between PdO reduction, PdH formation and H spillover is observed at high H$_2$ pressures, while at 6.6 kPa evidence of Pd^{2+} to Pd^0 (inset of Fig. 3) is indicated by the change in the pre-reduction rate when hydrogen uptake is about 45 μmol of H$_2$ g^{-1}. At H$_2$ pressures higher than 69 kPa lower pre-reduction rates are observed. The final H$_2$ uptake is a function of the pressure (about 705 and 680 μmol of H$_2$ g^{-1} for 133 and 69 kPa respectively) and independent of the temperature. In the case of the runs performed at 6.6 kPa, the low H$_2$ pressure used limits the final total uptake (about 80 μmol of H$_2$ g^{-1}). Fallah et al. [17] have established that ceria reduction easily occurs only if water partial pressure is not higher than 10^{-4} atm. Padeste et al. [19] have shown different kinetics for the reduction/oxidation reaction carried out by cycling between H$_2$ and O$_2$: the reduction rate being diffusion controlled whereas the oxidation rate is very fast. They showed that the consumption of H$_2$ during the reduction and reoxidation time are lowered in the presence of water. Accordingly, the presence of water could also lower the rate of reduction of our Pd/CZ80. Notably that water can reoxidize reduced ceria with evolution of H$_2$ at rt as well as at elevated temperature, even with low partial pressure of water [19].

The effect of pre-reduction conditions on the chemisorption rate of H$_2$ at 25 °C and 16 kPa is shown in Fig. 4A

and B. Analysis of the chemisorption kinetics reveals the following important facts: (i) greater rates for initial stage are obtained for samples pre-reduced at 50 °C than at 25 °C; (ii) an intermediate stage with constant chemisorption rate is observed (Fig. 4B), independently of the pre-reduction temperature; (iii) Fig. 4C and IR measurements (not reported) support the observation that the final H$_2$ uptake depends on the H$_2$ pressure during the pre-reduction. Note that during the pre-reduction of Pd/CZ80 at 80 °C and 133 kPa, 705 μmol of H$_2$ g^{-1} were consumed in less than 100 s (Fig. 2), while after evacuation, in the subsequent chemisorption at 80 °C and 133 kPa, 355 μmol of H$_2$ g^{-1} were consumed in about 500 s (Fig. 4C). In addition, significant ceria irreversible reduction has been observed during H$_2$ pre-reduction of Pd/CZ80 even at 30 kPa and 80 °C. In fact, the appearance of an IR band at 2120 cm^{-1} during in situ IR experiments clearly indicates the formation of oxygen vacancies with concomitant water evolution [20]. It is worth noting that decreasing the H$_2$ pressure to 3 kPa results in a weakening of the band at 2120 cm^{-1} and therefore in a decline of the degree of reduction. Moreover, H$_2$ chemisorption experiments on Pd/CZ80 indicates that the lower the H$_2$ pre-reduction pressure, higher the final H$_2$ uptake (Fig. 4B and IR). Therefore, strong pre-reduction conditions (high temperature [14] or high p(H$_2$)) decrease the rate and total H$_2$ uptake during the chemisorption. It has
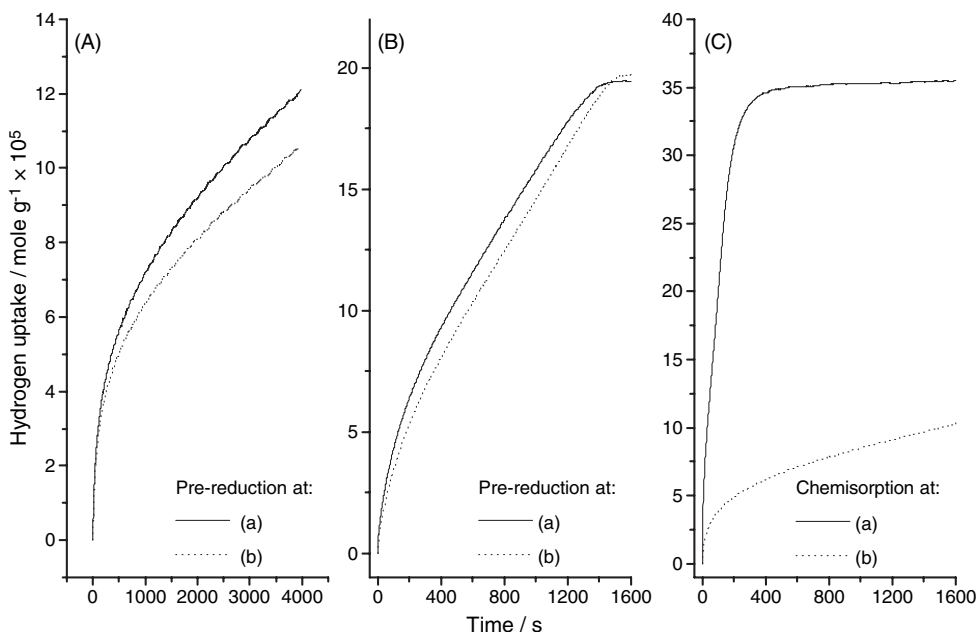
Fig. 4. (A and B) Effect of pre-reduction conditions on the H_2 chemisorption rate at 25 °C and 16 kPa. Reduction at 133 kPa (A) and 6.6 kPa (B): (a) 50 °C and (b) 25 °C. (C) H_2 chemisorption rate at (a) 80 °C and (b) 25 °C and 133 kPa after pre-reduction at 80 °C and 133 kPa.

been shown that the H_2 activation and spillover capacity of noble metals can be electronically deactivated by the presence of significant fraction of reduced ceria [2]. Usually this effect is observed after reduction of NM/CeO$_2$ catalysts at $T > 450$ °C, while after high temperature reduction, chemisorption capacity deactivation due to Pd particle agglomeration, Pd–Ce intermetallic formation and/or partial covering of Pd particles by ceria is observed [14]. The low pre-treatment temperature adopted ensures the absence of structural and morphological changes. Therefore, the decrease of H_2 uptake capacity of Pd/CZ80 during chemisorption should be associated with both the partial dehydroxylation of the surface and the presence of Ce(III) which may electronically deactivate the palladium, as confirmed by in situ IR experiments.

4. Conclusions

The following results can be summarized for the present investigation of the interaction of H_2 with surface and bulk homogeneous high surface area Pd/Ce$_{0.8}$Zr$_{0.2}$O$_2$.

Fast pre-reduction rates are observed for Pd/CZ80, which are negatively affected by the water partial pressure. Distinction between PdO reduction/PdH$_x$ formation and CZ80 reduction can be achieved only at low H_2 pressure.

An E_{app} of 58 kJ mol^{-1} can be estimated for the pre-reduction process.

H_2 uptake and chemisorption rate on Pd/Ce$_{0.8}$Zr$_{0.2}$O$_2$ are significantly decreased on samples deeply pre-reduced with respect to samples weakly pre-reduced.

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