Significant room temperature oxygen storage over 0.58% Pt/$Ce_{0.68}Zr_{0.32}O_2$ when H_2 is used as a reducing agent

N. Hickey,[a] P. Fornasiero,[a] J. Kašpar,*[a] M. Graziani,[a] G. Blanco[b] and S. Bernal[b]

[a] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy. E-mail: kaspar@univ.trieste.it*
[b] *Departamento de Ciencia de los Materials e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Apartado 40, Puerto Real, 11510, Spain*

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The investigation of the oxygen storage/release capacity (OSC) of 0.58 wt% Pt/$Ce_{0.68}Zr_{0.32}O_2$ catalyst by oscillating the feed-stream between reducing and oxidising conditions showed that a high OSC could be measured at room temperature, even for redox-aged sample, by using H_2 as the reducing agent.

The so-called oxygen storage/release capacity (OSC) of a three-way catalyst (TWC) is the ability to attenuate the negative effects of rich/lean oscillations of exhaust gas composition. By maintaining a stoichiometric composition at the catalyst, the highest conversion efficiency of the exhaust is attained. OSC, which in the modern TWCs is achieved by adding a CeO_2–ZrO_2 mixed oxide component, is usually discussed in terms of the ability to regulate the oxygen partial pressure in the exhaust through the Ce^{3+}/Ce^{4+} redox couple [eqn. (1)]:

$$CeO_2 \underset{H_2O-CO_2}{\overset{H_2-CO}{\rightleftarrows}} CeO_{2-x} + x/2O_2 \qquad (1)$$

Formation of vacancies is therefore either implied or assumed. Following the pioneering work of Yao and Yu-Yao,[1] dynamic-OSC measurement involves alternately pulsing the chosen reducing agent (usually CO but sometimes H_2) and O_2 over the material under investigation. More recently the oxygen buffering capacity (OBC) technique has been developed by Bernal *et. al.*[2] In this method O_2 is pulsed over the sample in a flow of inert gas, which effectively corresponds to oscillations between mildly reducing and oxidising conditions.

Here, we demonstrate that it is possible, using H_2 as reducing agent, to measure significant dynamic-OSC over Pt/$Ce_{0.68}Zr_{0.32}O_2$ under conditions where vacancy creation is unlikely (room temperature, r.t.). Such high r.t. OSC is not observed when either CO is used as reductant or when the OBC method is employed. The evidence suggests that this dynamic-OSC may be associated with the phenomenon of spillover. This opens the possibility that spilled-over H_2 can be a contributing factor to OSC measurements even at higher temperatures. The presence of H_2 in exhaust effluent in a ratio of *ca.* 1:3 with respect to CO[3] makes this finding a potentially important piece of information.

0.58 wt% Pt/$Ce_{0.68}Zr_{0.32}O_2$ and 0.53 wt% Pt/CeO_2 were prepared and supplied by RHODIA as part of the CEZIRENCAT network.[4] 0.5 wt% Pt/γ-Al_2O_3 (γ-Al_2O_3: Alfa products) was prepared using $Pt(NH_3)_2(NO_2)_2$ as precursor. An *in situ* oxidising cleaning procedure[5] (heating in flow of O_2 at 823 K for 1 h) was applied before all experiments, giving a sample designated as fresh. Redox-aged sample was prepared as follows: reduction up to 1273 K in 5 % H_2 in Ar (25 ml min^{-1}), holding at 1273 for 15 min, flushing in Ar at 1273 K; slow cooling to 700 K; re-oxidation at 700 K and cooling to 423 K in 5% O_2 in Ar; and, finally, cooling to r.t. in Ar (60 ml min^{-1}). Quantitative dynamic-OSC measurements were performed by increasing the temperature in a stepwise manner and, during the isothermal steps (60 min), alternately pulsing every 70 s H_2 (500 or 100 μl, H_2-OSC) or CO (100 μl, CO-OSC) and O_2 (250 or 100 μl) over the sample (20 mg, maintained in a flow of Ar of 25 ml min^{-1}). OSC was measured using a thermal conductivity detector as the uptake of O_2 from the O_2 pulse. Steady-state values are reported. When CO was used as the reducing agent, the evolved CO and CO_2 were separated on a Porapak Q column. TPR-MS profiles were obtained up to 1273 K as above reported for redox-ageing. OBC measurements were carried out as reported previously.[2] Hydrogen chemisorption measurements were conducted at 298 and 195 K.[6]

The redox behaviour was first investigated by means of the TPR-MS technique. The TPR profiles (not reported) of fresh and redox-aged Pt/$Ce_{0.68}Zr_{0.32}O_2$ showed single reduction features centred around 500 and 400 K, respectively. This behaviour is fairly consistent with a recent report[6] and is attributed to an initial reduction of supported PtO, which in turn results in support reduction through spillover of hydrogen species. The degree of reduction, *i.e.* the overall transferable oxygen, was measured by O_2 uptake at 700 K after the TPR experiment as previously reported.[6] An O_2 uptake of 20 ml g^{-1} was obtained for both fresh and redox-aged samples.

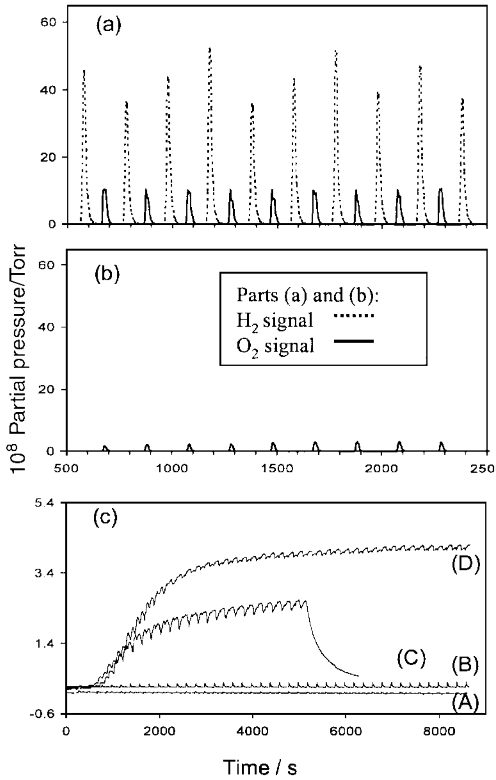

Fig. 1 H_2-OSC measured at r.t. H_2 (*m/z* = 2) and O_2 (*m/e* = 32) profiles over fresh/reduced at 500 K Pt/Al_2O_3 (for clarity this trace is displaced) (a) and Pt/$Ce_{0.68}Zr_{0.32}O_2$ (b), and water production (*m/e* = 18) (c) over: (A) fresh/reduced 500 K Pt/Al_2O_3, (B) fresh Pt/$Ce_{0.68}Zr_{0.32}O_2$; (C) redox-aged Pt/$Ce_{0.68}Zr_{0.32}O_2$, reaction stopped at 5000 s; (D) fresh/reduced 500 K Pt/$Ce_{0.68}Zr_{0.32}O_2$. MS was tuned to enhance the sensitivity to H_2 compared to O_2. 200 mg of sample and loop volumes of 1 ml were employed.

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Table 1 Oxygen storage and chemical/textural characterisation of the Pt/$Ce_{0.68}Zr_{0.32}O_2$ catalyst

Sample	Oxygen storage capacity[a]/OBC[b]				H_2 chemisorption[c]			N_2 physisorption Surface area/m^2 g^{-1}
						H_2 update/ml g^{-1}		
	T/K	H_2-OSC[d]/ ml O_2 g^{-1}	CO-OSC/ ml O_2 g^{-1}	OBC (%)	T/K	0 Torr	20 Torr	
Pt/$Ce_{0.68}Zr_{0.32}O_2$ fresh/reduced	r.t.	6.3	0.0		298	6.78	7.09	100
	373	7.1	0.7		193	0.31	0.37	
	473	7.5	1.7					
	673	8.1	> 2.6	4				
	773	8.9	> 2.6	20				
Pt/$Ce_{0.68}Zr_{0.32}O_2$ redox-aged	r.t.	2.8	0.0		298	2.62	2.76	30
	373	4.1	0.0		193	0.09	0.09	
	473	9.1	0.1					
	673	9.8	> 2.6	8				
	773	11.6	> 2.6	21				
Pt/CeO_2 fresh/reduced	r.t.	4.2			298	3.88	4.02	88
					193	0.30	0.31	
Pt/CeO_2 redox-aged	r.t.	0.6			298	0.47	0.45	7
					193	0.04	0.04	
Pt/Al_2O_3 fresh/reduced	r.t.	0.3			298	0.28	0.30	99
					193	0.26	0.27	

[a] Quantitative analysis using TCD, standard deviation ± 0.4 ml O_2 g^{-1}. Steady state values measured as O_2 uptake (ml g^{-1}). For CO / O_2 experiments, an OSC of 2.6 ml O_2 g^{-1} corresponds to a maximum O_2 uptake using the experimental setup described in the text. [b] OBC (%): [100 ($A_{NA} - A_A$)/A_{NA}]; A_{NA}: area under non-attenuated pulse; A_A: area under the attenuated pulse. Pulse volume 0.25 ml of 5% O_2 in He. [c] Sample reduced at 500 K for 1 h, followed by evacuation at 673 K for 4 h. A range of H_2 pressure of 2 –20 Torr was employed. Adsorbed volumes were determined by extrapolation to zero pressure of the linear part of the adsorption isotherm (0 Torr). Cumulative H_2 adsorption at $p = 20$ torr is also given. [d] Using loop volumes of 100 µl for H_2 and O_2 a full O_2 uptake, *i.e.* 2.6 ml O_2 g^{-1}, was observed in all experiments.

Fig. 1 compares the H_2-OSC behaviour at r.t. of Pt/$Ce_{0.68}Zr_{0.32}O_2$ and Pt/Al_2O_3. Table 1 summarises quantitative OSC measurements and also some characterisation data. Fresh/reduced Pt/Al_2O_3 does not exhibit appreciable H_2-OSC at r.t. In contrast, a very high consumption of both H_2 and O_2 is observed over fresh/reduced Pt/$Ce_{0.68}Zr_{0.32}O_2$, indicating the crucial role of the $Ce_{0.68}Zr_{0.32}O_2$ in providing sites for the storage process. Water evolution is also observed in the latter case [Fig. 1(c), trace D], ruling out any kind of chromatographic effect. Negligible water production is observed over the fresh Pt/$Ce_{0.68}Zr_{0.32}O_2$, [Fig. 1(c), trace B], indicating that reduced Pt is necessary to promote hydrogen activation. In an attempt to establish the origin of this high r.t. H_2-OSC, H_2 chemisorption measurements were carried out on the Pt/$Ce_{0.68}Zr_{0.32}O_2$ at 193 and 298 K. Spilling of H_2 at 193 K is negligible allowing determination of H/Pt ratios.[7] 0.31 ml H_2 g^{-1} are adsorbed at 193 K which correspond to a dispersion of 94% upon assumption of H : Pt = 1 : 1 stoichiometry. The low H_2 uptake indicates that titration of hydrogen/oxygen adsorbed on the metal cannot be responsible for the observed H_2-OSC. Conversely, the amount of H_2 adsorbed/spilled over the support at 298 K is of the same order of magnitude of the values of H_2-OSC, suggesting a relevant role of the spillover phenomena in the oxygen storage. A higher relative pressure of H_2 during the H_2 pulse and presence of H_2O could account for the high values of O_2 uptake compared to the spilt H_2 detected in the chemisorption measurement. In fact, H_2 and O_2 consumption close to stoichoimetry is measured in the H_2-OSC experiment. Redox-ageing decreases both the surface area and the amount of adsorbed H_2 at 298 K by a factor of three. The H_2-OSC decreases by a factor of two. The important role of hydrogen spillover in giving high H_2-OSC at r.t. is supported by the data reported for Pt/Al_2O_3 and Pt/CeO_2. In particular, very small r.t. H_2-OSC is observed for the latter catalyst after redox-ageing, when spillover is negligible.

The comparison with CO as reducing agent and the OBC measurements is striking. Irrespectively of the pre-treatment, fresh/reduced or recycled, significant CO-OSC is observed only at and above 473 K, while OBC starts being significant at 673 K. In both these experiments, the reduction process may be envisaged as a measure of the oxygen diffusion towards the surface where it is removed either by interaction with CO or simple desorption, provided that surface processes are not rate limiting.[8] The very high H_2-OSC clearly points to a crucial role of H_2 in affecting the redox properties of these systems at low temperatures.

In conclusion, there is a dramatic dependence of the results obtained on the nature of the reducing environment with significantly high dynamic-OSC particularly apparent at low temperatures using H_2. At r.t. spillover phenomena seem to be a dominant factor. The implications of these findings need to be carefully considered when the results of such measurements are extended to the extremely complicated conditions encountered in three-way catalysis.

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