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Reactivation of aged model Pd/$Ce_{0.68}Zr_{0.32}O_2$ three-way catalyst by high temperature oxidising treatment†

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A deactivated (aged under redox-cycled model TWC feedstream) Pd/$Ce_{0.68}Zr_{0.32}O_2$ catalyst is remarkably reactivated when subjected to a high temperature oxidising treatment whereas this effect is only marginal for Pd/Al_2O_3, which indicates the key role of such treatment in restoring the Pd–$Ce_{0.68}Zr_{0.32}O_2$ interactions leading to highly active catalysts.

Extremely demanding limits for durability (life-time up to 120 000 miles, equivalent to 10 years' vehicle use) and activity (conversion over 98%) have been set up by US TIER2 and European legislation on the abatement of automotive pollution. The state of the art automotive three-way catalysts (TWCs) contain NMs (noble metals: Pt, Rh and Pd) supported on high surface area CeO_2–ZrO_2 mixed oxides and Al_2O_3; which are in turn supported on honeycomb-type supports.[1] These systems show very high catalytic efficiency when fresh, whereas the issue of deactivation has received relatively scant attention. Catalyst poisoning due to Zn and P contained in the engine oil and thermal sintering of Al_2O_3, CeO_2–ZrO_2 and the supported metal particles represent the major pathways for the deactivation processes.[2,3] Thermally stable CeO_2–ZrO_2–Al_2O_3 composites have been suggested as a suitable way for preventing sintering of these components.[4,5] In contrast indications of how to efficiently prevent NM sintering are missing. Accordingly, strategies to stabilise nano-dispersed metal particles have been extensively investigated.[6,7] Here we show that a high temperature oxidative treatment of an aged Pd/$Ce_{0.68}Zr_{0.32}O_2$ is capable of restoring activity levels comparable to the fresh catalyst. This effect is particularly noticeable because the aging induces a strong sintering of the catalyst. The use of $Ce_{0.68}Zr_{0.32}O_2$ as support plays a fundamental role in this mechanism.

Pd 0.64 wt%/$Ce_{0.68}Zr_{0.32}O_2$ (BET surface area 104 $m^2\ g^{-1}$) indicated as PdCZ Fresh, was supplied by Rhodia. A reference Pd 0.51 wt%/Al_2O_3 (BET surface area 148 $m^2\ g^{-1}$) catalyst was also employed. Catalytic tests and ageing treatments were performed using model exhaust oxidising and reducing mixtures: C_3H_6, 900 ppm; NO, 900 ppm; CO_2, 10%; H_2O, 10% and N_2 to balance; CO, 1.6% and O_2, 0.465% were employed for the reducing mixture (air-to-fuel (A/F) = 14.13); CO, 0.4% and O_2, 1.26% for the oxidizing mixture (A/F = 15.17). Notice that A/F = 14.63 at stoichiometry. The accelerated ageing procedure[8] was performed by heating at 8 K min^{-1} from 373 to 1173 K and ageing for 5 hours at 1173 K under the above quoted model exhaust mixtures using a cycling frequency of 0.0055 Hz. The samples were cooled to 423 K either under the cycled feedstream (cycling frequency of 0.0167 Hz) (sample Aged-Cyc) or under the oxidising reaction mixture (sample Aged-Ox) and then to room temperature in N_2 flow. The ageing conditions, 1173 K under a redox cycling mixture, were chosen to ensure strong sintering of both Pd and $Ce_{0.68}Zr_{0.32}O_2$ support while avoiding extensive NM encapsulation.[9] Before testing, the catalysts were reduced for 1 hour at 573 K in a H_2 (5%)/N_2 flow. Light-off experiments were conducted under cycled conditions (1 Hz) using a space velocity of 125 000 h^{-1}. Dynamic oxygen storage and release capacity using CO as reducing agent (CO-OSC) was measured as reported previously.[10] H_2O (10%) was added to the carrier gas flow (Ar) through a saturator at 319 K. HREM, SEM-EDS, temperature programmed desorption, reduction and oxidation (TPD, TPR, TPO), XRD and CO and H_2 chemisorption studies were performed as already described.[4,11]

The effects of ageing procedures on PdCZ and Pd/Al_2O_3 are summarised in Table 1. Despite the fact that an equal degree of sintering was experienced by the PdCZ catalysts (BET area drops from 104 $m^2\ g^{-1}$ (fresh) to 30 $m^2\ g^{-1}$ in both Aged-Cyc and Aged-Ox) and equal pre-treatment (reduction at 573 K), there is a remarkable difference in terms of catalytic efficiency of the two aged catalysts: PdCZ Aged-Ox features a conversion efficiency that is comparable to that of PdCZ-Fresh.

Both TPD and TPO experiments performed on the PdCZ Aged-Cyc and Aged-Ox samples revealed evolution of traces of adsorbed H_2O and CO_2 consistent only with some unavoidable sample contamination upon exposure to air. This rules out the presence of surface carbonaceous residuals as responsible for the deactivation of the PdCZ Aged-Cyc compared to Aged-Ox. Noteworthy is the decrease of CO and O_2 conversion efficiency induced by the Aged-Cyc procedure which leads to an increase of light-off (50% conversion) temperature, T_{50}, by about 150–160 K compared to Aged-Ox. Re-oxidation of the Aged-Cyc PdCZ at 1173 K leads to significant recovery of the activity, indicating the crucial role of the final oxidising part of the ageing procedure in preventing the deactivation. Only a minor difference in the activity with the ageing procedure was found for a Pd/Al_2O_3 catalyst, which indicates the critical role of the $Ce_{0.68}Zr_{0.32}O_2$ support in favouring this unexpected regeneration of the catalyst induced by the "Ox" part of the ageing procedure.

A bifunctional reaction mechanism is typically invoked for the NM/CeO_2-based catalysts where the activity of the NM is promoted by the support, and particularly by its highly efficient redox capability (OSC).[12] Dynamic CO-OSC was measured (Fig. 1, Table 1) to assess the effects of the support. It shows that: i) CO-OSC, *i.e.* "support mediated" CO oxidation by O_2, is marginally affected by addition of water whereas occurrence of water gas shift reaction (WGSR) was detected, as revealed by concurrent H_2 production; ii) both CO-OSC and WGSR occur only to a small extent over PdCZ Aged-Cyc, iii) high CO-OSC/WGSR activity is observed over the PdCZ Aged-Ox; and remarkably iv) high temperature oxidation (1173 K) of PdCZ Aged-Cyc restores high activity in both CO-OSC and WGSR. Thus these data confirm that the "Ox" treatment has restored the promoting capabilities of the $Ce_{0.68}Zr_{0.32}O_2$ support. Consistently, HREM revealed a statistically significant difference between Aged-Ox and Aged-Cyc $Ce_{0.68}Zr_{0.32}O_2$ nanocrystal morphology (Fig. 2). Sharply defined nano-facets are typically found in Aged-Cyc whereas rounded, less-faceted morphology was detected in Aged-Ox sample. No Pd particles could be detected by HREM.

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† Electronic supplementary information (ESI) available: XRD data. See http://www.rsc.org/suppdata/cc/b3/b308321g/

Table 1 Effects of ageing procedures on the light-off temperature, T_{50}, for CO, NO and C_3H_6 conversion, CO-OSC, BET surface areas and chemisorption properties of $Pd/Ce_{0.68}Zr_{0.32}O_2$ and Pd/Al_2O_3 catalysts.

	T_{50} / K			Dynamic CO-OSC[a] (without H_2O)			
Catalyst	CO	NO	C_3H_6	O_2 uptake/ml g^{-1}	BET Area/ m^2 g^{-1}	H/Pd[b]	CO/Pd[b]
PdCZ Fresh	406	549	523	6.3 (7.1)	104	9.1	0.64
PdCZ Aged-Ox	413	541	530	4.1 (3.5)	30	1.1	0.14
PdCZ Aged-Cyc	588	628	598	1.8	30	0.10	0.06
PdCZ Aged-Cyc-Ox[c]	508	610	540	4.1			
PdAl Aged-Ox	567	584	569	< 0.4	123	0.09	0.08
PdAl Aged-Cyc	589	608	588	< 0.4	119	0.03	0.04

[a] CO-OSC measured as O_2 uptake at 573 K. Note that non stoichiometric values of CO_2 produced/CO consumed in comparison to O_2 consumed were observed in the presence of H_2O due to concurrent H_2 formation *via* WGSR. H_2 production was confirmed by MS (Fig. 1). For comparison O_2 uptakes of 0.9 and < 0.4 ml g^{-1} are observed respectively over fresh $Ce_{0.68}Zr_{0.32}O_2$ and Pd/Al_2O_3. An uptake of 0.5 ml O_2 g^{-1} is calculated for the Pd/PdO redox process assuming that all Pd is involved. Standard deviation 0.4 ml O_2 g^{-1}. [b] Sample reduced at 573 K; measured in the range of pressures 2–20 torr to minimize formation of Pd hydride and CO adsorption on the support; almost no CO_2 evolution was detected following the O_2 pulse in the CO-OSC experiments over these samples in agreement with negligible CO adsorption over the support. [c] Sample oxidized at 1173 K for 15 min in the oxidizing mixture and then cooled to 423 K in the same mixture or (CO-OSC) oxidized by pulses of O_2 (250 μl every 70 s) at 1173 K for 5 h and then cooled under O_2 pulses.

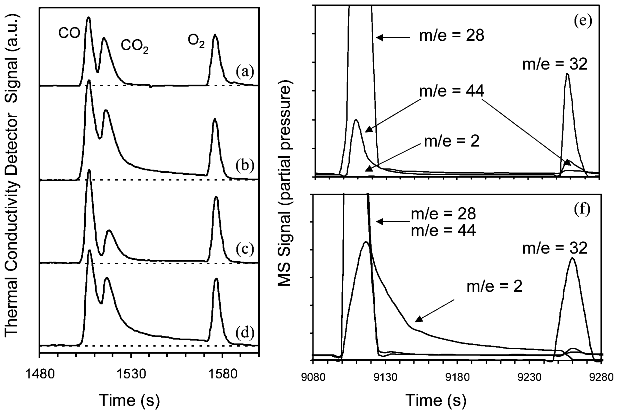

Fig. 1 Effect of H_2O addition and ageing procedures on dynamic CO-OSC at 673 K over $Pd/Ce_{0.68}Zr_{0.32}O_2$: (a) Aged-Ox in the absence of H_2O, (b) Aged-Ox in the presence of H_2O, (c) Aged-Cyc in the presence of H_2O, (d) Aged-Cyc-Ox (sample Aged-Cyc from experiment (d) oxidized *in situ* at 1173 K) in the presence of H_2O, (e) Aged-Cyc-Ox in the absence of H_2O, (f) Aged-Cyc-Ox in the presence of H_2O. The tailing of peaks in (b)–(d) is due to H_2 evolution (WGSR) that occurs under the CO and CO_2 peaks, as revealed by the MS traces (compare (e)–(f)).

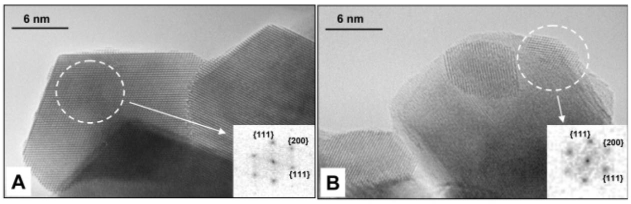

Fig. 2 HREM micrograph of Pd/ $Ce_{0.68}Zr_{0.32}O_2$: (A) Aged-Cyc and (B) Aged-Ox. In the insets DPP patterns showing the presence of *t*-phase.

Pd redispersion[13] over the support, induced by the "Ox" treatment that affects the delicate – support-dependent – PdO/Pd equilibrium,[14] can be invoked as one of the factors for this catalytic behaviour: evidence for some Pd redispersion were found by XRD.[15] However, the small CO/Pd values measured over the two systems suggest similar Pd exposed area, particularly when compared to the fresh sample. Both TPR profiles and H_2 chemisorption showed much more efficient low temperature H_2 activation and spillover in the PdCZ Aged-Ox compared to PdCZ Aged-Cyc. This cannot be associated with a simple Pd redispersion effect, but, as indicated by the HREM, CO-OSC and TPR studies, by a simultaneous occurrence of chemical and nano-structural changes affecting both the metal phase and, particularly, the mixed oxide support. CeO_2–ZrO_2 supports play a key role in these phenomena.[11,12]

In summary, the observed critical importance of the ageing/reactivation conditions, and, particularly, of the high temperature oxidation, in maintaining high catalytic efficiency of these Pd-CZ materials is relevant not only to TWCs but may also suggest novel strategies for development of efficient and durable catalytic systems for reactions related to on-board H_2 production from fuels, *e.g.* fuel-reforming and WGSR, where catalyst deactivation is an important issue.[16]

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Notes and references

1 E. S. J. Lox and B. H. Engler, Environmental Catalysis – Mobile Sources in *Environmental Catalysis*, eds. G. Ertl, H. Knozinger and J. Weitkamp, Wiley-VCH, Weinheim, 1999, pp. 1–117.
2 C. Larese, F. C. Galisteo, M. L. Granados, R. Mariscal, J. L. G. Fierro, M. Furio and R. F. Ruiz, *Appl. Catal. B: Environ.*, 2003, **40**, 305.
3 J. Kaspar, P. Fornasiero and N. Hickey, *Catal. Today*, 2003, **77**, 419.
4 R. Di Monte, P. Fornasiero, J. Kaspar, M. Graziani, J. M. Gatica, S. Bernal and A. Gomez Herrero, *Chem. Commun.*, 2000, 2167.
5 A. J. Zarur and J. Y. Ying, *Nature*, 2000, **403**, 65.
6 A. T. Bell, *Science*, 2003, **299**, 1688.
7 Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto and N. Hamada, *Nature*, 2002, **418**, 164.
8 J. R. Gonzalez-Velasco, M. A. Gutierrez-Ortiz, J. L. Marc, J. A. Botas, M. P. Gonzalez-Marcos and G. Blanchard, *Ind. Eng. Chem. Res.*, 2000, **39**, 272.
9 G. W. Graham, H. W. Jen, W. Chun and R. W. McCabe, *Catal. Lett.*, 1997, **44**, 185.
10 N. Hickey, P. Fornasiero, J. Kaspar, M. Graziani, G. Blanco and S. Bernal, *Chem. Commun.*, 2000, 357.
11 J. M. Gatica, R. T. Baker, P. Fornasiero, S. Bernal and J. Kaspar, *J. Phys. Chem. B*, 2001, **105**, 1191.
12 A. Trovarelli, *Catal. Rev. – Sci. Eng.*, 1996, **38**, 439.
13 N. M. Rodriguez, S. G. Oh, R. A. Dallabetta and R. T. K. Baker, *J. Catal.*, 1995, **157**, 676.
14 R. J. Farrauto, J. K. Lampert, M. C. Hobson and E. M. Waterman, *Appl. Catal. B: Environ.*, 1995, **6**, 263.
15 Compare supplementary material†.
16 D. L. Trimm and Z. I. Onsan, *Catal. Rev. – Sci. Eng.*, 2001, **43**, 31.