

Redox behaviour of Pd-based TWCs under dynamic conditions: analysis using dispersive XAS and mass spectrometry†

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The redox behaviour of Pd-based TWCs is studied under dynamic, cycling conditions (e.g. lambda oscillations) on a 50 millisecond scale. Pd temporal response to gas inlet mixture changes is governed by metal-promoter interface properties.

Three way catalysts (TWCs) are used to control pollutant emissions from gasoline engine powered vehicles. Pd-based cerium-promoted systems have become a widely used TWC standard for the automobile industry.¹ For such systems, the nature and properties of the metal–promoter interface appear to be key factors for the optimization of the catalytic properties.^{1,2} Metal (Pd) and promoter (Ce) characteristics have been extensively studied under light-off or isothermal conditions but much less is known for cycling conditions, typical of TWC operation, in which the stoichiometry of the gas atmosphere (the oxidant to reducing molecule balance) oscillates around the stoichiometric point with a frequency of ca. 1–3 Hz.^{1–3} To contribute to this last point, here we describe a time resolved XAS (X-Ray Absorption Spectroscopy) study of the active noble metal component in real, operating conditions. It must be noted that the Pd chemical state is one of the key parameters governing system catalytic behavior.³

Dispersive XAS provides a route to both structural and electronic property determinations in catalysts for reactions occurring in a timescale of under a second.⁴ Here we recorded XANES (X-Ray Absorption Near Edge Structure) spectra at the Pd K-edge on ID24 at ESRF using a plug-flow reactor configuration which ensures that meaningful spectroscopic data are obtained.⁵ Three catalysts were used, all containing 1 wt.% Pd but supported on three different supports: alumina (PdA), 10 wt.% CeO₂ on alumina (PdCA), and 10 wt.% CeZrO₄ on alumina (PdZCA). These have been fully characterized elsewhere⁶ and allow the analysis of the relationship between the promoter nature and the noble metal performance. Samples were sieved to a fraction between 100–150 μm, calcined *in situ* under a diluted oxygen flow at 723 K and subjected to a 0.1% C₃H₆ + 0.1% NO + 1% CO (He balance) flowing gas mixture with different concentrations of O₂ (1.10–0.49%) at 723 K, with a GHSV ca. 80 000 h⁻¹. The redox power of the gas mixture is typically determined by a lambda parameter; λ equals 1 for a stoichiometric mixture and is greater (smaller) than 1 for net oxidising/lean (reducing/rich) mixtures (see ESI†). Detection of XAS was made

using a Peltier cooled, phosphor masked Princeton CCD camera, with typical acquisition time of 50 ms. XAS measurements were made at the gas inlet end of the catalysts bed and consisted in the accumulation of 15 spectra. The horizontal focus of the Si(311) polychromator mounted in a Bragg configuration was 500 μm (FWHM). The composition of the gas stream was measured at the outlet of the reactor with a mass spectrometer (0.5 s).

It is well known that noble metal oxidation (under a net-oxidising exhaust atmosphere) of previously reduced entities (obtained on contact with exhaust gas mixtures with λ ≤ 1) is a rather slow process;⁷ accordingly, full bulk oxidation was completed with our XAS set-up (λ ca. 1.01) only after 10 min. This means that the core of Pd particles must remain essentially in a zero-valent state when going from rich to lean conditions under cycling operation in real conditions, assuming Pd(0) as the initial state of the noble metal after light-off (the predominance of the reduced Pd oxidation state mainly depends on gas inlet composition and operation temperature).⁶ A combined XAS/Raman/IR study, adding surface sensitivity to our data, would be needed to address in a more complete way the Pd behavior in the corresponding rich to lean step change. So, XAS analysis with sub-second sampling was restricted to characterising the transient response of Pd to a gas mixture step-change from λ 1.01 to 0.98, simulating a typical oscillation from lean to rich conditions.^{1–3} The normalised XANES spectra obtained for the three samples are given in the supplementary information.† The edge position of the initial spectrum (Fig. 1; Table 1) is typical of an oxidised Pd(II)-like species while the shape may be influenced by the presence of hydrocarbon-derived adsorbed species.⁸ A small shift (as measured by the derivative spectrum) to lower energy is detected from PdA to PdZCA, indicating an increasing contribution from reduced Pd species. The final spectrum edge position (Table 1) indicates Pd(0) to be the dominant species but again the XANES shape may be affected by adsorbed species.⁸ A small red shift is visible for the 4f Continuum Resonance (CR), located at ca. 24.390 eV, for PdZCA with respect to the other two samples (Fig. 1B); this red shift indicates an increase of the Pd–Pd nearest distance most likely associated with the dissolution of C atoms on the Pd fcc structure and the incipient formation of a carbide phase under rich conditions.^{8,9} Differences between samples can be ascribed to a different Pd(0) particle size and morphology.⁶

Factorial analysis unequivocally shows the presence of two chemical species for each sample throughout the experiment (see ESI† for details concerning statistical test results). As can be deduced from the previous paragraph, these two Pd chemical species must be Pd(II), dominating the initial XANES spectrum, and Pd(0), the only species present at the end of the step change.

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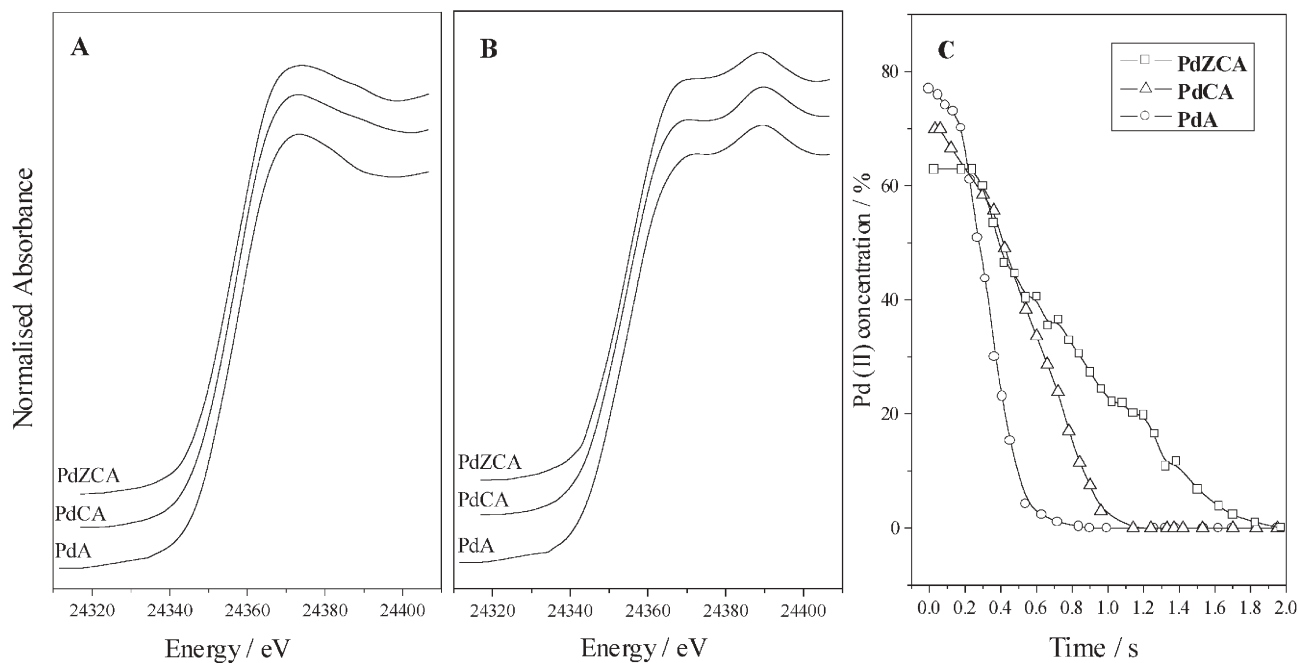


Fig. 1 Pd K-edge results: (A) initial, (B) final species XANES spectra, and (C) Pd(II) concentration profiles through the step experiment.

Table 1 Energy position (eV) of the edge and 4f Continuum Resonance (CR) present in XANES spectra displayed in Fig. 1. Values relative to the Pd foil

Sample	Series (Fig. 1)/Condition	Edge	4f CR
PdA	A/lean	4.3	—
	B/rich	0.0	39.5
PdCA	A/lean	4.0	—
	B/rich	0.0	39.6
PdZCA	A/lean	3.7	—
	B/rich	0.0	37.9

This can be further confirmed by using iterative target testing procedures.⁸ The statistical analysis allows the quantification of the Pd oxidation state evolution (Fig. 1C). Although the initial Pd(II) concentration is not 100% (this justifies the edge-shift displayed in Table 1 for the initial XANES spectrum—Series A), the main point is that the nature of the support affects the temporal response of Pd to the gas mixture step-change. While PdA shows a quick and sigmoidal-like curve of reduction, the presence of a Ce-containing promoter retards the reduction of the noble metal. Also, the nature of the promoter, CeO₂ vs. CeZrO₄, influences the response; a significant stabilisation of the oxidized Pd state is achieved in presence of the novel CeZrO₄ promoter.

The corresponding gas composition changes allow the interpretation of the solid response. Fig. 2 displays the gas composition at the reactor outlet for the samples. Blank tests with alumina ensure that the profiles shown in Fig. 2 display the catalytic response of the solids. The gas phase step change from lean ($\lambda = 1.01$) to rich ($\lambda = 0.98$) conditions increases NO and decreases CO conversion. As well known, CO is more sensitive than the hydrocarbon to lambda oscillations;^{3,10} and thus differences among samples become most apparent in the corresponding profiles. Fig. 3 compares Pd(II) and CO concentration profiles through our step experiment. This latter molecule is oxidized in the metal-promoter interface with the help of oxygen atoms from the

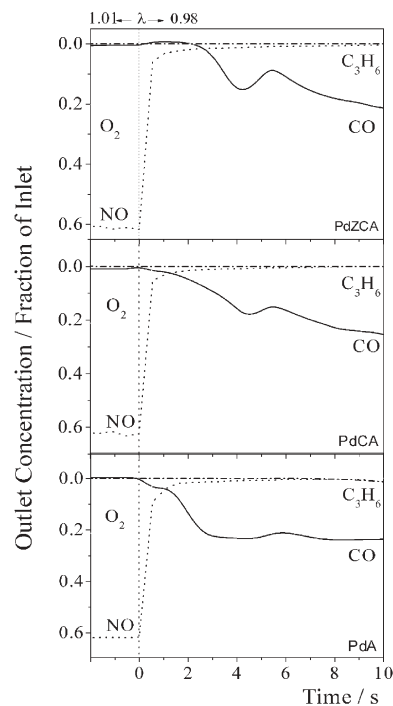


Fig. 2 MS signals during the step change of gas atmosphere for the Pd-containing samples.

promoter.^{2,6,11} The larger redox potential of CeZrO₄ vs. CeO₂ at the experiment temperature is customarily ascribed to the participation of bulk anions, in addition to the surface ones, characteristic of CeO₂.^{2,3} Considering the different time resolution of the XAS/MS experiments (which would justify the existence of an apparent small shift in the CO profile response with respect to the Pd(II) concentration profile) Fig. 3 would indicate that CO conversion decreases for PdA when no more PdO is detected while

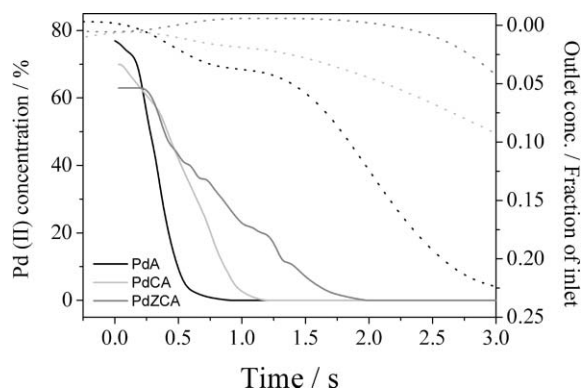


Fig. 3 Pd(II) (full line) and CO MS signal (dotted line) during the step change.

a conversion near 100% is detected above the full reduction of the Pd phase for PdCA but particularly for PdZCA. The comparative analysis of these latter two samples, which have a similar weight percentage of the promoter (and thus, a smaller number of Ce atoms in the case of CeZrO_4), shows that Zr presence in the oxide promoter is rather efficient in enlarging the oxygen transfer under dynamic conditions, smoothing the catalytic effect originating from the lack of gas phase oxygen (e.g. the loss of CO conversion) in reducing/rich conditions.

On the other hand, if the reduction of the catalyst starts at the metal–promoter interface, before extending the process to the noble metal and, finally, to the promoter areas far from the interface,¹² the differences observed in the noble metal response can be interpreted as originating from different kinetics of Pd reduction. In fact, a kinetic analysis of the Pd reduction data (not shown) displays a different reaction order with respect to the Pd oxidation state in presence (ca. 0.5) and absence (ca. 1.5) of the promoter phase, with smaller differences between the two promoted, PdCA and PdZCA, systems studied. These results are relevant in the sense that the Pd oxidation state defines the behavior of the catalyst, particularly at low-medium temperature; the presence of oxidised palladium species appears critical for adequate activity in hydrocarbon oxidation and this in turn influences the behavior of the system in the elimination of other (CO, NO) pollutants.^{13,14} Such a behavior becomes crucial during the warm up of the TWC system, where the majority of the hydrocarbon emissions is produced.¹⁵ The presence of carefully engineering noble metal–promoter contacts may thus be envisaged as a new way to improve the behaviour of the catalyst during the

cold start period. This would compete with or complement alternative procedures based on the use of different noble metal particle sizes (which are typically associated with the metal fractions supported on alumina and the cerium-containing promoter), adequately selected to maximize activity in oxidation (hydrocarbon) or reduction (NO) elimination reactions.^{3,15}

In brief, we believe that the experimental results outlined are direct evidence for the oxygen transfer effect occurring at the metal–promoter interface of TWC systems under dynamic conditions (e.g. lambda oscillations), and establish a procedure to quantify it.

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