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Metal–promoter interface in Pd/(Ce,Zr) O_x /Al₂O₃ catalysts: effect of thermal aging

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Abstract

The behavior of Pd three-way catalysts promoted with Ce–Zr mixed oxides and supported on alumina subjected to thermal degradation treatments has been examined during light-off tests under stoichiometric $CO+NO+O_2$. Attention was paid to the region of aging temperature 1273–1373 K, where phase segregation of the ceria–zirconia promoter occurs. Characterization of the samples was performed using X-ray diffraction and Raman spectroscopy. In situ XANES/DRIFTS studies of the Pd chemical state at the surface and in the bulk of the materials were conducted to determine the noble metal response to the gas atmosphere during light-off. Electron paramagnetic resonance was used to analyze the promoter surface and to study the redox response of the materials in contact with the reactant gases. Thermal degradation appears to sinter both the noble metal and promoter components of the catalyst but also stabilizes oxidized Pd entities in contact with the promoter prior to the occurrence of the Ce–Zr phase segregation reaction. Additionally, it enriches the promoter surface in the lanthanide cation. The influence of these physicochemical phenomena on the catalytic properties of the Pd-based TWC is discussed. © 2003 Elsevier Inc. All rights reserved.

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1. Introduction

Regulations concerning automotive emissions are becoming more stringent in the most advanced countries (see, as an example, Directive 98/69/EC of the European Parliament), driving the industry to an effort to diminish the environmental impact of pollutants emitted by vehicles. In this context, the development of more efficient and resistant catalytic converters, able to maintain maximum durability while decreasing pollutant emissions to minimum levels, is necessary. Three-way catalysts (TWC) constitute, up to now, the most satisfactory and efficient solution to diminish pollutant emissions from gasoline-engine-powered vehicles [1,2]. These mainly act through simultaneous oxidation of carbon monoxide (CO) and hydrocarbons (HC) and reduction of nitrogen oxides (mainly NO). In recent years, typical TWC formulations have included Pd as the active metal, fluoritetype oxides, such as ceria-zirconia, as promoters, and alumina as support, as well as other minor components, mainly present in order to enhance thermal stability and/or resis-

* Corresponding author. *E-mail address:* m.fernandez@icp.csic.es (M. Fernández-García). tance to poisons [1,3]. The use of Pd in TWCs is restricted by the presence of lead in the fuel, which may strongly deactivate the noble metal by poisoning [4]. On the other hand, ceria–zirconia (CZ) materials having Ce:Zr atomic ratios close to 1 and tetragonal or pseudo-cubic structures replace the classical ceria component due to their better thermal and oxygen-handing properties [5,6].

During operation, TWCs display a general loss of catalytic activity by the effect of a diversity of phenomena, which include fouling and mechanical, chemical, and thermal effects [7]. Among them, it is well established that thermal ones are the major problem due to their irreversible character [1,8,9]. The latter category comprises a series of phenomena affecting the different components of TWCs. As is already well known [1-6], a key factor limiting thermal aging effects is maintenance of catalyst surface area, a fact directly related to the stabilization of the gamma alumina particle size and, more importantly, to the inhibition/delay of phase transition(s) leading to theta or delta polymorphs and finally to the low-surface-area alpha (alumina) phase. Among the TWC components, the CZ promoter is known to help in stabilizing alumina; however, for Ce:Zr atomic ratios close to 1, this component may suffer phase segregation above 1273 K, leading to a significant decrease in catalyst surface area [5,6]. Additionally, the CZ catalytic role may be altered by this phase segregation reaction, as significant growth of promoter particle size and strong modification of its surface composition and redox properties have been reported [5,6]. Thermal aging can also influence the number of noble metal sites as a consequence of Pd sintering and/or encapsulation [9–11], affecting catalytic activity mainly by the concomitant loss of metal–promoter interface sites [1–4, 9–11]. All of these phenomena are interrelated but to a large degree depend on the interface interactions between the noble metal and promoter as well as between the promoter and the alumina carrier, which are in turn largely responsible for the stabilization of the corresponding components during aging of TWCs.

Although thermal aging has been also studied in classical, ceria-promoted automotive catalysts [12], much less is known about the physical phenomena occurring in the more complex case of CZ-promoted TWCs. As above mentioned, a basic understanding of the interface effects between components may help to understand the chemicophysical phenomena associated with the thermal aging and their catalytic consequences. To this end, we have studied a typical Pdbased TWC, paying attention to the effects of thermal degradation in the high-temperature region 1273-1373 K, where experience shows the occurrence of an abrupt degradation of the CZ component properties [5,6]. A model stoichiometric $CO + NO + O_2$ mixture will be used to test the effect of aging in two of the main toxic exhaust emission gases, CO and NO [1-3]. In an attempt to separate some of the above mentioned effects, model systems in which Pd has been impregnated over an aged CZ component supported on alumina have been included in the study. These Pd-TWC systems have been analyzed using a multitechnique approach involving XRD, TEM-XEDS, Raman, and EPR for catalyst characterization and catalytic activity in combination with in situ DRIFTS and XANES techniques to evaluate the catalytic performance in the $CO + NO + O_2$ reaction.

2. Experimental

2.1. Catalyst preparation

A ceria–zirconia/alumina support (CZA) of 10 wt% of mixed oxide, expressed as $Ce_{0.5}Zr_{0.5}O_2$, was prepared using γ -Al₂O₃ Condea Puralox as carrier and an adaptation of the microemulsion method used previously for preparing the unsupported oxide, hereafter called CZ [13]. Full details of the procedure can be found elsewhere [14]. After drying overnight at 393 K, portions of these alumina, ceria–zirconia, and ceria–zirconia/alumina supports (hereafter called A, CZ, and CZA, respectively) were calcined at 773 K for 2 h under dry air flow or aged under air by a treatment at 1273 (CZA-m1273) or 1373 (CZA-m1373) K for a total of 12 h for each step. Chemical analysis (by ICP-AES) of the CZ and CZA materials gave Zr/Ce atomic ratios of 1.0 ± 0.1 .

A, CZ, CZA, CZA-m1273, and CZA-m1373 supports were impregnated by the incipient wetness method with aqueous solutions of Pd(NO₃)₂ to give a 1.0 wt% metal loading. The resulting catalysts were calcined following the same drying/calcination procedure described above for the supports (773 K, 2 h) and are referred to as fresh PdA, PdCZ, and PdCZA samples or PdCZA-m1273 and PdCZA-m1373 model systems. Oven aging of the fresh PdA, PdCZ, and PdCZA materials was performed by successive treatments at 1273 K (samples PdA-a1273, PdCZ-a1273, and PdCZAa1273) and 1373 K (PdA-a1373, PdCZ-a1373, and PdCZAa1373) under air for a total of 12 h for each step. Therefore, the fresh sample for each support (PdA, PdCZ, PdCZA), as well as model PdCZA-m and aged PdA-a, PdCZ-a, and PdCZA-a series, have been prepared. Note that only the support underwent high-temperature (1273-1373 K) aging in materials denoted with an -m suffix, while both the noble metal and support are jointly aged for materials denoted with an -a suffix.

2.2. Catalytic tests

Catalytic tests using a 1% CO + 0.1% NO + 0.45% O₂ (N₂ balance) stoichiometric mixture at 30,000 h^{-1} were performed in a pyrex glass reactor system. After grinding and sieving, catalyst particles in the range 0.12 to 0.25 nm, for which internal diffusion effects were minimized, were employed for these tests. Gases were regulated with mass flow controllers and analyzed on-line using a Perkin-Elmer 1725X Fourier transform infrared (FTIR) spectrometer coupled with a multiple reflection transmission cell (Infrared Analysis Inc.; path length 2.4 m). Oxygen concentrations were determined using a paramagnetic analyzer (Servomex 540A). Prior to catalytic testing, in situ calcination was performed in diluted oxygen (2.5% O₂ in N₂) at 773 K, followed by cooling under the same atmosphere and subsequent N₂ purge at room temperature (RT). A standard test consisted of increasing the temperature from 298 to 823 K at $5 \text{ K} \text{min}^{-1}$.

2.3. Characterization techniques

Powder XRD patterns were recorded on a Seifert diffractometer using nickel-filtered Cu-K_{α} radiation, operating at 40 kV and 40 mA, and with a 0.02° step size, using a continuing time of 5 s. Fitting of XRD data was performed using Pearson VII functions and the Winfit! Program (by S. Kumm; http://www.geol.unerlangen.de). BET surface areas were determined from N₂ adsorption isotherms in a Micromeritics 2100 automatic apparatus.

Raman spectra were acquired with a Renishaw Micro-Raman System 1000 equipped with a cooled OCD detector (200 K) and a holographic super-Notch filter that removes the elastic scattering. The samples were excited with the 514 nm Ar line. The spectra acquisition consisted of 60 accumulations of 10 s acquisition time for each sample, with a typical running power of 25 mW.

DRIFTS analysis of adsorbed species present on the catalyst surface under reaction conditions was carried out using a Perkin-Elmer 1750 FTIR fitted with a MCT detector. Analysis of the NO conversion at the outlet of the IR cell was performed by chemiluminescence (Thermo Environmental Instruments 42C). The DRIFTS cell (Harrick) was fitted with CaF₂ windows and a heating cartridge that allowed samples to be heated to 773 K. Portions of ca. 65 mg were calcined in situ with synthetic air (20% O_2 in N_2) and then cooled to 298 K in the same atmosphere before introduction of the reaction mixture and subsequent heating at 5 K min⁻¹ up 573 K, recording one spectrum (4 cm⁻¹ resolution, average of 50 scans) generally every 15 K. The gas mixture $(1\% \text{ CO} + 0.1\% \text{ NO} + 0.45\% \text{ O}_2, \text{N}_2 \text{ balance})$ was prepared using a computer-controlled gas blender with $60 \text{ cm}^3 \text{ min}^{-1}$ passing through the catalyst bed. Following runs under reaction conditions, the samples were cooled under inert gas flow. Subsequently, CO (3% in N2) was flowed at RT and finally $CO_{(g)}$ was flushed out with N₂.

XANES experiments at the Pd *K*-edge were performed on line 9.2 at SRS, Daresbury. A Si(220) double-crystal monochromator was used in conjunction with a rejection mirror to minimize the harmonic content of the beam. Additionally, a detuning of 30% was used. Transmission experiments were carried out using Kr/Ar-filled ionization chambers. The energy scale was simultaneously calibrated by measuring the Pd foil using a third ionization chamber. Samples as self-supported discs (absorbance ca. 0.5) were placed in a controlled-atmosphere cell for treatment. XANES spectra were taken every 15 K during a 5 K min⁻¹ temperature ramp up to 723 K, in the presence of the CO + NO + O₂ flowing mixture (similar to that employed for catalytic activity tests).

Results obtained in XANES experiments were subjected to normalization using standard procedures and analyzed using principal component analysis (PCA) [15-17], which assumes that the absorbance in a set of spectra can be mathematically modeled as a linear sum of individual components, called factors, which correspond to each one of the palladium species present in a sample, plus noise [18]. To determine the number of individual components, an F-test based on the variance associated with factor k and the summed variance associated with the pool of noise factors is performed. A factor is accepted as a "pure" chemical species (i.e., a factor associated with signal and not noise) when the percentage of significance level of the F-test, %SL, is lower than a test level set in previous studies at 5% [15,16]. The ratio between the reduced eigenvalues, R(r), which approaches one for noise factors, was also used in determining the number of factors. Once the number of individual components was set, XANES spectra corresponding to individual palladium species and their concentration versus temperature profiles were generated by an orthogonal rotation (varimax rotation) which should align factors (as close as possible) along the unknown concentration profiles, followed by iterative transformation factor analysis (ITFA). ITFA starts with delta function representations of the concentration profiles, associated with each chemical species, located at temperatures predicted by the varimax rotation, which are then subjected to refinement by iteration until error in the resulting concentration profiles is lower than the statistical error extracted from the set of raw spectra [15–17].

Electron paramagnetic resonance (EPR) spectra were recorded at 77 K with a Bruker ER 200 D spectrometer operating in the X-band and calibrated with a DPPH standard (g = 2.0036). Portions of the samples were placed inside a quartz probe cell with greaseless stopcocks, using a conventional dynamic high-vacuum line for the different treatments. Oxygen adsorption treatments were initiated by admitting a dose of 210 µmol of O2 per gram of sample at 77 K. This treatment was followed by thorough outgassing at 77 K (aiming to minimize magnetic interactions with nonchemisorbed oxygen) and referred to as O₂ adsorption at 77 K. Subsequent 30 min warming to room temperature (RT) will be denoted as O_2 adsorption at RT. Some of the experiments were continued by subsequent outgassing at RT. These experiments were designed on the basis of former work, in order to get maximum intensity and optimum resolution of superoxide signals formed upon oxygen interaction [6,19,20]. Pretreatments under CO or CO + NO were performed by admitting at RT, respectively, 100 Torr of CO or, in a consecutive way, 100 Torr of CO and 10 Torr of NO, followed by heating at 453 K for 1 h and outgassing at 453 K for 0.5 h. Computer simulations were employed in some cases to determine spectral parameters or contributions of individual signals.

3. Results

3.1. Catalytic tests

Results obtained during the light-off tests for the Pd-CZA, PdCZA-m1273, PdCZA-a1273, PdCZA-m1373, and PdCZA-a1373 systems are depicted in Fig. 1. Comparison with the reference PdA and PdCZ systems is presented in Table 1 on the basis of conversion values at a 50% level (T_{50}) for fresh and 1273-K-aged materials.

Aging by thermal effects seems to have a significant impact on the CO and NO conversions displayed by the PdCZA system (Figs. 1A and B). Thus, an increase in the T_{50} temperature of 60/25 and 25/35 K is detected in the CO/NO elimination reactions in comparing, respectively, PdCZA and PdCZA-a1273 samples and the two aged PdCZA-a catalysts (Fig. 1; Table 1). The physicochemical effects taking place during aging of the CZA support seem of lesser importance in defining catalytic performance; this follows from the fact that both model systems, PdCZA-m1273 and PdCZAm1373, show close or improved performance in both CO



Fig. 1. CO (A) and NO (B) conversion profiles, NO₂ production (C), and N₂ selectivity (D) during CO + NO + O₂ light-off tests.

Table 1 50% conversion temperatures (K) observed for fresh and 1273-K-aged Pd-CZA, PdCZ, and PdA systems

Treatment	PdCZA		PdCZ		PdA	
	СО	NO	CO	NO	CO	NO
Fresh	435	475	360	465	470	420
Aged: 1273 K	495	500	550	565	515	515
Difference	60	25	190	100	45	95

and NO elimination reactions with respect to the fresh Pd-CZA catalyst. The samples do not display significant differences in the NO reduction selectivity during the light-off tests, reaching 100% N₂ yield a few degrees after the temperature of full NO conversion (Fig. 1D). Small differences are, however, encountered in the production of NO₂, which is typically negligible for Pd-based systems operating under stoichiometric conditions [21] but here visible for PdCZAa1373 and, more clearly, for PdCZ-a1273. NO₂ formation thus appears to be related to systems containing CZ particles of significant dimensionality (vide infra).

The influence of the support nature on the CO and NO elimination catalytic activity is briefly illustrated in Table 1. The third row for each type of catalyst reports the difference in T_{50} values between the fresh and 1273-K-aged catalysts.

The strongest deactivation is clearly produced for the PdCZ system. Comparison between PdCZA and PdA shows moderate differences in CO oxidation activity. These are much stronger for NO reduction activity, in particular due to the relatively strong increase in the T_{50} value displayed by PdA after aging.

3.2. Characterization of the calcined samples

Powder X-ray diffraction patterns are displayed in Fig. 2. Reflections are here indexed for Ce-rich phases (pseudocubic t" or cubic c phases; Ce:Zr \geq 1) as derived from the cubic Fm3m cation lattice symmetry, while Zr-rich ones (tetragonal t', t) have been indexed using a P4₂/nmc space group symmetry. It can be noted that the poor resolution of the XRD data, inherent in the heterogeneity of the CZArelated materials, does not allow a simple resolution of the tetragonal splitting of the corresponding Ce–Zr mixed oxides, as discussed previously for the CZA support [6]. Analyses of the cell parameters and particle size obtained from the XRD data as well as the BET area of the supports/catalysts are summarized in Table 2. The XRD data indicate the presence of several transitional alumina phases as a function of the aging treatment suffered by the CZA-



Fig. 2. XRD diffractograms of support and Pd-containing samples. Peaks corresponding to ceria–zirconia mixed phases are indexed; C or Z prefixes refer to Ce-rich or Zr-rich phases, respectively. Peak positions corresponding to PdO are indicated by vertical dashed lines. Greek letters indicate presence of different alumina phases (* symbol corresponds to diffraction peaks which can be associated with several transitional phases). See text for details.

Table 2 Main characterization results for calcined materials

Sample	$S_{\rm BET} ({ m m}^2{ m g}^{-1})$	Cell parameter (Å)	Particle size (nm) ^a
А	200	_	_
A-a1273	84	_	-
A-a1373	7.5	-	-
CZ	130	5.30 ^b	4.5
Pd/ZC-a1273	5	5.36 ^b , 3.63/5.26 ^c	15,7
Pd/ZC-a1373	2	5.37 ^b , 3.63/5.23 ^c	27, 24
CZA	203	5.30 ^b	3
PdCZA	201	5.30 ^b	3
CZA-a1273	83	5.33 ^b	12
PdCZA-a1273	77	5.34 ^b	10
CZA-a1373	37	5.37 ^b , 3.62/5.29 ^c	28, 19
PdCZA-a1373	38	5.37 ^b , 3.61/5.32 ^c	26, 15

^a When adequate, first average particle size is reported for t''/c phases while the second correspond to t'/t tetragonal phases.

^b Fluorite-type cell with Fm3m symmetry is considered for phases ascribed to cubic c or tetragonal t" phases assigned according to Raman results.

 $^{\rm c}$ Tetragonal-type with $P4_2/nmc$ symmetry is considered for t'/t phases.

containing materials. Concerning these phases, the practical absence of differences between the behavior under aging of the support (for which data obtained under the same conditions can be found elsewhere [6]) and the Pd-containing catalyst (Fig. 2) can be noted.

Peaks related to the CZ component (discussed elsewhere in Refs. [5,6]) are dominated by the cation sublattice of the corresponding mixed oxide compound. The XRD study (Fig. 2 and Table 2) indicates the absence of significant differences between the support and Pd-containing catalysts in either the fresh or the aged states. Up to 1273 K, a growth of CZ particle size and a small variation of the cell parameter are detected (Table 2); this suggests that the integrity of the CZ component is mostly maintained, although the asymmetry of the peaks indicates a certain degree of heterogeneity (see, as an example, the zone corresponding to the c(111) reflection of Fig. 2; note also that higher index peaks with better resolved splittings do not yield a definitive conclusion in this respect, due to their lower intensity and/or overlapping with peaks from other compounds). Upon aging at 1373 K, the Ce-Zr phase compositional homogeneity abruptly breaks, giving rise to two discernible phases (Fig. 2 and Table 2), one with Ce/Zr atomic ratio close to 3.3, according to the value of its lattice parameter [5,6,22], and the other exhibiting Zr enrichment and composition, which cannot be determined on the exclusive basis of XRD due to the rough steadiness of cell parameters for Ce/Zr compositions below 1 [5,22]. In the case of the PdCZ system, the phase segregation reaction is already visible after the treatment at 1273 K. Indeed, Table 2 indicates a degree of Ce-Zr phase segregation for PdCZ-a1273 similar to that for PdCZA-a1373, in spite of the fact that particle size appears to evolve in a roughly similar way with temperature for both CZ- and CZA-supported systems. A mutual stabilization between the promoter and the alumina carrier then becomes apparent. The tetragonal character of the Zr-rich t phase is





Fig. 3. Raman spectra of support and Pd-containing materials. Peaks related to Ce-containing components are marked with a cross; other peaks are associated with the PdO phase.

better developed in the PdCZ-a1373 sample, according to the presence of all characteristic reflections of its $P4_2/nmc$ symmetry (marked in Fig. 2).

Peaks attributable to Pd-containing phases are only detected for aged PdCZA samples, independent of the thermal treatment (Fig. 2). PdO peaks are shown as vertical dashed lines in Fig. 2 and their absence is noted in the PdCZ series, indicating some limitation in the growth of the noble metal with respect to the PdCZA series. In fact, TEM/EDS analysis (not shown) gives evidence that large Pd particle sizes are associated with sample regions depleted in ceria–zirconia and are thus characteristic of PdA-like regions.

In contrast to the cation-dominated information yielded by XRD, Raman spectra of fluorite-related phases are dominated by lattice oxygen vibrations [23] and are obviously sensitive to crystalline symmetry. Raman spectra of the CZA support after the different treatments (Fig. 3) give evidence of the presence of a pseudo-cubic, tetragonal t" Ce–Zr phase, which accounts for the ca. 470 and 618 cm⁻¹ phonon modes [6,14,22], irrespective of the treatment temperature. An additional peak at 251 cm⁻¹ has been also detected in supported ceria specimens [24], and could be ascribed either to a localized defect or an impurity-derived vibration mode. The ca. 470 cm⁻¹ band is first order anion-lattice associated vibration [23], whose characteristic frequency displays low sensitivity to changes in Ce/Zr composition near the unity [6]. A point to stress is the apparent absence of well-resolved bands from the Zr-rich phase formed upon phase segregation as a consequence of the aging treatment at T > 1273 K. In this respect, for t'/t phases, apart from other vibration modes, a Zr–O stretch mode should be easily detected at around 235 cm⁻¹ for a Zr-rich (Ce/Zr ca. 0.33) phase or below ca. 260 cm⁻¹, the corresponding value of the tetragonal ZrO₂ phase [25]. The absence of such features suggests a significant structural disorder in the anion sublattice of the Zr-rich phase, in accordance with EXAFS results reported for such phases [26].

The model systems obtained from the aging treatment of the CZA support (PdCZA-m1273, PdCZA-m1373; Fig. 3) do not show a significantly perturbed Raman shape with respect to the support alone. A difference is the presence of a band at ca. 650 cm⁻¹ ascribable to the B_{2g} Raman mode of PdO [27], which, on the other hand, is absent in the fresh PdCZA catalyst [28], but discernible in PdCZ aged specimens (Fig. 3). A general decrease in Raman intensity can be also noticed in the model systems and could be mostly associated to the colour change in samples. The presence of a better crystallized PdO phase is detected in the aged PdCZA-a1273 and PdCZA-a1373 samples; the numerous peaks associated with this well-developed noble metal oxidic phase are readily ascribable by comparison with the spectra of the PdA-a1273 system (Fig. 3). It must be noted that possible attribution of these bands to some of the transitional alumina phases observed by XRD (Fig. 2) is discarded on the basis of comparison with the spectrum of PdCZ-a1273 (Fig. 3). On the other hand, the presence of the noble metal in the PdCZA-a series of catalysts affects to some extent the CZ component. A loss of Raman peak intensity of CZ-associated bands is detected in the PdCZAa1273 spectrum (see, for instance, the peak at ca. 475 cm^{-1} in Fig. 3), which suggests that a certain loss of anion-lattice ordering is produced in that phase upon aging at 1273 K. The intensity of such features (particularly evident for the ca. 475 cm⁻¹ band) is, however, significantly recovered after the phase segregation induced by the aging treatment at 1373 K (Fig. 3). Preliminary studies in a similar series of ceria/alumina supported specimens indicate the exclusivity of such interaction to the ceria-zirconia-containing aluminasupported materials, although similar effects may be present in Pd/Ceria systems, as formation of a Pd-Ce solid solution has been reported [29].

3.3. In situ DRIFTS

DRIFTS spectra obtained under reaction conditions for the fresh PdCZA (Fig. 4A), model PdCZA-m1273 (Fig. 4B), and PdCZA-m1373 (Fig. 4C) systems and the aged PdCZAa1373 catalyst (Fig. 4D) show a general evolution of CO_g (as



Fig. 4. DRIFTS spectra of (A) PdCZA, (B) PdCZA-m1273, (C) PdCZA-m1373, and (D) PdCZA-a1373 samples in the presence of nitrogen (a) and a flow of 1% CO, 0.45% O₂, 0.1% NO, N₂ balance at (b) 303, (c) 318, (d) 333, (e) 348, (f) 363, (g) 378, (h) 393, (i) 408, (j) 423, (k) 438, (l) 453, (m) 468, (n) 483, (o) 498, (p) 513, (q) 528, (r) 543, (s) 558, and (t) 573 K.

a barely discernible doublet in the region $2050-2250 \text{ cm}^{-1}$) and $\text{CO}_{2,g}$, which roughly correlates with catalytic activity results (Fig. 1). NO_g is typically not detected in the employed conditions due to its lower absorption coefficient and concentration in the feed [21]. Analysis of the PdCZA sample has been provided elsewhere [21]. In brief, the presence of carbonyls adsorbed on Pd(II) sites (2140–2160 cm⁻¹), on Pd(I) (ca. 2110– 2120 cm⁻¹), and atop (2096–2050 cm⁻¹) and bridge (1975– 1945 cm⁻¹) Pd(0) sites is observed at low temperatures [21,28,30–32]. Carbonyls adsorbed onto threefold Pd(0) sites are also visible as a red shoulder of the bridge carbonyl contribution extending to ca. 1880 cm^{-1} . After contact with the reactive mixture at room temperature, differences between the fresh PdCZA sample and PdCZA-m systems mainly concern the easier detection of Pd(0) surface species for the fresh catalyst and the larger intensity, among carbonyls characteristic of oxidized Pd species, of those adsorbed onto Pd(I) sites for PdCZA-m catalysts. On the other hand, the PdCZA-a1373 sample (Fig. 4D) does not show features ascribable to adsorbed species, in agreement with previous studies for the sample aged at 1273 K [32]. This is consistent with a significant sintering of the noble metal phase.

When the temperature is raised, transformation of Pd(II) and Pd(I) surface sites to Pd(0) is observed; except for the aged PdCZA-a1273 catalyst, carbonyls adsorbed onto oxidized Pd species are detected up to about 423 K. When increasing the temperature of reaction, the carbonyls adsorbed on atop and bridge zerovalent surface sites display the characteristic red shift induced by changes in adsorbed-CO dipole coupling by the effect of decreasing CO coverage as the CO oxidation reaction progresses [28,30-32]. Differences between the fresh and model PdCZA systems (PdCZA-m series) are also detected during the light-off ramp and concern the behavior of Pd(0) centers with temperature. Considering carbonyls adsorbed on Pd(0) atop sites, a continuous decrease in frequency is detected for fresh PdCZA while the model catalysts appear to have two contributions, one at 2096–2094 cm^{-1} , invariant up to 423 K, and another at lower wavenumber, which apparently begins to shift downwards at lower temperature. Concerning bridge Pd(0) sites, it can be noted that these are populated by CO from room temperature (RT) and display invariant frequency up to ca. 423 K in the PdCZA case; contrarily, practical absence of bridge carbonyls intensity is evident in both model systems at low temperature, beginning to appear at T above ca. 400 K.

In the fresh PdCZA sample, two bands at ca. 2240 and 2211 cm^{-1} are detected at temperatures close to 400 K. The first is assigned to isocyanate (NCO) species adsorbed onto aluminum cations [21,32,33], while the second may be described as NCO bending species also adsorbed onto the support. An alternative assignment to NO2⁺-related species [34] is possible, although such adspecies are unlikely to form under stoichiometric conditions. NCO species are formed by N-O bond dissociation and reaction with CO at metal surfaces followed by spillover to the support. The large intensity of NCO when adsorbed on alumina makes it a useful (though approximate) fingerprint for monitoring the NO dissociation process. In the model systems (Figs. 4B, 4C), a band at 2168 cm^{-1} is detected instead of at 2211 cm^{-1} . The band intensity runs parallel to the NCO one. This contribution can be assigned to ionic (NCO)⁻ species absorbed on metallic surfaces [35,36] or CN⁻ species probably adsorbed onto alumina [37]. The thermal stability of such adspecies, present at temperatures up to ca. 600 K (Figs. 4B, 4C), favors the second assignment [35,37]. CN^- group could be obtained from NCO decomposition on the metal surface [35,36] or, less likely, may indicate C–O bond dissociation, either directly or through the Boudouart reaction ($2CO \rightarrow C + CO_2$). Interesting here is the existence of a visible correlation between the onset of NCO detection and the intensity changes with temperature above described for bridge-bonded Pd(0) carbonyls; however, details of the correlation vary with sample and will be further analyzed in Section 4.

To examine the state of the metal surfaces on completion of the reaction runs and in the absence of thermally driven adsorption effects, the reactants were flushed at 623 K and the sample was cooled under N_2 to room temperature and subsequently exposed to 3% CO/N2 before the cell was flushed again with N2. Spectra recorded during this treatment are displayed in Fig. 5. All spectra, except that corresponding to PdCZ-a1273, show contributions from the already assigned bands of on-top (2105, 2095-2085, 2044 cm⁻¹) and bridge-bonded (1992–1979 cm⁻¹) carbonyls on Pd(0) sites; contributions from CO molecules adsorbed on Pd(II) centers $(2147-2144 \text{ cm}^{-1})$ can be also observed in the fresh PdCZA and PdCZA-m1273 systems (Fig. 5). A first point to note is that the atop to bridge intensity ratio differs from the fresh to model PdCZA systems; the larger ratio of the PdCZA sample clearly indicates a more dispersed Pd phase and, consequently, a lower average particle size [21,28,30]. On the other hand, the aging procedure induces a general, strong decrease of the carbonyl-related intensity, consistent with previous reports [32]; however, some differences are clearly visible among our samples. The influence of the support nature on the aging effects exerted on the noble phase is described after the treatment at 1273 K. The PdCZA-a1273 spectrum (Fig. 5) shows a strong resemblance to the spectrum corresponding to PdA-a1273, while adsorbed species are absent in the spectrum of PdCZ-a1273 (Fig. 5). A more subtle effect of the aging treatment in the



Fig. 5. DRIFTS spectra following experiments shown in Fig. 4 after exposure to CO and subsequent flushing with N_2 .

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PdCZA system is the presence of two atop species (2105, 2044 cm^{-1}), which may indicate a more heterogeneous distribution of noble metal particle size.

3.4. In situ XANES

Factor analysis results at the Pd K-edge (Table 3) for Pd-CZA, PdCZA-m1273, PdCZA-m1373, and PdCZA-a1273 obtained during a light-off run under $CO + NO + O_2$ are consistent with the existence of two different chemical species in all cases. The number of species is clearly indicated by sharp variation in the %SL and R(r) values displayed in Table 3. In Fig. 6, the fraction of these chemical species as a function of reaction temperature is depicted. This plot shows that Pd is initially present as a single chemical species which evolves into a single final state. Small differences in the onset of the initial species disappearance for fresh and model systems can be noted. As can be expected, the aged PdCZAa1273 evolves much later. Differences between the fresh and model PdCZA catalysts are somewhat maximized at intermediate stages of the reaction run; the temperature of maximum rate of initial-state (chemical species) disappearance is ca. 510, 550, 570, and 640 K, respectively for PdCZA, PdCZA-m1273, PdCZA-m1373, and PdCZA-a1273. For the fresh and model systems, only one species is detected above ca. 625 K, while this is true above 700 K in the PdCZAa1273 case. It may thus become apparent that, according to XANES, differences between the fresh and model PdCZA catalysts are absent at the onset and final reduction temperatures, while the aged specimens reduction starts about 75 K later.

When compared with the reference spectrum of PdO (Fig. 7A), the shape of the XANES spectrum of the samples in their oxidized state shows only slight differences, which may be a consequence of the limited particle size of the oxidic Pd-containing entities and/or some interaction with the support. This suggests a similar oxidation state, Pd(II), local geometry (D_{2h}) , and oxygen first-shell coordination distance for all the samples displayed in Fig. 7A. Similarly, the XANES spectra of the final species detected in the reaction (Fig. 7B) do not show significant differences between the fresh and model samples and can be readily identified in all cases as Pd particles in a zerovalent oxidation state. A higher intensity of the 5sp and 4f continuum resonances (CRs) and a different energy position of the former CR are, however, detected for the aged PdCZA-a1273 specimen. As these CR energy positions have a geometrical contribution with an inverse dependence on the coordination distance [17], it appears that the XANES technique is able to evidence differences in particle size only between the aged (PdCZA-a) series and the remaining systems. Differences between the fresh and model PdCZA particle size are thus not visible in the XANES spectra. On the other hand, the similar XANES shapes detected for oxidized and reduced Pd-containing species of fresh and model PdCZA systems indicates a reasonable similarity in electronic properties.

Factor	Eigenvalue	%SL	R(r)	Variance
		A. PdCZA		
1	458.49	0.00	1334.23	99.930
2	0.31594	0.00	194.34	0.070
3	0.00149	10.24	1.45	0.001
4	0.00092	12.38	2.06	0.001
5	0.00040	25.48	1.23	
6	0.00029	29.50	1.22	
7	0.00021	34.36	1.01	
8	0.00018	35.02	1.10	
	В	. PdCZA-m127	73	
1	677.54	0.00	490.2	99.810
2	1.2837	0.00	361.4	0.189
3	0.03283	7.19	1.21	0.001
4	0.02503	4.57	3.42	
5	0.00067	23.75	1.19	
6	0.00051	26.59	1.46	
7	0.00032	35.77	0.95	
8	0.00030	34.93	0.97	
	(C. PdCZ-m137	3	
1	459.32	0.00	475.32	99.808
2	0.87895	0.00	267.41	0.191
3	0.00298	5.99	1.93	0.001
4	0.00137	9.85	2.89	
5	0.00042	29.90	1.18	
6	0.00031	33.75	1.14	
7	0.00023	37.81	1.03	
8	0.00019	40.26	0.99	
	Ľ	. PdCZA-a127	3	
1	383.46	0.00	494.32	99.819
2	0.68891	0.00	162.43	0.179
3	0.00372	8.79	2.61	0.001
4	0.00123	22.53	1.43	
5	0.00072	28.37	1.57	
6	0.00038	40.02	0.91	
7	0.00033	40.13	1.07	
8	0.00023	46 49	1.06	

Table 3 \mathbf{P}_{1}

Variances lower than 10^{-3} are not reported.

8



Fig. 6. Concentration profiles during the temperature-programmed reaction run for Pd-containing species. See text for details.



Fig. 7. XANES spectra for PCA predicted chemical species. (A) Pd initial, oxidized species; (B) Pd final, reduced species. Reference compound, PdO (4A), as dotted line.

3.5. EPR analysis

As shown elsewhere [6,19,20,38,39], O₂-probe EPR is a powerful technique for obtaining insight into surface structural characteristics and redox properties of ceriumcontaining samples. A previous report has shown in detail the characteristics of the superoxide signals obtained upon O₂ adsorption at 77 K on the CZA support outgassed at 773 K in either the fresh (calcined at 773 K) or the aged (at 1273 or 1373 K) states [6]. From these results, presence of dispersed CZ entities (in the form of two-dimensional patches or 2D-CZ) on the surface of the alumina was revealed. No strong change in the characteristics of these 2D-CZ entities was apparently produced as a consequence of the aging treatment [6]. Significant changes are, however, produced on the surface characteristics of bulk-like, aggregated three-dimensional CZ particles (3D-CZ entities). Insight into these surface and redox characteristics can be experi-



Fig. 8. EPR spectra following oxygen adsorption at RT (and subsequent RT outgassing) on the samples outgassed at 773 K. (a) CZA; (b) CZA-m1273; (c) CZA-m1373. Computer simulations are overlapped as dotted lines on the experimental spectra.

mentally achieved by performing a treatment consisting of outgassing of the sample at 773 K followed by O2 adsorption at RT and subsequent RT outgassing [6,39]. Fig. 8 shows the results obtained after this treatment for the fresh and aged supports. The spectra are basically constituted by the overlapping of two kinds of signals: first, an orthorhombic signal OZ at $g_z = 2.033 - 2.032$, $g_y = 2.009$, and $g_x = 2.002$, which corresponds to superoxide species chemisorbed on zirconium cations ($O_2^{-}Zr^{4+}$ species) [6,19,40]. Second, quasiaxial signals type OC with $g_{\parallel} = 2.040 - 2.031$ and $g_{\perp} = 2.011 - 2.010$, which correspond to superoxide species chemisorbed on cerium cations $(O_2^--Ce^{4+} \text{ species})$ [6,19, 20,38,39]. The main differences between the samples concern changes in the relative contributions of type OC and OZ signals. Thus, the results in Fig. 8 clearly show relative contributions of OC signals increasing with the aging temperature; according to computer simulations, the OZ/OC ratio of integrated intensities is 1.9, 0.9, and 0.6 for CZA, CZA-m1273, and CZA-m1373, respectively. This indicates that cerium surface enrichment is gradually produced with aging in the 3D-CZ particles, in line with previous studies of the aging process of unsupported Ce-Zr mixed oxide samples [41,42]. Another subtle difference concerns the appearance of a type OC signal feature at g = 2.040 for the aged samples (Figs. 8b and c). According to a previous work [39], this is characteristic of the formation of relatively large 3D-CZ particles, which interact less strongly with the underlying alumina, as a consequence of the sintering process.

Redox properties of some of the catalysts (the PdCZAm and -a series treated at 1273 K) have been analyzed by monitoring the evolution of EPR signals formed after oxygen adsorption on samples pretreated under either CO or CO + NO at 453 K. Different O_2^- -Ce⁴⁺ species, attribut-



Fig. 9. Overall intensity of O_2^- -Ce⁴⁺ signals obtained after O_2 adsorption on the samples indicated. (A) O_2 adsorption at 77 K, sample pretreated under CO at 453 K; (B) O_2 adsorption at 77 K, sample pretreated under CO + NO at 453 K; (C) O_2 adsorption at RT, sample pretreated under CO at 453 K.

able on the basis of previous works to species formed on 2D- and/or 3D-CZ entities at either promoter or Pd-CZ interface sites [21,28,43], are observed in the spectra. For the sake of simplicity and considering its higher relevance for this study, exclusively the analysis of the evolution of the overall integrated intensity of these signals as a function of the treatment is presented (Fig. 9). The results show a general decrease of intensity either upon warming to RT after O₂ adsorption at 77 K on the samples reduced under CO at 453 K or by effect of introducing NO in the pretreatment at 453 K. This decrease must be in both cases a consequence of oxidation of surface cerium cations, previously reduced by CO, in accordance with previous reports [21,28,43]. Thus, the decrease observed upon RT warming of the samples with O₂ adsorbed at 77 K indicates a deeper progress in the electron transfer from the sample surface toward oxygen (within the generally accepted oxygen adsorption scheme, e.g., $O_2 \rightarrow O_2^- \rightarrow O_2^{2-} \rightarrow \cdots \rightarrow 2O^{2-}$), giving rise to the formation of diamagnetic species, e.g., peroxide or oxide anions [43]. On the other hand, the decrease produced in the presence of NO indicates that some cerium sites are reoxidized upon NO interaction [21,44]. It must be noted that the magnitude of the electron transfer process responsible for the surface reoxidation can be related to the reduction degree achieved in each case after the treatment under CO, not only in global terms but also at a local level [20,44]. On this basis, the analysis of Fig. 9 indicates the higher general redox activity induced by the presence of Pd. Among Pd-containing samples, it appears that the redox activity follows the order PdCZA-a1273 < PdCZA < PdCZA-m1273.

4. Discussion

4.1. Physicochemical effects

Thermal aging influences the size/morphological as well as chemical properties of all the TWC components, the noble metal, the promoter, and the carrier. In this section we discuss the main physicochemical effects exerted by thermal degradation. As already mentioned in the Introduction, previous reports have analyzed these in terms of the noble metal particle sintering and/or its covering (by support components) as well as the promoter sintering and phase segregation reaction [8–12], but much less is known about the specific interaction between the noble metal and the promoter and the corresponding influence upon the catalytic properties of the systems.

Concerning the metal component, our study displays results similar to those of previous reports [9,12]; XRD only detects a PdO phase in the case of the aged PdCZA samples (PdCZA-a series), while XRD and Raman give evidence of the larger crystallinity of the oxidic Pd phase in the PdCZA system with respect to similarly aged PdCZ samples (Figs. 2 and 3). Additionally, the absence (or significant decrease) of noble metal presence at the surface of the PdCZ material is evidenced by the DRIFTS study of CO adsorption after reaction (Fig. 5). The comparative study of CZ- and CZAsupported catalysts shows therefore that Pd is significantly covered in the aged PdCZ samples, limiting the growth of the noble metal (or metal oxide) particle size [11]. On the other hand, data presented in Section 3.2 give evidence that Pd sintering in the PdCZA system under thermal degradation is more acute in zones depleted in promoter presence and thus may be primarily associated with PdA-like zones.

The thermal aging treatment also sinters the promoter and the carrier, although previous results on the CZA-support clearly evidence the beneficial mutual influence between these two components [6,14]. Comparative study of the CZA support and PdCZA system subjected to thermal aging shows the absence of significant differences in terms of particle size of the CZ component as well as main compositional parameters (Ce, Zr-content of the final phases) before and after the promoter phase segregation (Fig. 2; Table 2). Additionally, Pd is not expected to exert an effect in the surface Ce-enrichment detected in the promoter patches (Fig. 8). It could be thus concluded that the noble metal does not influence the evolution of bulk and surface properties of the promoter upon aging. A clear effect is, however, visible in the Raman spectra displayed in Fig. 3; at temperatures below occurrence of the phase segregation reaction, the ceria-zirconia promoter appears to lose anion-lattice ordering to some extent, a fact that is attributable to the presence of the noble metal and may be associated with the stabilization of fully oxidized Pd(II) species forming part of the ceria-zirconia solid solution [29]. This effect might be also present in the aged PdCZ samples, but the bulk-averaged Raman technique is not able to detect it, due to the significant fraction of the promoter that presumably does not remain in contact with the noble metal. This noble metal-promoter interaction is lost after the phase segregation reaction, as shown by the recovery of the Raman intensity of the ca. 470 cm^{-1} peak (compare Figs. 3f and 3g). The Raman spectra thus suggest that a minor part of Pd remains stabilized, probably in a fully oxidized Pd(II) chemical state, in close contact with the promoter after aging at 1273 K, and that the phase segregation may allow this to evolve as Pd single species, likely maintaining a certain proximity with the promoter.

4.2. Catalytic effects

In systems of unsupported Pd or Pd on fairly inert supports (the Pd/Al₂O₃ can be considered among these latter), it is well known that the CO oxidation is essentially a structurally insensitive reaction [45], while NO reduction is strongly sensitive due to the structural dependence of the two steps, NO dissociation and N recombination, which may be involved in the rate-determining step depending on the noble metal particle size [30,46]. Recent evidence shows, however, that CO oxidation may display a weak sensitivity to structure in the case of small Pd particles [47]. In any case, when both reactants are present in the reactive mixture, the kinetic regime and the corresponding surface coverage(s) at the metal particles vary with particle size, in turn affecting the elimination rates of each specific reactant [48]. Additionally, in the presence of a Ce-containing promoter, the size and morphology of the noble metal and the promoter become critical, since the centers active at low temperature are located at the metal-promoter interface [21,28,32,43,44, 49,50]. In PdCZ and PdCZA systems it is therefore obvious that the "structure sensitivity" concerns size and morphology factors of the metal-promoter interface. It is also inferred from this that, in addition to geometric/electronic factors affecting the active metal or metal/promoter interface for the CZA-supported systems, the metal distribution achieved over the complex support is of relevance (i.e., whether the metal shows a preference for interacting with the CZ or the alumina component). The dynamic nature of the catalytic system upon interaction with the reactant atmosphere during a light-off run requires monitoring the formation of the potential active phases during the course of the reaction. In this sense, comparison of catalytic activity (Fig. 1) and DRIFTS/XANES results (Figs. 4-7) indicates that the lightoff profile roughly parallels the reduction of the noble metal and its concomitant aggregation, a fact reported in previous studies [21,47,51]. This fact indicates that the metallic state (either at the surface or in the bulk) is the most active for any of the examined reactions, e.g., CO oxidation and NO reduction. In this respect, the higher difficulty for achieving the metallic state displayed, according to XANES experiments (Fig. 6), by the aged systems (-a series) can be considered as one of the main factors to account for their lower activity in general terms. Nevertheless, as mentioned above and according to previous experience on TWC systems [21,28, 32,43–50], the main factors affecting the catalytic activity are different for each of the reactions and are therefore discussed separately.

With regard to CO oxidation, as briefly outlined above and in accordance with previous works [28,32,43,45,46,48], the main factors governing the catalytic activity of TWC systems are the palladium dispersion (for active sites constituted by particles in contact with the alumina component, and considering the mentioned structural insensitivity of this reaction) and the number and specific properties of Pd-CZ interface sites. In cases where a sufficient number of the latter sites are present, e.g., enough contact between the Pd and CZ components in PdCZA, they have been shown to dominate the CO oxidation catalytic activity at low temperatures [28,32,43]. Another factor to be considered when examining this reaction in the presence of NO concerns the catalytic interferences induced by occupation of active sites on the metallic particles by species derived from NO chemisorption [21,48-50]. This interaction produces a kind of self-poisoning effect as a consequence of the oxidation of the sites over the metallic particles, clearly visible in the DRIFTS spectra (Fig. 4).

Taking all the above mentioned factors into account, the lower activity of the PdCZA-a systems (Fig. 1) as well as the higher difficulty for Pd reduction (Fig. 6) in them is simply interpreted as a consequence of the significant Pd sintering produced upon aging (evidenced by XRD and Raman, Figs. 1 and 2), which induces the concomitant decrease in the relative number of Pd-CZ interface sites with respect to the nonaged PdCZA system. On the other hand, the comparison between the fresh PdCZA system and those of the PdCZA-m series, where only the support suffered the aging process, appears quite interesting. The absence of significant differences between them or even the highest CO oxidation activity shown by the PdCZA-m1273 system suggests differential properties for the Pd-CZ interface sites when PdCZA-m systems are compared with the fresh PdCZA one. First, it can be noted that analysis of the DRIFTS spectra in Figs. 4B and 4C confirms that Pd-CZ interface sites, and not particles in contact with the alumina component, are the active sites for CO oxidation in the PdCZA-m systems. To show this, we must note that the observation of an atop carbonyl maintaining its frequency at a relatively high value (ca. 2095 cm⁻¹) for $T \leq$ ca. 423 K is a typical fingerprint of the behavior of Pd particles in contact with the alumina component [45,48]. The onset of CO oxidation in such unpromoted systems coincides with the point at which a red shift is produced in that band (taking into account, as mentioned before, that the frequency of that band is determined by dipolar coupling effects and that the reaction is basically limited by thermally induced desorption of CO). However, the temperature at which the mentioned shift in the carbonyl band is detected (ca. 423 K) is well above the onset of CO oxidation in the PdCZA-m systems. A careful analysis of the atop carbonyl region in Figs. 4B and 4C shows the presence of another component which begins its red shift at lower temperatures and which, in accordance with previous experience with systems of this kind [21,32,43], must be related to the palladium particles in contact with the CZ component, which could then be considered as the most active sites for this reaction. The fact that DRIFTS observation of features related

to Pd particles in contact with alumina is more apparent for the PdCZA-m systems in comparison with the fresh PdCZA system suggests that a higher proportion of the Pd is in contact with the alumina component for the former catalysts, as expected when considering the lower general CZ dispersion in the model systems (Fig. 2 and Table 2). The results thus indicate a higher CO oxidation catalytic activity of the Pd-CZ interface sites of the PdCZA-m systems with respect to the fresh PdCZA sample. This can be related to the changes observed in the surface characteristics of the CZ component upon aging; as revealed by EPR (Fig. 8) and reported in previous studies [52], the promoter surface is enriched in Ce. In turn, the EPR results of Fig. 9 evidence a strong parallelism between redox and catalytic activity; therefore, a correlation can be established between the CO potential to create vacancies at the metal-promoter interface and, associated to this, the reoxidation ability of such vacancies upon interaction with oxygen. The comparison between model and aged series of catalysts shows that the CZ phase segregation reaction only produces a moderate effect on CO oxidation.

NO reduction is a structure-sensitive reaction which should be dependent on noble metal size/morphology properties, particularly influencing NO dissociation and N recombination steps [30,46,48]. The analysis of metal particle size and its effect in the reaction can be extracted from DRIFTS experiments (Fig. 4). This technique evidences differences in palladium particle size already from the starting point of the reaction; model systems show a larger surface coverage by N-containing adspecies, which yield Pd(I) surface states after NO dissociation, as well as absence of bridge-bonded carbonyls until the NO-product(s) disappears from the metal surface concomitantly to NCO formation. These aspects indicate a stronger NO interaction with Pd particles in the PdCZA-m systems in comparison to the fresh PdCZA catalyst. Additionally, the CO adsorption on used samples (Fig. 5) gives further evidence of the larger particle size, according to the higher bridge-to-atop intensity ratio, of model systems (PdCZA-m series). All these data are in agreement with the fact that model systems have a larger metal particle size already from the onset of the reaction (also observed in the Raman spectra, Fig. 3, of calcined materials) and show higher efficiency than fresh Pd-CZA in the NO adsorption/dissociation process [48]. All the "structural" factors, e.g., higher size of the Pd particles and lower amount of Pd–CZ contacts, are, generally speaking, in favour of a higher NO reduction activity of the PdCZA-m systems, in which active sites for this reaction are probably related to Pd particles in contact with the alumina component. Nevertheless, differences between PdCZA-m1273 and PdCZA-m1373 may suggest a certain role for the metalpromoter interface. In fact, the EPR study (Fig. 9) shows that NO dissociation affects the CZ component, at least at low temperature, and appears somewhat more favored in the presence of Ce-enriched promoter surfaces. This may be grounded in the fact that the Ce content of the surface governs the nature (isolated vs associated) and number of

anion vacancies present in the promoter, which in turn affects the NO activation processes [6,21,38,43,44]. We may thus suggest that thermal aging affects NO reduction in Pd-CZA systems by decreasing the number of surface Pd atoms (sintering of the noble metal) as well as stabilizing Pd(II) species before the phase segregation reaction, but also may have a positive effect driven by the Ce enrichment of the promoter surface in cases where the NO dissociation is involved in the slow rate step [46]. Pd particle size and, to a limited extent, Ce concentration at the promoter surface appear as the key physicochemical factors affected by thermal aging and influencing catalytic activity for NO elimination.

5. Conclusions

The behavior of a Pd-based ceria–zirconia-promoted TWC system has been analyzed for the CO oxidation and NO reduction processes under the influence of thermal aging effects. As already well known, the aging process aggregates the noble metal and promoter components and induces ceria–zirconia phase segregation above 1273 K. Encapsulation of the noble metal seems of relatively low importance in our alumina-supported Pd TWC. The thermal degradation process also appears to increase the surface Ce concentration of the CZ component and to influence the redox state of the active metal fraction in close contact with the promoter; aging below 1273 K seems to stabilize Pd in a presumed oxidized state, forming part of a solid solution with promoter components. Such interaction decreased after the promoter phase segregation reaction.

The light-off behavior of the Pd-based fresh and aged TWC samples under the $CO + NO + O_2$ atmosphere appears dominated by the reduction of the noble metal component and its sintering. Comparison with the model PdCZA-m series gives evidence that promoter aging only plays a limited role in the general decreasing of catalytic activity induced by thermal effects through the loss of metal–promoter contacts and, indirectly, by the loss of alumina surface area. This comparison also shows that the interface between Pd and ceria–zirconia is critical for CO oxidation and less important for NO conversion, although the enrichment in cerium detected during promoter aging after the phase segregation phenomenon may have a positive influence in the NO dissociation process.

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