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On the effect of reduction and ageing on the TWC activity of Pd/$Ce_{0.68}Zr_{0.32}O_2$ under simulated automotive exhausts

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ABSTRACT

The activity of a Pd/$Ce_{0.68}Zr_{0.32}O_2$ catalyst was studied under complex gas mixtures simulating those in automotive exhaust gases, analysing the evolution of CO, C_3H_6, O_2 and NO conversion and nitrogen compounds formed. The effects of pre-reduction and ageing treatments in cycled redox feedstreams at 1173 K, where the composition of oxidizing and reducing streams and cooling environment were changed, were investigated. The obtained results are compatible with the presence of two active palladium species on the catalyst surface whose predominance is temperature-dependent: Pd(I)-like species in the low-temperature range, and Pd(0) in the high temperature range.

1. Introduction

In Three-Way Catalysis (TWC), the appropriate choice of precious metal, among Pt, Rh, Pd or their combinations, depends on the emission control to be achieved, the operating conditions chosen and the cost objectives [1]. Traditionally, the standard system was based on Pt–Rh, but modern three way catalytic converters incorporate a front Pd-only monolith [2]. Although Pd is known to be a good oxidation catalyst, its activity concerning NO_X reduction is less effective [3]. In order to achieve the more drastic regulations concerning NO_X emissions, a Pt/Rh monolith is set after the Pd-only monolith [2].

The use of Pd presents some major interest, as it is the cheapest precious metal applicable in TWCs and it shows some performance advantages under certain operating conditions [4]. In order to achieve high nitrogen oxides, carbon monoxide and hydrocarbon efficiencies, many works have been carried out modifying the precious metal function with different supports: Al_2O_3 [5–7], La_2O_3 [7–10], $LaFeO_3$ [11], MoO_3 [12], ceria [6,13–15], ceria and zirconia [16], ceria–zirconia [11,17–20] or modified ceria–zirconia [21–26], and other metals [27–30].

The role of palladium has been particularly studied in methane [16,31–41] or VOCs combustion [42–44]. It has been underlined that the crystallite size, the dispersion and, particularly, the oxidation state of Pd are very important parameters in the catalytic performance. The presence of oxidized palladium species in the catalysts has been related to higher activities [16,42,45,46]. The redox nature of the reacting gas and the treatment temperature have been underlined as very important parameters in the formation/decomposition of PdO [47].

The catalytic activity of supported Pd catalysts has been investigated in conditions close to the TWC application by the use of complex gas mixtures and actual exhaust gases. It was shown that the reactivity was dependent on the support [48] and the pre-treatment atmosphere [3]. Ceria is widely used as promoter in TWCs because of its ability to store and release oxygen (OSC) [49–51], to improve dispersion of noble metals [49,51,52], and to promote water–gas shift reaction [53]. However, ceria is known to present low structural stability when submitted to high temperature treatments, losing many of its interesting properties. It has been reported that the addition of zirconia into the ceria lattice, sometimes combined with rare earths, in a reasonable proportion leads to a significant improvement of the OSC [19,54–56] and the thermal stability [21,57,58] of ceria. TWCs have been aged in the field [59] and under simulated conditions [20,30]. It has been reported that support sintering has relatively low effect in the loss of catalytic activity, the main effect related to Pd sintering and weakness in the Pd–Ce interaction. Besides, CO oxidation is much more affected by ageing than C_3H_6 oxidation.

Most studies reported in the literature on Pd supported on ceria–zirconia (alumina) TWCs deal with particular reactions [42,56,60,61], or simulated stationary mixtures [62,63]. The

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Table 1
Treatments applied to the different catalyst samples.

Sample	Ageing environment	A/F range	Cooling environment	Reduction
F-O	Fresh	–	–	No
F-R	Fresh	–	–	Yes
A-HOR	Cycled redox complex mixtures	15.13–14.13	Oxidizing complex mixture	Yes
A-HCR	Cycled redox complex mixtures	15.13–14.13	Cycled redox complex mixtures	Yes
A-LOR	$O_2/H_2O/N_2$–$H_2/H_2O/N_2$	19.62–12.98	O_2/N_2	Yes
A-LRR	$O_2/H_2O/N_2$–$H_2/H_2O/N_2$	19.62–12.98	H_2/N_2	Yes

interest of using complex redox cycling gas mixtures for catalytic activity measurements is that they simulate the behaviour in the actual application of the catalyst while the inlet gas composition is easily controlled. This kind of activity measurements constitutes a good way to compare different catalysts, particularly when studying deactivation effects or durability. The durability of a catalyst submitted to severe ageing depends on the metal, the support and the ageing treatment. A specific ageing treatment can induce a strong deactivation of the catalyst or, on the contrary, improve its activity.

In this article, we have studied the effect on the activity of a $Pd/Ce_{0.68}Zr_{0.32}O_2$ catalyst under simulated cycled redox exhaust gas mixtures of: a reduction treatment, and different ageing treatments under cycled redox streams at 1173 K in the presence of water, modifying the composition of the oxidizing and reducing streams, the duration of the treatment at 1173 K, and the cooling environment. The evolution of CO, HC, NO and O_2 light-off curves and the corresponding nitrogen compounds produced (NH_3 and N_2O) have been detailed and correlated to the presence of different palladium species on the catalytic surface.

2. Experimental

2.1. Preparation of fresh and aged catalysts

The $Pd/Ce_{0.68}Zr_{0.32}O_2$ catalyst used in this study was supplied by Rhodia, with a palladium content of 0.64 wt.%. The catalyst consisted of a very fine powder (average particle size 29.5 μm) and was pelletized to a particle size in the range 0.5–1.0 mm in order to avoid unacceptable pressure drop in the reactor. The catalyst in pellet form was cleaned by an oxidation treatment consisting of heating up to 823 K under a flow of 5% O_2/N_2 for 1 h. The catalyst thus cleaned constituted for us the fresh catalyst (F-O) in the activity measurements.

The fresh catalyst was submitted to a mild reducing treatment in a flow of 5% H_2/N_2 for 1 h at 573 K. The catalyst thus reduced constituted for us the fresh reduced catalyst (F-R) in the activity measurements. This reduction treatment was always performed immediately before an activity measurement and in the same experimental equipment, in order to prevent reoxidation of the catalyst.

Before ageing, the fresh catalyst was kept for 12 h at 373 K in a flow of N_2. Catalyst ageing was carried out by submitting the fresh catalyst to a hydrothermal treatment at 1173 K in which the gas flow was cycled between mixtures with oxidizing and reducing character. After switching the gas to the cycled ageing flow, the catalyst was heated from 373 K to 1173 K at a rate of 8 K/min, then kept at this temperature (1173 K) for several hours and, after switching the gas to the cooling flow, finally slowly cooled down first to 423 K, where the gas flow was again switched to N_2, and then to room temperature.

Differently aged catalysts were obtained by changing: oxidizing and reducing gas flow compositions during cycled ageing, duration of the ageing treatment, and composition of the gas flow during the cooling stage. Thus, four aged catalysts were prepared as follows.

Table 2
Textural properties of fresh and aged catalyst samples.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
Fresh (F-O, F-R)	103	0.228	8.8
Aged (A-HOR, A-HCR)	30	0.153	20.5
Aged (A-LOR, A-LRR)	30	0.122	16.5

The first group of aged catalysts (A-HCR and A-HOR) was aged using as oxidizing and reducing gas mixtures those used in the cycled activity measurements, that is:

Oxidizing:	10.0% CO_2, 0.4% CO, 900 ppm C_3H_6, 900 ppm NO, 1.26% O_2, 10.0% H_2O and N_2 to balance.
Reducing:	10.0% CO_2, 1.6% CO, 900 ppm C_3H_6, 900 ppm NO, 0.46% O_2, 10.0% H_2O and N_2 to balance.

which were alternatively fed to the reactor with a frequency of 0.55×10^{-3} Hz (that is, each feedstream was changed every 15 min), with an amplitude in the air to fuel ratio (A/F) of ±0.5 units around the stoichiometric point (A/F = 14.63). This cycled flow was kept during heating, and for the 5 h treatment at 1173 K. After this, two possibilities were used in the cooling stage until 423 K: either keeping the same cycled flow, but with a cycling frequency of 0.017 Hz (each feedstream was changed every 30 s; A-HCR catalyst); or switching to the oxidizing gas mixture during cooling (A-HOR catalyst).

The second group of aged catalysts (A-LRR and A-LOR) was aged using as oxidizing and reducing gas mixtures the following:

Oxidizing:	5.0% O_2, 10.0% H_2O and N_2 to balance.
Reducing:	5.0% H_2, 10.0% H_2O and N_2 to balance.

which were alternatively fed to the reactor with a frequency of 0.55×10^{-3} Hz (that is, each feedstream was changed every 15 min), with an amplitude in A/F of 6.6 units (A/F between 19.62 and 12.98). This cycled flow was kept during heating, and for the 6 h treatment at 1173 K. After this, again two possibilities were used in the cooling stage until 423 K: either switching to a reducing flow of 5% H_2/N_2 (A-LRR catalyst), or switching to an oxidizing flow of 5% O_2/N_2 (A-LOR catalyst).

All aged catalysts were submitted to reduction for 1 h at 573 K in a flow of 5% H_2/N_2 immediately before an activity measurement. Table 1 summarizes the different fresh and aged $Pd/Ce_{0.68}Zr_{0.32}O_2$ catalysts studied.

Specific surface area (S_{BET}), pore volume and average pore radius of fresh and aged catalyst samples have been measured with N_2 at 77 K using a Micromeritics ASAP 2010C apparatus. Before the measurements, the samples were outgassed for 12 h at 573 K and a vacuum of 100 mPa. Table 2 shows the results obtained for the different catalyst samples.

2.2. Activity measurements

Ageing treatments and activity tests were carried out in a conventional continuous-flow reactor previously described [64]. Before the activity measurements, the catalysts were kept for 4 h at 373 K in a flow of N_2. Catalyst activity was tested by determination of both light-off curves and stoichiometric windows.

Light-off experiments consisted of flowing through the catalyst sample (ca. 1.8 g of pellets, in a catalytic bed of 3.5 cm^3) 125,000 h^{-1} of a gas mixture whose composition was continuously cycled around the stoichiometric value (A/F = 14.63, amplitude of ±0.5 A/F) by alternating the following oxidizing and reducing feedstreams:

Oxidizing:	10.0% CO_2, 0.4% CO, 900 ppm C_3H_6, 900 ppm NO, 1.26% O_2, 10.0% H_2O and N_2 to balance.
Reducing:	10.0% CO_2, 1.6% CO, 900 ppm C_3H_6, 900 ppm NO, 0.46% O_2, 10.0% H_2O and N_2 to balance.

with a frequency of 1 Hz, while the temperature was increased from 373 K to 873 K at 3 K/min. The conversion data were continuously evaluated by non-dispersive infrared (CO, CO_2, NH_3 and N_2O), flame ionisation (C_3H_6), magnetic susceptibility (O_2) and chemiluminiscence (NO and NO_2).

Stoichiometric window experiments were carried out immediately after the light-off experiments. After finishing the measurements at 873 K, the flow was switched to N_2 and the temperature set to 773 K. Once the temperature stabilised, seven feedstreams (see Table 3) were successively passed through the fixed bed from the most reducing (A/F = 14.13) to the most oxidising (A/F = 15.13), at 125,000 h^{-1}. Change between feedstreams was carried out in N_2. Each feedstream was fed for about 10 min for stabilisation before measuring the conversion values.

Finally, after the stoichiometric window experiment was finished, a test was carried out in order to determine to what extent water–gas shift (WGS) and steam reforming (SR) reactions took place on the catalyst. Thus, the flow through the catalyst was switched to N_2 for about 10 min. Then, a stationary mixture composed of CO (1.0%) and H_2O (10.0%) diluted in N_2 to a total space velocity of 125,000 h^{-1} was fed to the reactor and the exit conversion measured after about 10-min stabilisation. The flow was again switched to N_2 for cleaning and then to a stationary mixture composed of C_3H_6 (900 ppm) and H_2O (10.0%) diluted in N_2 to a total space velocity of 125,000 h^{-1}. After about 10-min stabilisation, exit conversion was measured and the flow switched again to N_2. The temperature was successively set to 773, 673, 573 and 473 K; and the conversion measured with the two feed-streams at each temperature. Change between temperatures was carried out in N_2.

3. Results

3.1. Light-off experiments

Fig. 1 shows the results of CO, O_2, C_3H_6 and NO conversion versus temperature in the light-off experiments with fresh catalysts. The only difference between F-O and F-R catalysts is that the latter has been submitted to reduction before activity measurements. Table 2 shows that the catalysts present a high surface area of 103 m^2/g. The palladium dispersion of the catalysts has been estimated as CO/Pd = 0.64 [65]. At low temperature, CO reacts with oxygen to a high extent, only a limited amount of C_3H_6 reacts below 473 K, while NO conversion only occurs above this temperature. CO conversion presents a decrease at intermediate temperature which has not been observed when similar light-off experiments were carried out with the support in the absence of noble metal [66] or with Pd catalysts supported on cerium-promoted alumina [67].

Comparing the behaviour of F-O (Fig. 1a) and F-R (Fig. 1b) catalysts, we can see it is virtually identical below 423 K. Also, NO conversion starts at the same temperature, 473 K, which is coincident with the minimum observed in CO conversion curves (an auxiliary vertical line has been drawn in Fig. 1 to facilitate comparison). Total conversion of CO, O_2 and C_3H_6 is reached, the latter component being the one to reach total conversion at higher temperature. F-R presents a shift of about 60 K to higher temperature compared to F-O to reach total conversion of each one of the three components. NO does not reach total conversion, although a maximum of 97% is obtained with F-R at 723 K, and then decreases with temperature. The presence of this maximum in NO conversion with temperature has been associated to the contribution of WGS and SR reactions (see hollow symbols in Fig. 2) in the high temperature range, which allows for more oxygen availability in detriment of NO.

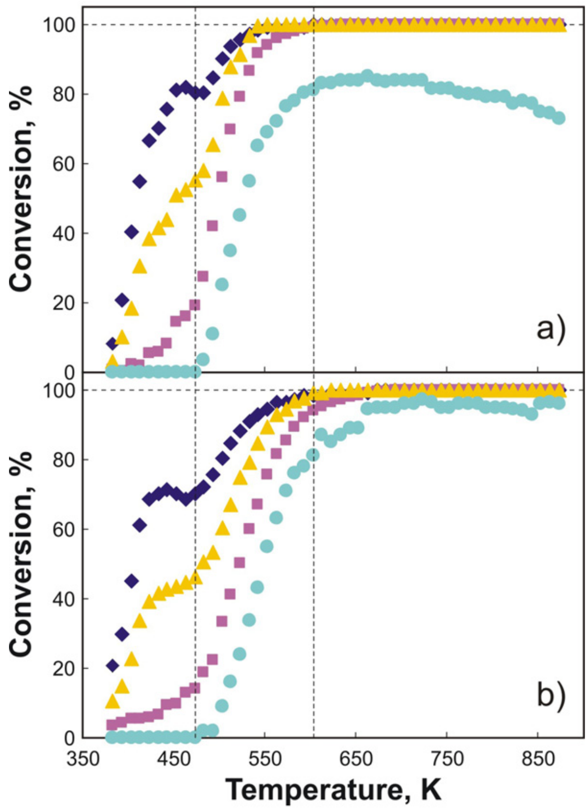

Fig. 1. Light-off curves obtained with fresh catalysts: (a) F-O, and (b) F-R. Symbols: ◆ : CO, ▲ : O_2, ■ : C_3H_6, and ● : NO.

Fig. 2 shows the light-off curves for the same components: CO, O_2, C_3H_6 and NO, obtained with the two catalysts aged under cycled redox complex mixtures. These ageing conditions were chosen to ensure strong sintering of both Pd and $Ce_{0.68}Zr_{0.32}O_2$ support while avoiding extensive encapsulation of the noble metal [68]. Table 2 shows that catalysts aged in these conditions have lost an important amount of surface area, with a final value of 30 m^2/g, and also of palladium dispersion, which has been estimated as CO/Pd = 0.14 for A-HOR aged catalyst, and as CO/Pd = 0.06 for A-HCR aged catalyst [65]. The only difference between these two aged catalysts is that A-HOR was cooled in oxidizing complex mixture, while A-HCR was cooled in cycled redox complex mixture.

Comparing the behaviour of A-HOR (Fig. 2a) and A-HCR (Fig. 2b) catalysts, we can see there are significant differences. Behaviour of A-HOR catalyst resembles that of fresh catalysts in Fig. 1, with virtually identical light-off curve for CO up to 473 K compared to that of F-O. Also, minimum CO conversion is coincident with the starting of NO conversion (an auxiliary line has been also drawn in Fig. 2), which is 20 K shifted to higher temperature in A-HOR compared to F-O. This effect produces a more pronounced minimum in CO conversion in the aged catalyst, which in this case can be also observed in the curve for oxygen. Total conversion of CO, O_2 and

Table 3
Composition of the stationary feedstreams used in stoichiometric window experiments.

Feedstream	A/F	CO_2 (%)	CO (%)	C_3H_6 (ppm)	NO (ppm)	O_2 (%)	H_2O (%)	N_2
I	14.13	10.0	1.6	900	900	0.465	10.0	Balance
II	14.33	10.0	1.0	900	900	0.448	10.0	Balance
III	14.53	10.0	1.0	900	900	0.724	10.0	Balance
IV	14.63	10.0	1.0	900	900	0.860	10.0	Balance
V	14.73	10.0	1.0	900	900	0.993	10.0	Balance
VI	14.93	10.0	1.0	900	900	1.254	10.0	Balance
VII	15.13	10.0	1.0	900	900	1.510	10.0	Balance

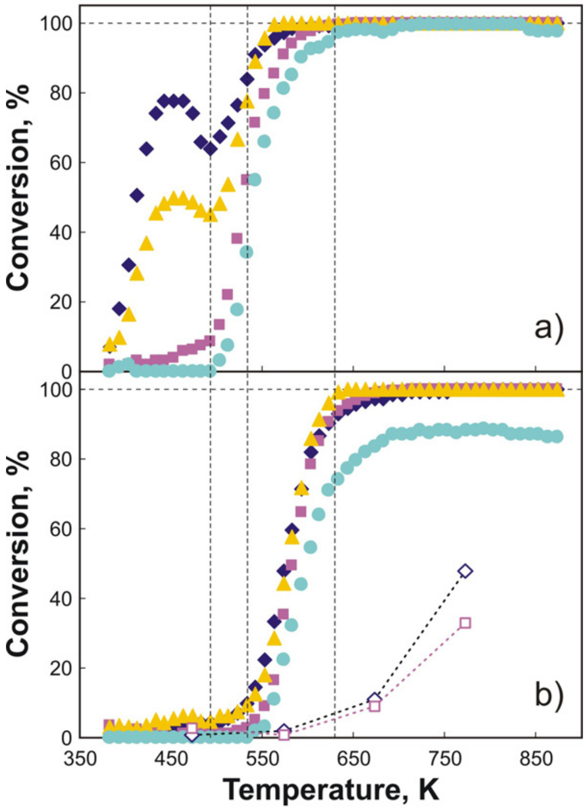

Fig. 2. Light-off curves obtained with catalysts aged under cycled redox complex mixtures: (a) A-HOR, and (b) A-HCR. Symbols: ◆ : CO, ▲ : O_2, ■ : C_3H_6, ● : NO, ◇ : CO in an experiment with only 1.0% CO + 10.0% H_2O in N_2 (WGS), and □ : C_3H_6 in an experiment with only 900 ppm C_3H_6 + 10.0% H_2O in N_2 (SR).

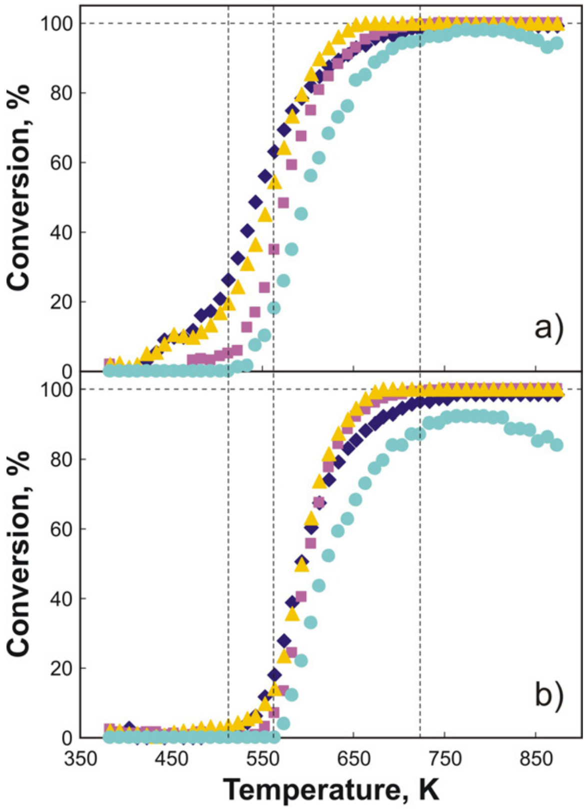

Fig. 3. Light-off curves obtained with catalysts aged under cycled $O_2/H_2O/N_2$–$H_2/H_2O/N_2$: (a) A-LOR, and (b) A-LRR. Symbols as in Fig. 1.

C_3H_6 is reached, also shifted 20 K to higher temperature compared to F-O. Concerning NO, virtually total conversion is reached around 773 K with A-HOR, although a small decrease at higher temperature is also observed as a consequence of WGS and SR.

A-HCR in Fig. 2b shows no significant CO, O_2 and C_3H_6 conversion below the temperature at which NO conversion starts which, in this case, is 533 K, that is 40 K above A-HOR (an auxiliary line has been also drawn), and 60 K above F-O and F-R. The curves for CO, O_2 and C_3H_6 are almost coincident in all the temperature range, with a shift of about 40 K with respect to those for A-HOR. The curve for NO reaches a lower maximum conversion as compared to A-HOR, in the same temperature range.

Fig. 3 shows the light-off curves for the same components: CO, O_2, C_3H_6 and NO, obtained with the two catalysts aged under cycled $O_2/H_2O/N_2$–$H_2/H_2O/N_2$ streams. In this case, the higher oscillation in the A/F ratio as compared to cycled redox complex mixtures and the longer duration has been designed to produce a more severe ageing in the catalysts. The results of surface area in Table 2 of the samples thus aged, however, do not show a significant difference compared to those aged in cycled redox complex mixtures. The only difference between A-LOR and A-LRR aged catalysts is that the former was cooled down in an oxidizing mixture, whereas the latter was cooled down in a reducing mixture.

Comparing the behaviour of A-LOR (Fig. 3a) and A-LRR (Fig. 3b) catalysts, we can see they are much more similar than those aged in cycled redox complex mixtures. Still, A-LOR catalyst presents small but significant conversion of CO, O_2 and (much less) C_3H_6 below the temperature at which NO starts reacting that, in this case, is 513 K, about 40 K above F-O and 20 K above A-HOR. A maximum of 98% NO conversion is reached around 773 K with A-LOR, with a clear decrease at higher temperature as a consequence of WGS and SR.

A-LRR presents no significant CO, O_2 and CO conversion below 563 K, the temperature at which NO starts reacting with this catalyst, in the same line than A-HCR, and total conversion of C_3H_6 is reached in both A-LRR and A-LOR around the same temperature. A maximum NO conversion of 92% is reached with A-LRR also around 773 K, with a pronounced decrease at higher temperature.

Figs. 4–6 show the evolution in the exit concentration of nitrogen compounds with temperature corresponding to the light-off experiments in Figs. 1–3, respectively. The same auxiliary lines than those included in the corresponding light-off

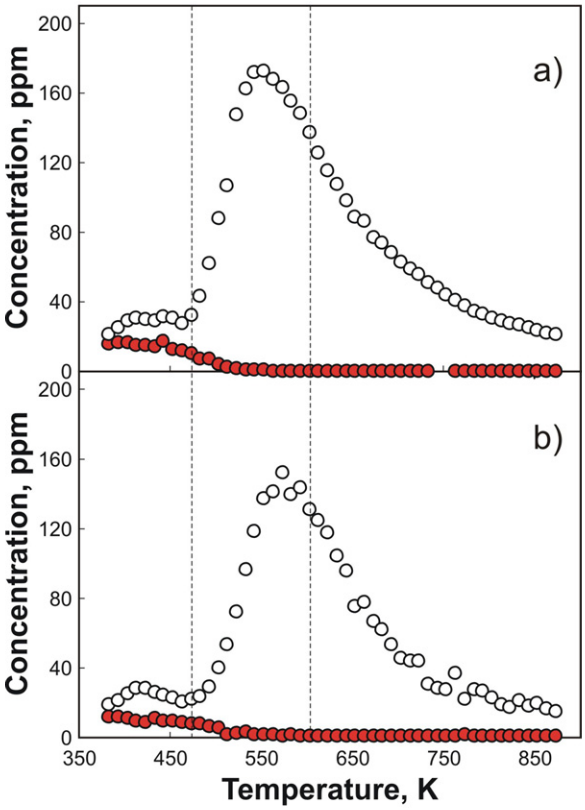

Fig. 4. Evolution in the outlet concentration of nitrogen compounds during light-off experiments in Fig. 1: (a) F-O, and (b) F-R. Symbols: ○: N_2O, and ●: NH_3.

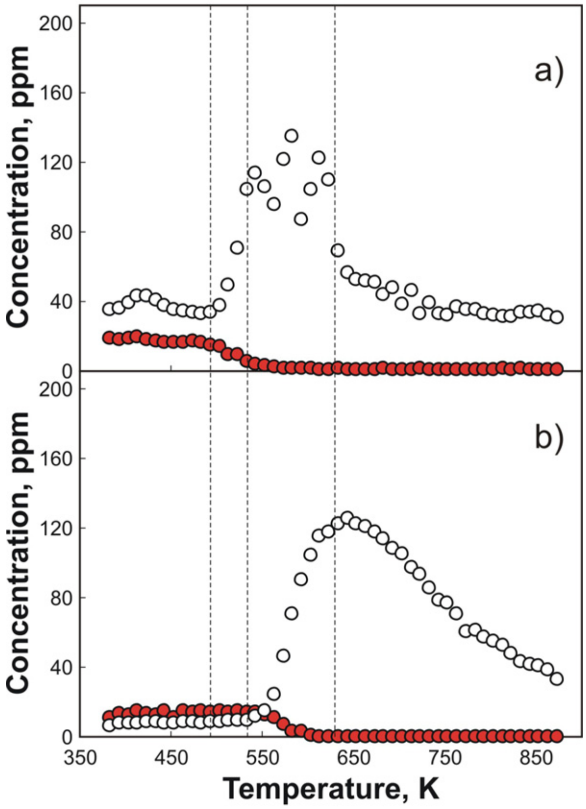

Fig. 5. Evolution in the outlet concentration of nitrogen compounds during light-off experiments in Fig. 2: (a) A-HOR, and (b) A-HCR. Symbols as in Fig. 4.

experiments have been added to the figures, to facilitate comparison.

Apart from N_2 and NO, only N_2O and NH_3 have been detected in the products, the latter in very small proportion, and only in the low temperature range, associated to the range of temperatures where C_3H_6 presents some degree of conversion but no conversion of NO is observed. N_2O is produced in two separate steps. The first one is also associated to the range of temperatures where C_3H_6 reacts, but not NO. The second one is related to NO conversion, as the concentration starts rising when NO conversion starts, and the peak temperature is set at about 70% NO conversion in the corresponding light-off curve.

3.2. Stoichiometric windows

Fig. 7 shows the results of the stoichiometric window experiments carried out in stationary conditions at 773 K with A-HOR, A-HCR and A-LOR catalysts. The data corresponding to an A/F ratio of 14.63, as compared to the results for the corresponding catalysts in Figs. 2, 3, 5 and 6, for conversion and nitrogen compounds exit concentration, respectively, shows the big differences found between the behaviour of the catalysts in cyclic and stationary conditions in NO conversion and exit concentration of nitrogen compounds.

While cyclic stoichiometric experiments in Figs. 2 and 3 show that NO conversion at 773 K is very high with aged catalysts cooled under oxidizing conditions (99.5% for A-HOR, and 98% for A-LOR) and somewhat lower with the corresponding aged catalysts cooled under cyclic or reducing conditions (88% for A-HCR, and 92% for A-LLR), stationary stoichiometric experiments in Fig. 7 show different behaviour: low NO conversion at 773 K, although the aged samples cooled under cyclic or reducing conditions still present lower values than the corresponding catalysts cooled under oxidizing conditions, and significantly higher values for catalysts aged under cyclic $O_2/H_2O/N_2$–$H_2/H_2O/N_2$ streams (49% for A-HOR, 43.5% for A-HCR, and 67% for A-LOR).

Concerning the distribution of nitrogen compounds, while cyclic stoichiometric experiments in Figs. 5 and 6 show that, at 773 K, no NH_3 is formed and N_2O concentration is relatively low (35 ppm for A-HOR, 60 ppm for A-HCR, 28 ppm for A-LOR, and 43 ppm for A-LRR), higher for aged samples cooled under cyclic or reducing conditions compared to the corresponding catalysts cooled under oxidizing conditions, stationary stoichiometric experiments in Fig. 7 show that: a significant amount of NH_3 is formed with aged catalysts cooled under oxidizing conditions (49 ppm for A-HOR, and 15 ppm for A-LOR), no NH_3 is formed with aged catalysts cooled under cyclic or reducing conditions, and much higher amount of N_2O is formed (121 ppm for A-HOR, 110 ppm for A-HCR, and 136 ppm for A-LOR), slightly higher for catalysts cooled under oxidizing conditions compared to the catalysts cooled under cyclic or reducing conditions, and for catalysts aged under cyclic $O_2/H_2O/N_2$–$H_2/H_2O/N_2$ streams compared to those aged under cyclic redox complex mixtures.

All these results clearly indicate that one should be careful when extrapolating conclusions obtained with experiments carried out in stationary conditions to actual catalyst behaviour in the automobile (cyclic) [69,70].

4. Discussion

The light-off experiments presented in Figs. 1–3 clearly point to changes in the active surface of the catalysts with temperature. Fernández-García et al. [71], using in situ Pd *k*-edge XANES and DRIFTS, studied the evolution with temperature of the chemical state of several oxidized palladium catalysts, under stationary streams simulating those of TWC. They observed that the evolution

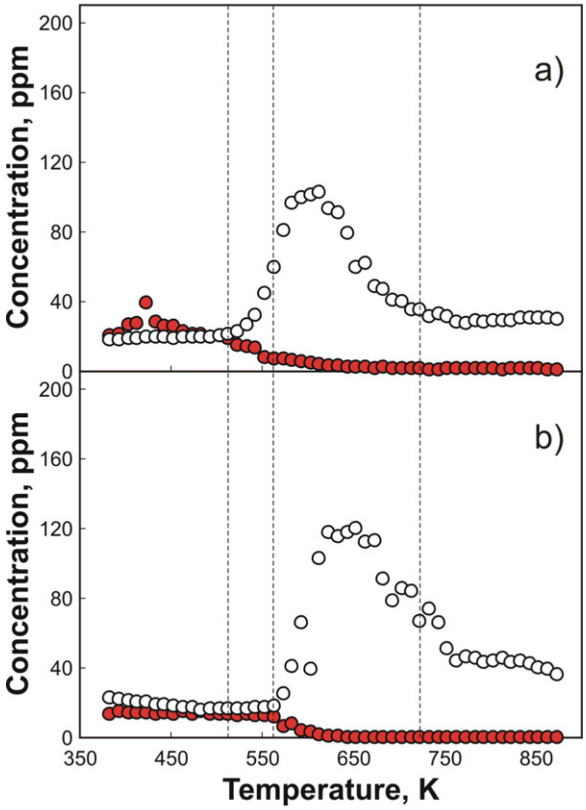

Fig. 6. Evolution in the outlet concentration of nitrogen compounds during light-off experiments in Fig. 3: (a) A-LOR, and (b) A-LRR. Symbols as in Fig. 4.

of surface palladium species was different in Pd/ceria–zirconia compared to Pd/alumina or Pd/ceria–zirconia/alumina catalysts, when C_3H_6 was present in the stream.

In their studies, initially, until 373 K, palladium was found completely oxidized as PdO (or PdO-like phase) on all catalysts. On Pd/alumina or Pd/ceria–zirconia/alumina, PdO was slowly converted to Pd(0) from around 400 K. In the absence of C_3H_6, Pd/ceria–alumina underwent a similar process. However, in the presence of C_3H_6, PdO on Pd/ceria–zirconia was slowly converted to an intermediate Pd(I)-like species with a certain metallic character which, after reaching a maximum around 550 K, was slowly converted to Pd(0), which was the only palladium species above 673 K.

Our experiments were carried out with a Pd/ceria–zirconia catalyst (Pd/$Ce_{0.68}Zr_{0.32}O_2$), in the presence of C_3H_6. Thus, stabilization of the intermediate Pd(I)-like phase is expected to occur. In fact, this explains very well the observed behaviour of the catalysts during the experiments.

A light-off experiment starts at 373 K, when conversion of PdO to Pd(I)-like species has begun. The certain metallic character of this palladium species is able to activate CO and C_3H_6, the former via carbonyl and the latter via polymeric species [71] which, in the fresh catalyst (Fig. 1), results in significant CO and C_3H_6 conversion. As the temperature increases, CO and C_3H_6 increases, in accordance with the observed increase in the amount of Pd(I)-like species in the catalyst. Above 473 K, evidence of the presence of Pd(0) species on the catalyst is given by the increase of NO conversion with temperature, activated on Pd(0). The presence of Pd(0) also produces the observed quick increase of CO and C_3H_6 conversion with temperature. Thus, the low-temperature activity of these catalysts can be associated to the presence of Pd(I)-like species, which seem to be only formed on Pd/ceria–zirconia catalysts in the presence of C_3H_6; and the high-temperature activity to Pd(0).

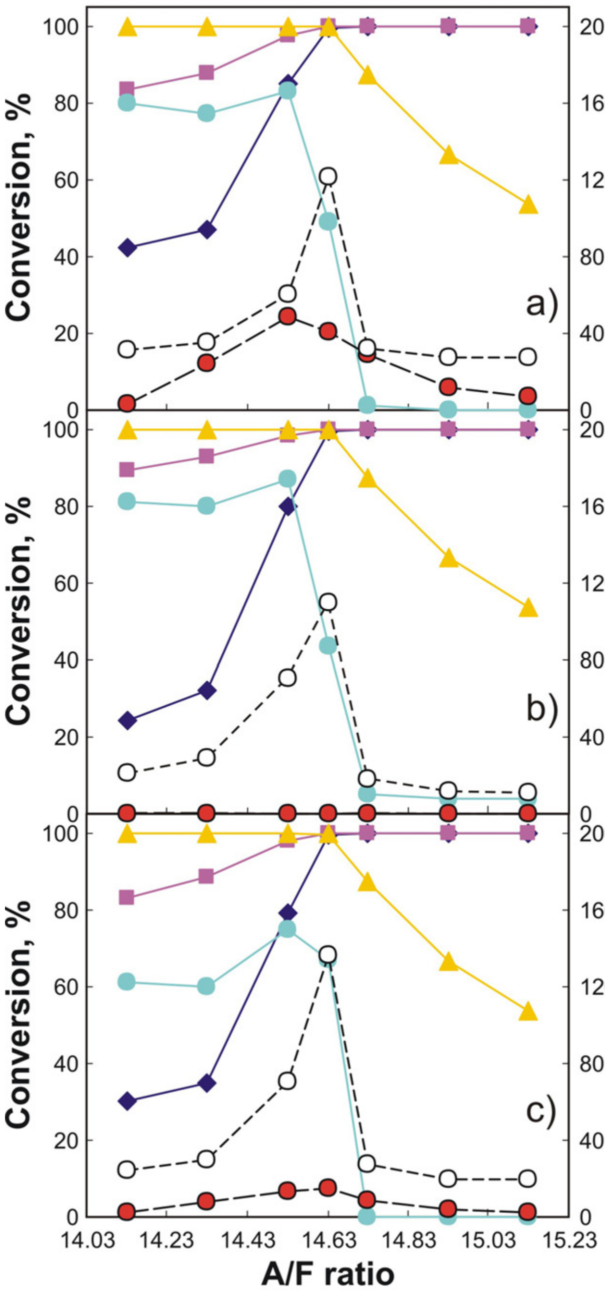

Fig. 7. Results of stoichiometric window experiments with the feedstreams in Table 3, obtained with several catalysts at 773 K: (a) A-HOR, (b) A-HCR, and (c) A-LOR. Symbols: ◆ : CO conversion, ▲ : O_2 conversion, ■ : C_3H_6 conversion, ● : NO conversion, ○: N_2O concentration, and ● : NH_3 concentration.

According to the results in Fig. 4, Pd(I)-like species are then responsible for the formation of the small amounts of NH_3 at low temperature, and also of a small amount of N_2O. However, no conversion of NO is observed in the low-temperature range. We considered the source of nitrogen to be NO adsorption during start-up of an experiment. However, we discarded this possibility as formation of NH_3 and N_2O had been observed previously at low temperature [61] in experiments carried out with a similar Pd/$Ce_{0.68}Zr_{0.32}O_2$ catalyst with simplified stationary feedstreams and long periods of stabilization between measurements at different temperature. There, the presence of C_3H_6 was observed to be necessary for NH_3 and N_2O to be formed, and also net consumption of N_2.

In the high-temperature range, on Pd(0), according to Figs. 4–6, in no case NH_3 is formed when experiments are carried out with cyclic feedstreams simulating the actual behaviour of the TWC in an automobile, no matter what the stationary experiments in Fig. 7 show.

F-O and F-R in Fig. 1a and b present the same surface area, and the same palladium dispersion, as the only difference between them is a mild reduction step. Although F-R was reduced, and palladium should have been completely transformed in Pd(0) as no stabilizing C_3H_6 was present during reduction, when the light-off experiment starts there seems to be not much difference between F-O and F-R samples, and Pd(I)-like species is present, probably stabilized during starting-up with the cycled feedstream. Reduction of the pure support [72] occurs above 573 K, and significant reduction of the support below that temperature occurs in the catalyst [73]. If reduced support were less efficient in stabilizing Pd(I)-like species or supplying oxygen, that would explain the lower value of maximum CO conversion in the low temperature range obtained with F-R.

At high temperature, when the conversion of CO, C_3H_6 and O_2 is complete, NO conversion is not complete because of the competence with WGS and SR reactions, which allow for more available oxygen in detriment of NO. Comparison between Fig. 1a and b shows that an oxidized support favours WGS and SR compared to a more reduced support. Thus, from the point of view of NO conversion, a reduction step before reaction is advisable, and that is the reason why all aged catalysts were reduced before the activity experiments.

When the catalysts are aged under cyclic redox complex mixtures, specific surface area and palladium dispersion is greatly decreased compared to the fresh catalysts. The cooling environment also affects palladium dispersion, which remains higher in the sample cooled in oxidizing complex mixture (A-HOR). Figs. 2a and 4a show that A-HOR presents the low-temperature activity characteristic of Pd(I)-like species, which indicates that there still remains enough palladium surface and enough contact between palladium and support for this effect to occur. The smaller palladium surface may be the cause for the 20 K shift of the transformation in Pd(0). On the whole, this aged catalyst is better than the fresh F-R catalyst, as it presents similar conversion of all the reactants during cold start, and practically total conversion of NO in normal operation conditions in the automobile (773 K) with a high selectivity to N_2.

The sample cooled in cyclic redox complex mixture (A-HCR) presents negligible low-temperature activity (Figs. 2b and 4b), which means that no significant Pd(I)-like species is formed. This fact, together with the shift to higher temperature of formation of Pd(0), indicates that there is a very small amount of surface palladium, at least in Pd(I)-like or Pd(0) state, perhaps by the stabilization of palladium oxidized species forming part of a solid solution with the support [47].

The catalysts aged under cyclic $O_2/H_2O/N_2$–$H_2/H_2O/N_2$ streams, present activity results (Figs. 3 and 6) compatible with a more severe ageing on the palladium side. Small, but still noticeable low-temperature conversion, indicative of the presence of Pd(I)-like species, can be observed for the catalyst cooled in oxidizing mixture (A-LOR), while negligible conversions are observed with the catalyst cooled in reducing mixture.

5. Conclusions

The light-off behaviour of a $Pd/Ce_{0.68}Zr_{0.32}O_2$ catalyst has been studied under cycled redox complex gas mixtures simulating those in automotive exhaust gases. Two zones in the light-off curves have been observed, associated to two ranges of temperature. In the low-temperature range, which has been associated to the presence of Pd(I)-like species with a certain metallic character on the catalyst surface, CO, O_2 and C_3H_6, but not NO, conversion occurs, and a small amount of NH_3 and N_2O are detected as products, what points to net conversion of N_2. Pd(I)-like species, present at low temperature, are not important during normal operation of a TWC in the automobile, but could be important during cold start, where the majority of CO and C_3H_6 emissions occur.

The high temperature range is defined by the temperature at which NO conversion starts, and has been associated to the presence of Pd(0) on the catalyst surface. In this range, no NH_3 is detected, but a significant amount of N_2O is formed with a maximum around 70% NO conversion, which decreases in favour of N_2 at higher temperature. Pd(0) species is the one predominating around 773 K, temperature of normal operation in a TWC.

The results have shown that no important effect is observed in the low-temperature behaviour of the fresh catalyst upon reduction, although a significant benefit is obtained in the conversion of NO under normal operation conditions, which has been associated to inhibition of WGS and SR reactions with a more reduced support. Thus, reduction of the catalyst is recommended before its use.

Hydrothermal ageing at 1173 K under cycled redox mixtures produces an important sintering of both palladium and support and, when the ageing procedure is more severe (high oscillation in the A/F ratio and for a longer time), stabilization of some palladium as Pd(II) probably by forming a solid solution with the support. This stabilization reduces the amount of palladium available to form Pd(I)-like and Pd(0) species, and thus the activity of the catalysts.

Cooling the aged catalysts under oxidising conditions, provided that sufficient palladium is not forming a solid solution with the support, increases palladium dispersion as compared to cooling under cycled redox or reducing conditions. If ageing is carried out in cycled redox simulated automotive exhaust gases, which probably reproduces better actual ageing in the automobile, the catalyst recovers almost completely its original activity, with comparable low-temperature behaviour (during cold start) and behaviour under normal operating conditions which even exceeds that of the fresh reduced catalyst. Thus, an oxidizing treatment to the catalyst from time to time during operation in the automobile would probably increase its durability and its behaviour during cold start by redispersion of palladium on the support. This oxidizing treatment should be followed by reduction, in order to keep the good catalyst performance towards NO in normal operation conditions. These treatments could be programmed to be carried out, for example, during annual maintenance operation of the automobile.

Finally, it has been shown that experiments carried out in stationary conditions, even with complex mixtures simulating average composition of actual automotive exhaust gases, do not provide adequate information on how the catalyst will behave in actual automobiles.

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References

[1] M. Härkönen, M. Kivioja, P. Lappi, P. Mannila, T. Maunula, T. Slotte, Soc. Automot. Eng. SP-1043 (1994) 303–316.
[2] H.J. Kwon, J.H. Baik, S.B. Kang, I.-S. Nam, B.J. Yoon, S.H. Oh, Ind. Eng. Chem. Res. 49 (2010) 7039–7051.
[3] S. Matsuura, A. Hirai, K. Arimura, H. Shinjoh, Stud. Surf. Sci. Catal. 92 (1995) 445–448.

[4] K. Nagashima, G. Zhang, T. Hirota, H. Muraki, Soc. Automot. Eng. SP-1544 (2000) 73–80.
[5] R.G. Silver, J.C. Summers, Stud. Surf. Sci. Catal. 96 (1995) 871–884.
[6] V.H. Sandoval, C.E. Gigola, Appl. Catal. A: Gen. 148 (1996) 81–96.
[7] H. Keskinen, J.M. Makela, R. Heikkinen, A. Suopanki, J. Keskinen, Catal. Lett. 119 (2007) 172–178.
[8] R.F. Hicks, Q.J. Yen, A.T. Bell, J. Catal. 89 (1984) 498–510.
[9] M. Andersson, K. Jansson, M. Nygren, Catal. Lett. 39 (1996) 253–259.
[10] H. Muraki, K. Yokota, Y. Fujitani, Appl. Catal. 48 (1989) 93–105.
[11] M.S. Kumar, A. Eyssler, P. Hug, N. van Vegten, A. Baiker, A. Weidenkaff, D. Ferri, Appl. Catal. B: Environ. 94 (2010) 77–84.
[12] H.S. Gandhi, H.C. Yao, H.K. Stepien, ACS Symp. Ser. 178 (1982) 143–162.
[13] S. Tagliaferri, R.A. Köppel, A. Baiker, Appl. Catal. B: Environ. 15 (1998) 159–177.
[14] L.S. Kravchuk, N.I. Ivashchenko, Russ. J. Appl. Chem. 70 (1997) 1423–1425.
[15] M.F. Luo, Z.Y. Hou, X.X. Yuan, X.M. Zheng, Catal. Lett. 50 (1998) 205–209.
[16] C.A. Franchini, D.V. Cesar, M. Schmal, Catal. Lett. 137 (2010) 45–54.
[17] A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, Appl. Catal. B: Environ. 31 (2001) 51–60.
[18] M. Shen, M. Yang, J. Wang, J. Wen, M. Zhao, W. Wang, J. Phys. Chem. C 113 (2009) 3212–3221.
[19] B. Zhao, G. Li, C. Ge, Q. Wang, R. Zhou, Appl. Catal. B: Environ. 96 (2010) 338–349.
[20] M.W. Zhao, M.Q. Shen, J. Wang, W.L. Wang, Ind. Eng. Chem. Res. 46 (2007) 7883–7890.
[21] B. Yue, R. Zhou, X. Zheng, W. Lu, Mater. Chem. Phys. 114 (2009) 722–727.
[22] Q.Y. Wang, G.F. Li, B. Zhao, R.X. Zhou, Appl. Catal. B: Environ. 100 (2010) 516–528.
[23] G.F. Li, Q.Y. Wang, B. Zhao, R.X. Zhou, J. Mol. Catal. A: Chem. 326 (2010) 69–74.
[24] M. Zhao, H.R. Wang, S.H. Chen, Y.L. Yao, M.C. Gong, Y.Q. Chen, Chin. J. Catal. 31 (2010) 429–434.
[25] Q.Y. Wang, B. Zhao, G.F. Li, R.X. Zhou, Environ. Sci. Technol. 44 (2010) 3870–3875.
[26] M.Q. Shen, J.Q. Wang, J.C. Shang, Y. An, J. Wang, W.L. Wang, J. Phys. Chem. C 113 (2009) 1543–1551.
[27] A. Iglesias-Juez, A.B. Hungría, A. Martínez-Arias, J.A. Anderson, M. Fernández-García, Catal. Today 143 (2009) 195–202.
[28] A. Iglesias-Juez, A. Martínez-Arias, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, M. Fernández-García, Appl. Catal. A: Gen. 259 (2004) 207–220.
[29] A.S. Ivanova, Kinet. Catal. 50 (2009) 797–815.
[30] G.F. Li, B. Zhao, Q.Y. Wang, R.X. Zhou, Appl. Catal. B: Environ. 97 (2010) 41–48.
[31] J.N. Carstens, S.C. Su, A.T. Bell, J. Catal. 176 (1998) 136–142.
[32] R.F. Hicks, M.L. Young, R.G. Lee, H. Qi, J. Catal. 122 (1990) 280–294.
[33] R.F. Hicks, M.L. Young, R.G. Lee, H. Qi, J. Catal. 122 (1990) 295–306.
[34] P. Briot, M. Primet, Appl. Catal. 68 (1991) 301–314.
[35] R. Zhou, B. Zhao, B. Yue, Appl. Surf. Sci. 254 (2008) 4701–4707.
[36] E.Y. Long, Y. Wang, X.Y. Zhang, Y.L. Li, M.C. Gong, Y.Q. Chen, Chin. J. Catal. 31 (2010) 313–316.
[37] X.Y. Zhang, E.Y. Long, Y.L. Li, J.X. Guo, L.J. Zhang, M.C. Gong, M.H. Wang, Y.Q. Chen, J. Nat. Gas Chem. 18 (2009) 139–144.
[38] S. Specchia, E. Finocchio, G. Busca, P. Palmisano, V. Specchia, J. Catal. 263 (2009) 134–145.
[39] F.X. Yin, S.F. Ji, P.Y. Wu, F.Z. Zhao, H. Liu, C.Y. Li, ChemSusChem 1 (2008) 311–319.
[40] S. Guerrero, P. Araya, E.E. Wolf, Appl. Catal. A: Gen. 298 (2006) 243–253.
[41] C. Bozo, N. Guilhaume, J.M. Herrmann, J. Catal. 203 (2001) 393–406.
[42] G. Wang, M. Meng, Y.Q. Zha, T. Ding, Fuel 89 (2010) 2244–2251.
[43] Q.B. Zhang, L.H. Zhao, B.T. Teng, Y.L. Xie, L. Yue, Chin. J. Catal. 29 (2008) 373–378.
[44] S. Zhao, R.J. Gorte, Appl. Catal. A: Gen. 248 (2003) 9–18.
[45] C. Thomas, O. Gorce, F. Villain, G. Djega-Mariadassou, J. Mol. Catal. A: Chem. 249 (2006) 71–79.
[46] M.F. Luo, Z.Y. Pu, M. He, J. Jin, L.Y. Jin, J. Mol. Catal. A: Chem. 260 (2006) 152–156.
[47] A. Iglesias-Juez, A. Martínez-Arias, M. Fernández-García, J. Catal. 221 (2004) 148–161.
[48] A. Lemaire, J. Massardier, H. Praliaud, G. Mabilon, M. Prigent, Stud. Surf. Sci. Catal. 96 (1995) 97–108.
[49] H.C. Yao, Y.F. Yu Yao, J. Catal. 86 (1984) 254–265.
[50] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, J. Catal. 114 (1988) 23–33.
[51] M. Yang, M.Q. Shen, J. Wang, J. Wen, M.W. Zhao, J. Wang, W.L. Wang, J. Phys. Chem. C 113 (2009) 12778–12789.
[52] E.C. Su, W.G. Rothschild, J. Catal. 99 (1986) 506–510.
[53] T. Shido, Y. Iwasawa, J. Catal. 136 (1992) 493–503.
[54] J.G. Nunan, W.B. Williamson, H.J. Robota, Soc. Automot. Eng. PT-123 (2006) 143–150.
[55] M.H. Yao, R.J. Baird, F.W. Kunz, T.E. Hoost, J. Catal. 166 (1997) 67–74.
[56] Z.Q. Han, J.Q. Wang, H.J. Yan, M.Q. Shen, J. Wang, W.L. Wang, M. Yang, Catal. Today 158 (2010) 481–489.
[57] J.P. Cuif, G. Blanchard, O. Touret, M. Marczi, E. Quéméré, Soc. Automot. Eng. SP-1207 (1996) 73–81.
[58] M. Pijolat, M. Prin, M. Soustelle, O. Touret, P. Nortier, J. Chem. Soc. Faraday Trans. 91 (1995) 3941–3948.
[59] I. Heo, J.W. Choung, P.S. Kim, I.S. Nam, Y.I. Song, C.B. In, G.K. Yeo, Appl. Catal. B: Environ. 92 (2009) 114–125.
[60] T. Bunluesin, R.J. Gorte, G.W. Graham, Appl. Catal. B: Environ. 14 (1997) 105–115.
[61] M.P. González-Marcos, A. Betolaza, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Int. J. Chem. Reactor Eng. 4 (2006) A34.
[62] H.J. Kwon, J.H. Baik, Y.T. Kwon, I.-S. Nam, S.H. Oh, Chem. Eng. J. 141 (2008) 194–203.
[63] B. Zhao, C. Yang, Q. Wang, G. Li, R. Zhou, J. Alloys Compd. 494 (2010) 340–346.
[64] J.R. González-Velasco, J.A. Botas, J.A. González-Marcos, M.A. Gutiérrez-Ortiz, Appl. Catal. B: Environ. 12 (1997) 61–79.
[65] N. Hickey, P. Fornasiero, R. Di Monte, J. Kašpar, J.R. González-Velasco, M.A. Gutiérrez-Ortiz, M.P. González-Marcos, J.M. Gatica, S. Bernal, Chem. Commun. (2004) 196–197.
[66] J.R. González-Velasco, M.A. Gutiérrez Ortiz, J.L. Marc, J.A. Botas, M.P. González-Marcos, G. Blanchard, Ind. Eng. Chem. Res. 39 (2000) 272–276.
[67] J.R. González-Velasco, J.A. Botas, R. Ferret, M.P. González-Marcos, J.L. Marc, M.A. Gutiérrez-Ortiz, Catal. Today 59 (2000) 395–402.
[68] G.W. Graham, H.W. Jen, W. Chun, R.W. McCabe, Catal. Lett. 44 (1997) 185–187.
[69] A. Kubacka, A. Martínez-Arias, M. Fernández-García, M.A. Newton, Catal. Today 145 (2009) 288–293.
[70] A. Iglesias-Juez, A. Martínez-Arias, M.A. Newton, S.G. Fiddy, M. Fernández-García, Chem. Commun. (2005) 4092–4094.
[71] M. Fernández-García, A. Iglesias-Juez, A. Martínez-Arias, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, J. Catal. 221 (2004) 594–600.
[72] J.L. Ayastuy, M.P. González-Marcos, A. Gil-Rodríguez, J.R. González-Velasco, M.A. Gutiérrez-Ortiz, Catal. Today 116 (2006) 391–399.
[73] B. Zhao, Q. Wang, G. Li, R. Zhou, J. Alloys Compd. 508 (2010) 500–506.