

Effect of Na, K, Ca and P-impurities on diesel oxidation ~~catalysts~~ reaction (DOCs)

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Abstract

In order to reach the limits of CO₂ emissions set by Kyoto protocol, the use of biofuels is becoming more interesting gaining momentum. However, the biofuels contains alkali and alkaline earth metals (Na, K and Ca) and phosphorus (P) species, which, which could decrease the efficiency of the after-treatment system are potential poisons for the post treatment system. The main aim of this study is to increase the knowledge of the effect of impurities contain on biofuel on the catalytic activity of the diesel oxidation catalysts (DOCs). The main aim of this study is to increase the knowledge of the effect of impurities in the diesel oxidation catalysts (DOCs). Both reference (PtPd/CeZrO₂/La-Al₂O₃) and modified catalysts were synthesized, characterized by several techniques and tested, concerning their physico-chemical, redox and catalytic properties. Based on the characterization results, the catalyst crystalline structure did not change was not modified after the impurities incorporation, however, the specific surface area was decreased in all cases. Both oxygen interaction and NO adsorption strength was were increased due to the low electronegativity of Na, K and Ca species, according to H₂-TPR and NO-TPD analyses. XPS analysis confirmed the formation of cerium phosphate, which can stabilize the Ce³⁺ oxidation state related to its higher Ce³⁺/Ce⁴⁺ ratio, diminishing the catalytic redox activity. The physico-chemical and redox properties modifications after Na, K and Ca impurities addition diminished have a negative influence on the CO and NO removal catalytic activity, however, the C₃H₆ conversion was improved. Besides, both CO and C₃H₆ oxidation were enhanced, while the NO to NO₂ conversion was disfavoured decreased in presence of P species.

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1 **Keywords:** biodiesel impurities, alkali and alkaline earth metals, phosphorus species,
2 afterpost-treatment system, diesel oxidation catalyst.

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3 4 1. Introduction

5 Governmental regulations concerning atmospheric pollution from combustion
6 engines are becoming increasingly stringent [1]. This imposes a continuous
7 improvement of existing after-treatment systems and the development of new
8 concepts that can accomplish future emission standards. For this purpose, the Euro VI
9 standard for heavy duty vehicles (NO_x and particle emissions) [2] established that the
10 exhaust gas afterpost-treatment systems must be equipped with a diesel oxidation
11 catalyst (DOC), a catalyst for the selective reduction of NO_x (SCR) and a diesel
12 particulate filter (DPF), with a required durability of 7 years or 700000 km.
13 Particularly, the DOC catalyst are mainly composed of noble metals (platinum,
14 palladium) supported on lanthanum-stabilised alumina and doped with ceria-zirconia-
15 mixed oxides (high oxygen storage capacity, providing a better resistance to redox
16 aging [3]). This catalyst facilitates the oxidation of carbon monoxide (CO), unburned
17 hydrocarbons (HC) and as well as the oxidation of NO towards NO₂, which is an
18 essential component for DPF regeneration and SCR or NSR (NO_x Storage Reduction)
19 catalysts. Indeed, the presence of high amounts of NO₂ accelerates the soot oxidation
20 in the DPF at low temperature and increases the NO_x conversion efficiency in the
21 urea-SCR and NSR systems [4]. Thus, the DOC catalyst plays a crucial role in the
22 complete after-treatment system. A deactivation of the DOC catalyst can therefore
23 have an impact on the post-treatment system as a whole.

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24 Moreover, the use of renewable energy sources has been gaining some
25 attention during the last few years. Biodiesel have the potential to replace
26 conventional diesel fuels due to similar calorific values to those of a traditional fuel.
27 In addition, it use decrease in a great extend the emissions of greenhouse gases as
28 carbon dioxide, carbon monoxide (CO), soot particles and hydrocarbon emissions.
29 However, increased NO_x emissions are observed in comparison to regular diesel fuel
30 [5]. Biofuels, particularly biodiesel, have the potential to replaee conventional diesel
31 fuels [6], which decrease in a great extend the emissions of greenhouse gases as
32 carbon dioxide, producing less carbon monoxide (CO), soot particles and
33 hydrocarbon (HC) emissions. However, increased NO_x emissions are observed in
34 comparision to regular diesel fuel [7]. Moreover, biofuels are indeed known to contain

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1 some alkali and alkaline earth metals (Na, K and Ca) or phosphorus (P), which can
2 affect the **afterpost-treatment** system. The alkali elements are present in the biofuel
3 due to the use of NaOH or KOH catalyst for the liquid-phase synthesis of biodiesel.
4 Although the biodiesel **is are** purified by impurities extraction and glycerine
5 separation after transesterification process some residual amounts of Na and/or K are
6 still present in the produced biodiesel. In addition, small amounts of calcium (Ca) can
7 also be incorporated to the fuel from the purification process [8,9] and detergent
8 additives. Moreover, phosphorus (P) species can be present in conventional diesel and
9 biodiesel fuels from the decomposition products of the antiwear/antioxidant additive
10 zinc dialkyldithiophosphate (ZDDP) [10–12].

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11 Regardless of the source, these inorganic compounds are converted into oxides,
12 sulphates, hydroxides or carbonates during the combustion process to form an ash that
13 can be deposited onto the exhaust emission control devices. According to the
14 literature, the alkali and alkaline earth metals can act as promoters or poisons for
15 catalysts, having an important effect on PdO reducibility [11], Pt sites blockage [12],
16 NO_x storage capacity [13] and relative adsorption strengths of reactants [14]. Contrary
17 to the alkaline and alkaline earth species, which are currently deposited on catalyst
18 surface, the **greater high** penetration depth of phosphorus species could favour the
19 formation of bonds and compounds directly with the support elements [15]. **As a**
20 **consequence, the catalytic activity of the inorganic containing-catalysts is affected,**
21 **decreasing the hydrocarbon and NO oxidation.** ~~As a consequence, the catalytic~~
22 ~~activity of the inorganic containing-catalysts is affected, decreasing the hydrocarbon~~
23 ~~oxidation and limiting the NO oxidation and reduction activity [12–16].~~ Nevertheless,
24 the soot combustion could be improved in presence of biodiesel impurities related to
25 the high species mobility [13].

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26 In this context, the aim of this study is to increase the knowledge of the effect
27 of biodiesel impurities **oin** the **afterpost-treatment** system of heavy-duty vehicles, and
28 more precisely **oin** the diesel oxidation catalyst. The reference catalyst
29 PtPd/CeZrO₂/La-Al₂O₃ was modified by wetness impregnation with Na, K, Ca and P,
30 simulating the incorporation of these compounds by the use of biodiesel for long
31 periods of time. Considering limits established by the European normative, the
32 amount of impurities added was chosen based on average fuel consumption of
33 35L/km for a truck fuelled exclusively by biodiesel during 700000 km [16]. Various
34 characterization techniques are used to evaluate the physico-chemical, structural,

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1 redox and surface properties of reference and modified catalysts. Finally, the
2 impurities effect on the catalytic CO, C₃H₆ and NO oxidation activity was studied.

3 **2. Experimental**

4 *2.1. Catalysts preparation*

5 Alumina support was prepared by calcination of γ -Al₂O₃ (Alfa Aesar) at
6 650°C for 5h under air flow (50 ml min⁻¹) containing 10% water. The alumina
7 calcined at 650°C was doped with 4 wt% of lanthanum by incipient wetness
8 impregnation, using an aqueous solution of La(NO₃)₃·6H₂O (Sigma Aldrich). Then the
9 support was dried at 100°C overnight and calcined under 10% water and 50 ml min⁻¹
10 of air flow. The alumina-supported ceria-zirconia supports were prepared by co-
11 impregnation of the lanthanum doped alumina with an aqueous solution of cerium
12 (III) nitrate hexahydrate (Sigma Aldrich) and zirconyl nitrate hydrate (Sigma Aldrich)
13 as precursors of cerium and zirconium, respectively. The CeZrO₂/Al-La support was
14 prepared with 10 wt% of ceria-zirconia oxides (Ce/Zr weight ratio of 2.5). This
15 material was dried again at 100°C overnight and calcined under the same conditions.
16 Finally, the reference catalyst was prepared by incipient wetness impregnation of the
17 support with an aqueous solution of Pt(NH₃)₄(NO₃)₂ (Sigma Aldrich) and Pd(NO₃)₂
18 (Sigma Aldrich); drying and calcination conditions after the impregnation were the
19 same as used for the support. In this way, the reference catalyst was obtained with
20 0.71 wt% Pt – 0.47 wt% Pd/CeZrO₂/La-Al₂O₃.

21 Once the reference catalyst was obtained, impurities were added by the same
22 procedure, the incipient wetness impregnation method of aqueous solutions of NaNO₃
23 (Sigma Aldrich), KNO₃ (Sigma Aldrich), Ca(NO₃)₂·4H₂O (Sigma Aldrich) or
24 (NH₄)₂HPO₄ (Sigma Aldrich). The amount of impurities added was related to real
25 percentage found on DOCs based on biodiesel fuel consumption of 35L/km for a
26 truck during 700000 km. The modified catalysts synthesized were: 1.6 wt% Na-, 0.5
27 wt% K-, 1.6 wt% Ca- and 5.6 wt% P-PtPd/CeZrO₂/La-Al₂O₃ catalysts.

28

29 *2.2. Catalyst characterization*

30 The chemical composition of the different catalysts was quantitatively
31 determined using inductively coupled plasma optical emission spectroscopy (ICP-
32 OES) on a flame Perkin Elmer M1100 spectrometer. Before the measurement, the

1 metal oxides were dissolved using a mixture of inorganic acids (H_2SO_4 , HNO_3 and
2 HF).

3 Powder X-ray diffraction (XRD) patterns of all catalysts were obtained using a
4 Bruker D8 diffractometer ($\text{CuK}\alpha$ radiation at 0.154184 nm) equipped with a Ni filter
5 and 1-D fast multistrip detector (LynxEye, 192 channels on 2.95°). The
6 diffractograms were collected at 2θ with steps of 0.02° from 4° to 80° for the total
7 acquisition time of 32 min. Phase identification was carried out using the Diffrac.Eva
8 software (Bruker) and the ICDD-PDF4+ database.

9 Nitrogen adsorption and desorption isotherms were measured at -196°C on a
10 Micromeritics ASAP 2020 surface area and porosity analyzer. Primary, the catalysts
11 were degassed at 300°C for 3h under vacuum. The specific surface area of each
12 catalyst was calculated from the linear part using the Brunauer-Emmett-Teller (BET)
13 method ($P/P_0 = 0.05\text{--}0.25$). The porous volume and the pore size distribution were
14 calculated using the Barrett-Joyner-Halenda (BJH) method.

15 Transmission electron microscopy (TEM) observations of the catalysts were
16 performed on a JEM-2100 microscope with EDX detector. All catalysts were
17 ultrasonically dispersed in ethanol and then dried over a copper grid coated with a
18 carbon film.

19 X-ray photoelectron spectroscopy (XPS) analysis over all catalysts were
20 carried out on a Kratos Analytical AXIS Ultra DLD electron spectrometer using the
21 $\text{AlK}\alpha$ (1486.6 eV) radiation source. In order to compare all the spectra recorded, the
22 $\text{Al}2p$ peak from Al_2O_3 present in the catalysts was selected as a binding energy
23 reference, and its value fixed at 74.6 eV.

24 The reducibility of the catalysts was examined by hydrogen temperature
25 programmed reduction (H_2 -TPR) using mass spectrometer detection (Hiden, HPR 20).
26 Prior to the test, the catalyst (about 100 mg) was firstly pre-treated at 600°C for 15
27 min in a synthetic air flow of 50 ml min^{-1} and then cooled down to room temperature
28 in an air flow. It was followed by 5 minutes of purge in an Ar flow, controlled by
29 residual O_2 analysis. 2% H_2/Ar with a flow rate of 50 ml min^{-1} as the reducing gas
30 was introduced and the reactor was heated from 25 to 650°C with a rate of $20^\circ\text{C min}^{-1}$.
31 H_2 consumption was quantitatively calculated by time integration of H_2 -TPR profiles.
32 Concomitant H_2O evolution was also recorded.

1 Temperature-programmed desorption (TPD) was performed using NO as the
2 adsorbate gas. Samples (ca. 0.1g) were loaded into a U-shaped quartz tube and pre-
3 treated at 250°C for 30 min, under a He flow of 50 ml min⁻¹. Adsorption was carried
4 out at room temperature in a 4000 ppm NO-He flow (50 ml min⁻¹) for 1 h. The
5 catalysts were then exposed to He for 0.5 h at room temperature to remove all the
6 physically adsorbed species before starting the desorption temperature program,
7 which consisted of a ramp of 5°C min⁻¹ until 600°C. Desorbed gases (NO, NO₂, N₂O,
8 CO₂) were analysed by infrared-ultraviolet spectroscopy (EMERSON IR/UV X-
9 STREAM Enhanced XEPG).

10 2.3. Catalyst activity measurements

11 The catalytic behaviour was tested in a U tubular quartz reactor with the
12 catalyst placed on a fritted quartz place (30 mm in length and 8 mm in internal
13 diameter). The reactor was heated with a furnace and the temperature measured with a
14 K-type thermocouple (Omega). The water content in the reaction mixture was
15 controlled using the vapour pressure of H₂O at the temperature of the saturator (28°C)
16 controlled by a heating bath. All lines placed downstream from the saturator were
17 heated above 100°C to prevent condensation. Catalytic tests were carried out using 50
18 mg of catalysts and a reactant mixture containing [NO] ≈ 500 ppm, [CO] ≈ 300 ppm,
19 [C₃H₆] ≈ 300 ppm, [CO₂] ≈ 5 vol.%, [O₂] ≈ 10 vol.%, [H₂O] ≈ 3.5 vol.% and He as
20 the carrier gas, with the total flow of 250 ml min⁻¹. **In agreement with the industrial
21 partner of the project, the gas hourly space velocity (GHSV) of the total gas mixture
22 was fixed at 135000 h⁻¹.** Temperature was increased and decreased by a ramp of 5°C
23 min⁻¹ from 80°C up to 600°C. Three consecutive catalytic cycles were performed to
24 analyse the catalytic stability. Gas effluents were analyzed with a micro gas
25 chromatograph (SRA % GC-R3000), a FID (Agilent Technologies GC-FID 6850
26 Network GC) and an infrared-ultraviolet spectroscopy (EMERSON IR/UV X-
27 STREAM Enhanced XEPG).

28 3. Results and discussion

29 3.1. Catalyst characterization

30 3.1.1. Chemical composition (ICP) and X-Ray diffraction (XRD)

31 The chemical composition and physico-chemical properties of synthesized
32 catalysts are listed in Table 1. The metal percentage found by chemical analysis

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1 [evidenced a decrease of percentage of platinum. This effect could be ascribed to](#)
2 [leaching of Pt after the second hydrothermal treatment.](#) **corresponded with the**
3 **expected theoretical one (see catalyst preparation).**

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4 Moreover, Figure 1 presents the XRD patterns of (A) reference catalyst
5 (PtPd/CeZrO₂/La-Al₂O₃), modified catalysts (B) Na-, (C) K-, (D) Ca- and (E) P-PtPd
6 PtPd/CeZrO₂/La-Al₂O₃ catalysts obtained using 2θ positions between 20 and 80°. The
7 reference catalyst diffraction pattern presented the peaks characteristics of γ-alumina
8 (45.8°, 47.6°, and 67°) and θ-alumina (33.3°, 37°, 39.5°) as well as two peaks at 28.6°
9 and 33.1°, which are related to the presence of CeO₂ with a cubic structure [17] and an
10 additional peak was found at 56.5°, associated with ceria-zirconia mixed oxide [18].
11 This ceria-zirconia mixed oxide could be favoured by the precursors used during
12 catalysis synthesis. Accordingly to [19], the different charge between anionic
13 Ce(NO₃)₆²⁻ and the cationic zirconyl (ZrO²⁺) could facilitate their interaction,
14 favouring the formation of a solid solution. Noble metals (Pt, Pd) were not detected
15 by XRD, which could be attributed to the quite homogeneous distribution on the
16 surface of the support and their very low metal-load on the catalysts.

17 In addition, peaks corresponding to Na, K and Ca impurities were not
18 observed on the XRD profiles of alkaline and alkaline earth containing catalysts.
19 These spectra showed only peaks attributable to γ-alumina, cerium oxide and ceria-
20 zirconia mixed oxide. Comparing modified catalysts spectra with reference one,
21 results suggest that metal addition do not modify the crystal structure of the catalyst.

22 **However, in the case of P-PtPd catalyst, the phosphorus additive appeared as cerium**
23 **phosphate at 2θ = 21° [20].**

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24 3.1.2. N₂-adsorption/desorption

25 [The N₂-adsorption/desorption analyses showed that the BET specific](#)
26 [surface area \(SSA\) of the alkaline and alkaline earth containing catalysts slightly](#)
27 [decreased in comparison to the reference catalyst. In order to verify if this effect was](#)
28 [associated with the impact of the second hydrothermal treatment after the](#)
29 [impregnation of the additives, a second hydrothermal calcination at 650°C was](#)
30 [performed to the reference catalyst \(Aged - PtPd\). The obtained results indeed](#)
31 [evidenced that the ageing treatments had an effect on the SSA of this catalyst, which](#)
32 [was decreased after treatment, phenomenon also observed by some other authors \[21\].](#)
33 **However, the decrease of SSA due to phosphorus addition was more severe, that**

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1 could be attributed to their physical deactivation (pore blocking) by phosphates [22],
2 according to XRD results. Thus, the amount of additives in the catalysts had an
3 important influence on the SSA and pore size distribution, as the catalyst with higher
4 percentage of additives presented the lower SSA value.

5 The BJH pore size distribution curves (not shown) presented a double
6 pore size distribution: smaller mesopores at around 3-4 nm and larger mesopores with
7 a pore diameter between 30-40 nm. The amount of the smaller mesopores (< 5 nm)
8 slightly decreased after impurities addition, in agreement with the decrease of SSA.

9 The N₂-adsorption/desorption analyses showed that the BET specific surface
10 area (SSA) of the alkaline and alkaline earth containing catalysts slightly decreased in
11 comparison to the reference catalyst. However, the decrease of SSA due to
12 phosphorus addition was more severe. This effect could be associated with the impact
13 of the second hydrothermal treatment after the impregnation of the additives. In order
14 to evaluate this effect, a second hydrothermal calcination at 650°C was performed to
15 the reference catalyst (Aged -PtPd). The obtained results indeed evidenced that the
16 ageing treatments had an effect on the SSA of this catalyst, which was decreased after
17 treatment [22].

18 Figure 2 shows the N₂-adsorption/desorption isotherms of the reference, aged
19 and Na-PtPd as an example of modified-catalysts. Figure 2 shows the N₂-
20 adsorption/desorption isotherms of the reference and aged catalysts. Both of them
21 exhibited a type IV isotherm based upon the Brunauer-Deming-Deming-Teller
22 (BDDT) classification, which is characteristic of mesoporous materials (2-100 nm)
23 with H3-type of hysteresis [23]. The isotherms obtained for all the modified catalysts
24 (not shown) had the same shape (e.g. Figure 2, Na-PtPd), namely the type IV
25 isotherm corresponding to mesopores distribution, which evidenced that these
26 additives did not modify the type of pores in the catalyst structure.

27 In addition, Figure 3 presents the BJH pore size distribution curves for the
28 reference, hydrothermally aged and modified catalysts. Both fresh and aged reference
29 catalysts presented a double pore size distribution: smaller mesopores at around 3-4
30 nm and larger mesopores with a pore diameter between 30-40 nm. However, it can be
31 observed that the amount of the smaller mesopores (< 5 nm) was decreased after
32 aging, while the amount of the larger mesopores (5-30 nm) was increased. This
33 phenomenon was in agreement with the decrease and the increase of SSA and total
34 pore volume, respectively, after the hydrothermal aging (Table 1). Comparing the

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1 pore size distribution of Na, K and Ca PtPd catalysts with that of the fresh catalyst, an
2 increase of the average pore size was detected, which was also observed for the aged
3 catalyst. In addition, the smaller mesopores amount was reduced in presence of
4 phosphorus. Nevertheless, the total pore volume remains constant comparing to that
5 of the fresh catalyst, which could be attributed to their physical deactivation (pore
6 blocking) by phosphates [24], according to XRD results. Thus, the amount of
7 additives in the catalysts had an important influence on the SSA and pore size
8 distribution, as the catalysts with higher percentage of additives had the lower BET
9 surface area and the most evident pore blocking.

10 3.1.3. Transmission electron microscopy (TEM)

11 Figure 34 showed TEM analysis results corresponding to: a) reference
12 (PtPd/CeZr/La-Al₂O₃), b) Na- and c) P-PtPd PtPd/CeZr/La-Al₂O₃ catalysts. These
13 observations were performed to better understand the morphological and structural
14 changes in synthesized catalysts after additives incorporation.

15 Firstly, it can be observed that no transition from the γ -phase to the α -phase
16 can be evidenced, as expected from the rather moderate ageing temperature used in
17 this study (650°C). According to the TEM images, the alumina support appears as
18 greyish, elongated, partly transparent particles. In the support material, EDX analysis
19 showed that dark dots correspond to ceria-zirconia, such as CeO₂ and CeZrO₂ mixed
20 oxide, according to XRD results. It could be also observed that the particles of ceria-
21 zirconia formed are uniform in size and covering alumina surface. As can be seen on
22 the encircled area in the micrographs, the lattice fringes are clearly visible with a d-
23 spacing of 0.316 nm, which can be assigned to the (111) plane of the cerium oxide
24 [24]. The detection of platinum and palladium was very difficult and no clear
25 evidence of Pt and Pd-particle growth was observed either in the fresh or modified
26 catalysts. In the elemental analyses (EDX), both elements were detected in different
27 areas of the ceria-zirconia oxides forming a bimetallic alloy in some places.

28 In the case of Na- (Figure 34b), K- and Ca- (not shown) PtPd catalysts, the
29 TEM images show the same trends. There are no changes in the alumina support or in
30 the platinum or palladium particles size. Again, ceria-zirconia oxides cover the
31 alumina surface with noble metals attached to them as a dispersed phase, according to
32 the EDX analysis. The presence of alkaline and alkaline-earth metals was detected by

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1 EDX in the alumina support, with no changes in its structure or in the platinum-
2 palladium particles.

3 Contrary, TEM analyses indicate some structural changes after phosphorus
4 addition. It can be observed in Figure 34c that alumina was covered by a phosphorus
5 (P)-containing layer, as well as cerium and zirconium oxides. The phosphorus-
6 containing layer covering cerium oxides could be responsible for the cerium
7 phosphate detected by XRD. In this case, platinum-palladium alloy was visible on the
8 phosphorous-containing layer, corresponding to an increased particles size after
9 phosphorus addition.

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10 3.1.4. Hydrogen temperature programmed reduction (H_2 -TPR)

11 In order to analyse the influence of the additives on the metal support
12 interaction and reducibility of the catalysts, TPR experiments were carried out from
13 room temperature to 650°C. The TPR profiles of reference and modified-catalysts are
14 depicted in Figure 45 and the H_2 consumption in Table 2.

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15 Firstly, the reference catalyst, PtPd/CeZrO₂/La-Al₂O₃, presented two main
16 sharp reduction peaks at low temperature and a broad peak at temperatures higher
17 than 450°C. The reduction peak located at 70°C could be attributed to the
18 simultaneous reduction of PdO species [25] and surface oxygen of CeO₂ around the
19 Pd species [26]. The reduction peak observed at 220°C can be assigned to the
20 reduction of PtO_x species and the superficial cerium oxide reduction, promoted by the
21 metal [27]. Finally, the broad peak detected at temperatures higher than 450°C could
22 be associated with the reduction of bulk ceria promoted by zirconium. Zirconium
23 promoting role in the bulk reduction of the solid solutions has been largely reported
24 [19,28]. The addition of zirconium to the lattice of ceria increases the number of
25 oxygen vacancies, which induces a largest mobility of oxygen and favours the
26 reducibility of the cerium-zirconium mixed oxide [19].

27 The H_2 -TPR profile for the Aged-PtPd catalyst (Figure 4) presented one peak
28 corresponding to PdO reduction at 87°C. The increase of the temperature reduction
29 can be correlated to the significant deterioration of the surface oxygen mobility after
30 second hydrothermal treatment [29]. In addition, the disappearance of the Pt reduction
31 peak for the aged-PtPd catalyst could be ascribed to its lower amount of Pt, which
32 was leached during hydrothermal aging.

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1 The H₂-TPR profile of modified catalysts (Figure 45) showed some
2 differences compared to the reference catalyst. In addition to the decrease of oxygen
3 diffusion after the second hydrothermal treatment, metal-support interaction was
4 increased after additives incorporation, shifting first reduction peak towards higher
5 temperatures, with a stronger effect in the case of Na, K and Ca. This effect could be
6 ascribed to differences in the electronegativity of the additives [30]. The
7 electronegativity of the additives used decreases as follow: Ca > K ≈ Na. Due to the
8 lower electronegativity of the alkali species, a higher interaction of metals with
9 oxygen was produced which increased the reduction temperature. According to this
10 electronegativity tendency, the lowest electronegativity of sodium and potassium
11 species increases the temperature corresponding to the first reduction peak. However,
12 the higher electronegativity of Ca comparing to that of Na and K compounds, leads to
13 the slightly higher reduction temperature than reference catalyst, with a less marked
14 effect than Na and K.

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15 Otherwise, the second reduction peak became broader after impurities addition.
16 With regard to reduction temperature, alkaline and alkaline-earth presence shifted
17 peak associated with PtO_x to slightly higher temperature than in the case of the
18 reference catalyst. In contrast, the second peak on the P-PtPd catalyst shifted to higher
19 temperature in comparison to the PtPd catalyst. These effects can be ascribed to the
20 lower amount of Pt found after impurities addition, probably due to leaching of Pt
21 during the hydrothermal calcination. The broad reduction peak of bulk ceria appears
22 at temperatures higher than 450°C in all the cases.

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23 The H₂ consumption of the PtPd/CeZrO₂/La-Al₂O₃ catalyst increases by
24 supplying Na, K and Ca additives. However, reduction peaks became broader after
25 alkali addition, being more difficult to integrate accurately. This finding indicates that
26 there might be a hydrogen spillover phenomenon on alkali-modified catalysts during
27 the TPR process, in which H₂ adsorbed on the metal atoms migrates to alkaline oxides
28 in close proximity to them [31]. This promotion effect is closely related to the
29 electron donation property of alkali metals. Ca-PtPd catalyst had a similar effect on
30 the H₂ adsorption, however a weaker promotion effect than the alkali metals was
31 exhibited, according to its higher electronegativity [33]. The consumption of
32 hydrogen measured after P addition was lower than the theoretical one, which could
33 be ascribed to CePO₄ formation as evidenced by XRD. Although only a small amount

1 of Ce is locked as Ce^{3+} in the CePO_4 phase, the phosphorus compound layer detected
2 by TEM could block and inhibit the reduction process [32].

3 3.1.5. *X-ray photoelectron spectroscopy (XPS)*

4 The XPS spectra obtained from the five catalysts studied yielded useful
5 additional information about the oxidation state of the catalysts. Firstly, the peaks
6 corresponding to XPS profiles of the Al 2p (Figure 56) are centred in the range of
7 74.4-74.8 eV for all catalysts, corresponding to $\gamma\text{-Al}_2\text{O}_3$, which evidenced that the
8 binding energy (BE) of the alumina was not modified after impurities addition. This
9 fact could be attributed to Al_2O_3 -stabilization with lanthanum, which was found as
10 carbonates in a BE range of 834-842 eV [33].

11 All catalysts presented the same peaks characteristic of pure CeO_2 (not shown),
12 according to the convention established by Burroughs [34]. Cerium was detected in
13 two oxidation states, namely Ce^{3+} and Ce^{4+} , with a higher amount of ceria species in
14 the more oxidized state (Ce^{4+} , see Table 2), which can be probably associated to the
15 oxidative atmosphere used during the catalyst synthesis. Note that the percentages of
16 the chemical states of cerium ($\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio) on the surface were calculated by
17 decomposition of Ce 3d spectra associated to these species. Moreover, the highest
18 $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio observed in the case of P-PtPd catalyst could be attributed to cerium
19 phosphates formed in this catalyst, according to XRD results. The formation of
20 cerium phosphate is expected to maintain the ceria in the reduced state (Ce^{3+}),
21 decreasing both redox properties and catalytic activity [35]. In addition, Zr 3d (182.1
22 eV) [36] also detected in two oxidation states, one its oxidation form Zr^{4+} and the
23 other one as some supra oxidized ZrO_x , promoted by the high amount of oxygen and
24 oxidized species around it [37].

25 Moreover, the Figure 67 shows the palladium chemical state on reference and
26 modified-catalysts. The Pd 3d spectra were characterized by the Pd $3d_{5/2}$ peak at
27 336.9 ± 0.5 eV, corresponding to Pd^{2+} (bulk PdO). Na and K impurities addition
28 produced a negative shift of the Pd-3d binding energies, which is indicative of an
29 increased electron density on the metal due to the presence of alkali ions [38].
30 Moreover, XPS profile of K-PtPd catalyst showed a second peak corresponding to
31 Pd^{2+} in contact with the support to form palladium-aluminate structures at 338.1 eV or
32 PdO_2 that induced the formation of new interfacial sites for the oxidation reaction [39].
33 The lower intensity of these peaks in presence of alkali impurities indicates that

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1 palladium is partly covered by the some components of the support, in fact by alkali
2 metal salts [40].

3 Platinum was also detected in an oxidized state, which was not possible to
4 specify exactly due to overlap of their corresponding binding energy with those of
5 zirconium oxides. Otherwise, atomic percentage of platinum and palladium could
6 neither be accurately measured due to the low metal amount presented on catalyst
7 surface.

8 The Na-PtPd catalyst presented a Na 1s peak with a maximum et 1072.2eV
9 BE [41], which may correspond to sodium carbonate, NaCO_x . In the case of Ca-PtPd
10 catalyst, Ca 2p region was overlapped by Zr 3d, so the principal oxidation state could
11 not be detected. However, the secondary state, Ca 2s, showed that calcium appeared
12 also in the form of carbonate, CaCO_x , at 439.8eV. The catalyst with potassium
13 additives followed the same trends, K was as K-O_x with K 2p BE equal to 296.5eV.
14 Finally, P-PtPd behaved differently; phosphorus was found in the form of phosphates,
15 as evidenced by XRD and TEM results, being P 2p BE equal to 134.4 eV.

16 3.1.6. NO temperature programmed desorption (NO-TPD)

17 NO-TPD was used to investigate the influence of the additives on the NO
18 adsorption capacity, which may be correlated with the NO conversion. Note that NO,
19 NO_2 and N_2O concentration in gas flows were followed by infrared spectroscopy
20 during the desorption ramp.

21 NO-TPD study (Figure 78) showed that only NO was detected in the outlet
22 gases flow under increased temperature for both reference and modified-catalysts. For
23 reference PtPd catalyst, three NO desorption peaks were observed in the 50-450°C
24 temperature range, whereas only two desorption peaks were detected for modified-
25 catalysts. The low temperature peak disappeared upon catalyst modification by the
26 additives. In addition, it can be observed that, with additives, desorption peaks are
27 generally more intense and shifted towards higher temperatures. Otherwise, the
28 phosphorus-modified catalyst showed a different behaviour. Contrary to the other
29 modified catalysts, only one low temperature desorption peak was detected, with an
30 intensity comparable to the one related to the first desorption peak of the reference
31 catalyst.

32 NO desorption peaks indicated the presence of NO reversibly adsorbed and
33 desorbed within low-temperature region (50-150°C) as well as in mid (150-350°C)

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1 and high (350-600°C) temperature regions. The three distinct features in the NO
2 desorption profiles suggest that three types of sites are available for NO adsorption.

3 ~~The first NO feature was associated with the weakly adsorbed NO, while the mid and~~
4 ~~high temperature desorption peaks have been attributed to monomeric and dimeric~~
5 ~~NO adsorbed species [44].~~ The first NO feature was associated with the weakly
6 adsorbed NO, while the mid and high temperature desorption peaks have been
7 attributed to more stable NO adsorbed species, as nitrites/nitrates species [42].

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8 Moreover, the total amounts of desorbed NO are presented in Table 3 for all
9 catalysts. Obtained results showed that the Ca-PtPd catalyst presented higher NO
10 desorbed amount than reference catalyst, while that Na and K-PtPd catalysts
11 presented similar NO desorbed quantities. Finally, in presence of phosphorus, the NO
12 desorbed quantity was the lowest one. The storage of NO in form of nitrites/nitrates
13 over Pt and Pd based catalysts was reported in the literature [43,44]. Otherwise, NO_x
14 storage-reduction (NSR) catalysts contain alkali or alkaline earth that can facilitate the
15 NO_x storage due to their higher basicity [42], which could explain the higher amount
16 of NO desorbed in presence of Ca.

17 In addition, previous studies showed that the addition of alkaline additives on
18 PtPd causes an increase in the strength of the metal-NO bond, accompanied by a
19 weakening of N-O bond of the adsorbed NO molecules, which facilitate the NO
20 dissociation [45,46]. This fact is ascribed to the low electronegativity of alkali
21 additives, which provides them with an electron donor behaviour, increasing the
22 interaction with NO, which has an electron acceptor character [30]. This is in
23 agreement with the results provided by NO-TPD experiments, which showed an
24 increase of desorption temperatures in presence of Na, K and Ca additives.

25 On the other hand, obtained results for P-PtPd catalyst showed that the NO
26 adsorption onto this solid was limited, according to the low amount desorbed and also
27 to the low temperature at desorption peak maximum. This fact could be ascribed to
28 the cerium phosphates formed on the catalyst surface, according to XRD and TEM
29 analysis, which hinder the NO adsorption on the active sites [21]. In addition, electron
30 transfer from Pt and Pd to ceria in oxidizing atmospheres has been reported [47]. This
31 interaction is expected to increase the strength of NO adsorption (NO electron donor)
32 on oxidized catalysts (Ce⁴⁺, electron acceptors; Ce³⁺, electron donors). However, XPS
33 results evidenced an increase of the percentage of Ce³⁺ in the presence of phosphorus,

1 which disfavoured NO adsorption in the presence of P due to the lower availability of
2 electron acceptor species.

3 3.2. Activity test results

4 The catalytic performances for CO, C₃H₆ and NO oxidation using Na, K, Ca
5 and P-PtPd catalysts (Figure 89) are discussed and compared with reference catalyst,
6 leading to evaluate the effect of the different additives on the catalytic conversions. In
7 order to better explain and compare the different results, reaction rates have been
8 calculated for each catalyst (Table 4) taking into account its actual metal content.

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9 Starting to the CO catalytic conversion, the results obtained for reference
10 catalyst showed that CO was the first compound to be consumed. The temperature at
11 50% conversion (T₅₀) was 188°C and the complete conversion was reached at around
12 200°C. Once CO oxidation was almost finished, the C₃H₆ conversion started, reaching
13 a 50% of C₃H₆ conversion quickly at 210°C and then, the complete conversion was
14 attained. As is well known, in the presence of oxygen and NO, the propene can be
15 consumed by: (i) oxidation with oxygen and (ii) selective catalytic reduction of NO
16 (SCR). However, although platinum based catalysts are known to be active for SCR at
17 low temperature, a significant amount of N₂O is also produced [48]. Thus, propene
18 conversion started at 183°C and, at a slightly higher temperature, the simultaneous
19 reduction of NO by propene (SCR) and N₂O production at around 225°C take place
20 (Figure 9). The maximum SCR conversion corresponded to the propene conversion
21 very close to 100%. Then, NO-N₂O conversion started to decrease, accompanied by
22 an increase in the NO conversion to NO₂. Finally, the NO conversion to NO₂ attained
23 a maximum of 22% at 370°C, decreasing at higher temperatures due to limitation by
24 the thermodynamic equilibrium.

25 Conversely, CO conversion values obtained with modified catalysts showed
26 the complete conversion in the temperature range of 200-250°C. Light-off curves
27 shifted towards slightly higher temperatures in presence of Ca, K and Na, showing
28 lower reaction rates calculated at 150°C (Table 4) than reference catalyst, notably in
29 the case of Ca-PtPd catalyst. As it is well known, CO strongly adsorbs on the active
30 sites of the catalyst at low temperatures, decreasing oxygen adsorption [33]. The use
31 of ceria-zirconia mixed oxide as an “active” support reduced this CO self-inhibition,
32 due to the role of surface oxygen vacancies in oxygen activation [51]. However, the
33 low electronegativity of alkali impurities produces an inhomogeneous electric field.

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1 which increase the metal-CO charge transfer [30], promoting CO adsorption and the
2 subsequent catalyst surface saturation.

3 Conversely, CO conversion values obtained with modified catalysts showed
4 the complete conversion in the temperature range of 200-250°C. Light off curves
5 shifted towards slightly higher temperatures in presence of Ca, K and Na, showing
6 lower reaction rates calculated at 150°C (Table 4) than reference catalyst, notably in
7 the case of Ca-PtPd catalyst. As it is well known, the CO oxidation on PtPd catalysts
8 occurs between adsorbed oxygen and adsorbed reactant on the catalyst surface [54].
9 Thus, the reaction rate increases with increasing oxygen concentration and is inhibited
10 by CO adsorption, which has the ability to strongly adsorb on the active sites of the
11 catalyst at low temperatures [33]. However, the use of ceria-zirconia mixed oxide as
12 an “active” support reduced this CO self-inhibition, due to the role of surface oxygen
13 vacancies in oxygen activation [57]. Hence, the combination of active sites for the
14 adsorption of CO, like the PdO species present on the catalyst surface as evidenced by
15 H₂-TPR and XPS analysis as well as the oxygen vacancies of the support lead to a
16 very active catalyst for the CO oxidation [58]. Therefore, the change in catalytic
17 activity observed for alkali and alkaline earth modified catalysts can be attributed to
18 an electronic factor [59]. Due to its low electronegativity, the contact between the
19 alkali metal ions and the metal surface produces an electron donor effect by the
20 neighbouring metal atoms. Thus, the CO adsorption on the metal surface could be
21 disfavoured due to the electron donor character of CO. However, P-PtPd catalyst
22 showed a more different behaviour, probably due to the higher amount of impurities
23 loaded in the catalyst. The light-off of the P-PtPd catalyst started at slightly lower
24 temperatures than that of the reference catalyst. However, the light-off curve was
25 displaced toward higher temperatures when almost complete conversion was attained.
26 As reported in Table 4, the P-PtPd reaction rate is higher than that of the reference
27 catalyst. This fact could be attributed to the phosphates formed in this catalyst,
28 detected by XRD and XPS, which inhibit CO adsorption, avoiding CO self-poisoning.
29 Moreover, the lower reducibility of Pt-Pd phase in presence of P favoured its
30 oxidation state, which is the active phase for CO oxidation.

31 Propene oxidation over reference catalyst follows a steady increase until
32 reaching the maximum conversion, in a similar trend than the CO light-off curve. It is
33 worth to be noticed that C₃H₆ adsorption is inhibited by competitive adsorption of
34 both CO and propylene during co-oxidation. CO adsorbs more strongly on active sites

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1 at lower temperature, inhibiting C₃H₆ oxidation. Thus, CO covers most of the active
2 sites until the temperature is high enough to oxidize, releasing active sites for
3 propylene adsorption [52].—

4 Propene oxidation over reference catalyst follows a steady increase until reaching the
5 maximum conversion, in a similar trend than the CO light-off curve. It can be also
6 noticed that their oxidation begins only after CO oxidation has started, leaving more
7 available active sites for C₃H₆ adsorption [57]. This fact is ascribed to the propene and
8 CO adsorption competition on the same sites, which has an important influence on
9 propene conversion.

10 Similarly to reference catalyst, when impurities were present, almost complete
11 conversion was achieved in a range between 200-250°C. The catalytic test results
12 showed that Na-PtPd light-off curve shifted towards higher temperatures, whereas K,
13 Ca and P-PtPd catalysts light-off curves shifted towards lower temperatures compared
14 to the reference catalyst, reaching the highest conversion faster than the reference
15 catalyst. Reaction rates calculated at 180°C are shown in Table 4, following this trend:
16 PtPd < Na-PtPd < P-PtPd < K-PtPd < Ca-PtPd. An enhancement of propene reaction
17 rate was noticed for all modified-catalysts, being more pronounced in presence of Ca
18 and K impurities. Note that the reference catalyst showed no conversion at this
19 temperature. The catalytic behaviour of Na- and Ca-PtPd catalyst for C₃H₆ conversion
20 could be attributed to the accumulation of carbonates (Na₂CO₃ or Ca₂CO₃) on the
21 catalyst surface (see XPS results), according to the literature [40]. These Na or Ca
22 species could block the active sites avoiding surface saturation by propene adsorption,
23 increasing their conversion. In addition, the electron-donor character of Na and K
24 could produce an enhancement of oxygen adsorption [54], improving propene
25 oxidation. In the same way, the highest catalytic activity of Ca-PtPd catalyst could be
26 associated to the higher electronegativity of alkaline-earth species compared to that of
27 Na and K species, which decrease the electron-donor effect and, as a consequence, the
28 oxygen interaction. As for CO oxidation, the formation of phosphates avoids C₃H₆
29 self-inhibition increasing reaction rate of P-PtPd catalyst compared to that of
30 reference catalyst.

31 In addition, NO-NO₂ conversions obtained for reference and modified
32 catalysts were compared. For the fresh catalyst, the maximum conversion (23%) is
33 achieved at 375°C, decreasing after that due to the thermodynamic equilibrium. The
34 same trend was found for modified catalysts however, with a total conversion that

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1 was always lower than for the reference. K-PtPd catalyst reached a maximum
2 conversion (18%) at 335°C, while Ca and Na-PtPd catalysts accomplished its
3 maximum of NO total conversion (~17%) at 430°C and 470°C respectively. Finally,
4 the P-PtPd catalyst showed its maximum conversion (17%) at 360°C. NO reaction
5 rates calculated at 230°C (Table 4) showed that K and P-PtPd catalysts had a higher
6 value of reaction rate than the reference catalyst. On the contrary, Na-PtPd and Ca-
7 PtPd showed a much lower reaction rate. The decrease in the NO-NO₂ maximum
8 conversion in the presence of alkaline additives could be due to the electron transfer
9 from alkaline to noble metals, which promotes the NO dissociation, increasing
10 decreased the adsorption strength of NO on the catalyst surface. In agreement with
11 Ciuparu et al. [55], this effect was accompanied by reinforcing the N-O bond,
12 avoiding the NO dissociation and decreasing catalytic activity. Otherwise, according
13 to NO-TPD analysis the presence of alkaline metal additives can create the new
14 adsorption sites on these modified catalysts, which are not involved in the reaction but
15 can store NO species [56]. Moreover, the higher reduction temperatures detected by
16 H₂-TPR analysis in the presence of Na, K and Ca additives made more difficult the
17 reduction of Pt and Pd species, diminishing the NO conversion as metallic Pt and Pd
18 are the active phase for NO oxidation. Finally, the decrease of NO conversion with
19 phosphorus addition could be correlated to the following conclusions: (1) the presence
20 of phosphates detected by XRD, TEM and XPS blocked the pores, decreasing the
21 BET specific surface area, which reduces the amount of NO adsorbed; (2) phosphates
22 species on catalysts surface can stabilize the Ce³⁺ oxidation state, according to the
23 higher Ce³⁺/Ce⁴⁺ ratio obtained by XPS analysis, decreasing the NO adsorption due to
24 its electron donor character and (3) the amount of NO desorbed obtained by NO-TPD
25 was the lowest, confirming the disfavoured NO adsorption detected by the rest of the
26 characterization methods.

27 Even in the presence of high amounts of oxygen, as encountered in the present
28 study, NO partial reduction was achieved by propene via the SCR reaction. The high
29 coverage of catalyst surface by C₃H₆ leads to not enough active sites available for NO
30 to react until hydrocarbon species react, which means NO reduction is secondary and
31 dependent on reduction of the active sites by C₃H₆ oxidation. N₂O and N₂ to a lesser
32 extent coming from NO partial reduction via C₃H₆-SCR were detected. To complete
33 the NO balance, the undesirable N₂O production was also evaluated for the reference
34 and modified catalysts.

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1 The reference catalyst presented a maximum of NO-N₂O conversion (13%) at
2 230°C (Table 4), while K-PtPd maximal NO-N₂O conversion (10%) was reached at
3 198°C. Na-PtPd achieved similar maximal conversion than K-PtPd catalyst (10%) but
4 at higher temperature and slightly lower than that of the reference catalyst. However,
5 Ca-PtPd and P-PtPd catalysts presented an almost negligible NO-N₂O conversion of
6 5% and 8% of maximum conversion, respectively. Moreover, the catalytic test results
7 showed that the NO-N₂O conversion started at the light-off temperature of propene
8 combustion, indicating the occupation of NO oxidation active sites by propene [48].
9 Comparing the results related to modified and reference catalysts, it can be seen that
10 the NO-N₂O conversion was lower for the K-PtPd catalyst than for the reference one.
11 An unexpected fact was the lower temperature at which the maximum conversion was
12 reached, reported to the electron donator role of the K additive. In the case of Na-PtPd,
13 the maximum conversion was found at higher temperature than over the reference and
14 K-PtPd catalysts. As stated before, alkali doping increases the strength of NO
15 chemisorption relative to C₃H₆, which induced a promotion phenomenon of NO
16 reduction. This enhancement follows a volcano type behaviour related to alkali
17 loading. The higher amount of Na compared to K added to the catalyst in the present
18 study probably overtook the optimum alkali amount, decreasing the promotion effect
19 related to alkali presence. As shown in Table 4, the maximum N₂O quantity produced
20 was similar to that obtained in the case of K-PtPd catalyst, lower than over the PtPd
21 catalyst. In addition, NO to N₂O conversion obtained over the Ca-PtPd catalyst was
22 almost negligible. Finally, the P-PtPd catalyst also disfavour SCR-C₃H₆ reaction,
23 according to the significantly lower NO-N₂O conversion and N₂O formation
24 compared to that of the reference and Na, K and Ca-PtPd catalysts.

25 4. Conclusions

26 The impact of biodiesel impurities, alkali and alkaline earth metals (Na, K and
27 Ca) or phosphorus species (P), on PtPd/CeZrO₂/La-Al₂O₃ diesel oxidation catalysts
28 physico-chemical, redox and catalytic properties was evaluated. The catalytic test
29 results for modified catalysts concerning CO, C₃H₆ and NO oxidation reactions have
30 shown that the presence of inorganic elements originating from biodiesel have a
31 significant impact on the performance of a DOC catalyst. Thus, the **electron-donor**
32 **effect-inhomogeneous electric field produced around** Na, K and Ca species increase

1 the oxygen interaction, according to H₂-TPR analysis. This fact results in a negative
2 effect on the CO catalytic oxidation due to the electron donor character of CO, which
3 ~~promotes its adsorption saturating the catalyst surface~~ avoids its adsorption. However,
4 the reaction between propene and oxygen is enhanced in presence of these inorganic
5 elements due to this higher oxygen interaction, improving the C₃H₆, oxidation activity.
6 ~~In addition, the presence of Na and Ca carbonates and phosphates species inhibited~~
7 ~~the catalyst surface saturation, avoiding CO and C₃H₆ self-poisoning.~~ In presence of P
8 species, both CO and C₃H₆ oxidation were improved, ~~while the NO conversion was~~
9 ~~disfavoured.~~ These results could be related to ~~the presence of phosphates species that~~
10 ~~inhibited the catalyst surface saturation, avoiding CO and C₃H₆ self-poisoning.~~ In
11 ~~addition,~~ the lower noble metals reducibility as well as to their higher oxidized state
12 ~~promotes their co-oxidation.~~ Na, K and Ca-PtPd catalysts also presented lower NO
13 catalytic activity than reference catalyst. These results could be attributed to the
14 electro-donor character of these additives, which increase the ~~Pt, Pd and~~ metal-NO
15 bond strength, according to the higher NO desorption temperature.

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