

## **Ceria-praseodymia mixed oxides: relationships between redox properties and catalytic activities towards NO oxidation to NO<sub>2</sub> and CO-PROX reactions**

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### **Abstract**

A series of Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2.5</sub> catalysts was prepared by co-precipitation method in alkali media. These catalysts were characterized by N<sub>2</sub> adsorption-desorption isotherms at -196°C, X-ray diffraction (XRD), thermogravimetry combined with mass spectrometry (TG-MS), and temperature-programmed reduction with H<sub>2</sub> and CO (H<sub>2</sub>-TPR and CO-TPR, respectively). Catalytic tests were performed for temperature programmed NO oxidation to NO<sub>2</sub> (from 25 to 750°C) and for the preferential oxidation of CO in H<sub>2</sub> rich stream (CO-PROX reaction) in the range of 150-500°C. The trends in the order of catalytic activities towards NO oxidation and CO-PROX are correlated with the redox properties of the catalysts and their composition.

Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2.5</sub> mixed oxides present very different catalytic behaviours towards NO oxidation and CO-PROX reactions. These experimental trends might be explained by the balance of several factors: the acid character of the NO and CO molecules, the different lattice oxygen mobility of the catalysts, the presence of surface carbonates species in the samples, and the catalysts' reducibility under H<sub>2</sub> and CO. The understanding of the features that govern the activity towards these environmentally relevant oxidation reactions is important in the designing of effective catalysts.

**Keywords:** NO oxidation; CO-PROX; ceria-praseodymia; redox properties; lattice oxygen.

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## 1. Introduction

The catalyzed oxidation of CO and NO has attracted interest of industry and academia as a major research topic for catalytic exhaust gas purification. Although most of the investigations are focused on catalytic performance of precious metals supported on inorganic oxides (such as ceria), great efforts have been devoted to understand and improve the special redox properties of noble metal-free ceria in the last years [1]. In this sense, one of the most interesting approaches to enhance ceria's redox behaviour is the addition of lanthanide cations in order to promote the low temperature redox response and the thermal stability. Among these elements, praseodymium, with variable oxidation states (+3/+4) deserves particular interest and, lastly, Pr-doped CeO<sub>2</sub> nanostructures are those to which more attention has been paid [2–4].

Preferential CO oxidation in the presence of excess of hydrogen (CO-PROX) is a cleaning-up process to remove CO impurities from reformat streams containing large amounts of hydrogen. Ceria based oxides with different morphologies or with some dopants have been intensively investigated for CO oxidation during the last ten years [1,3]. However, up to now and to the best of our knowledge, there are no studies about metal-free ceria based oxides for PROX reaction.

The corresponding mixed oxides, Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub>, can undergo more oxygen exchange at a lower temperature than pure ceria and it is also known that the Ce-Pr-O compositions are more promising than the trivalent rare-earth substituted ceria formulation. It could be assumed that Pr-containing mixed oxides should exhibit intermediate and close to optimal combination of capacity, stability and reactivity with respect to reversible oxygen evolution/uptake, but in catalytic oxidation reactions with practical application not all the *reactive* oxygen can be available and the establishment of redox-catalytic performances relationships in different environmental reactions could be of special interest [5].

The present work is devoted to prepare and characterize a series of Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> and to analyze the trends in catalytic activities towards the NO oxidation to NO<sub>2</sub> under O<sub>2</sub> rich atmospheres and the preferential oxidation of CO in H<sub>2</sub> rich stream (CO-PROX). The correlations between catalytic performances obtained and redox properties are explored and connected to the catalysts' composition.

## 2. Materials and methods

A series of mixed oxides with the general formula  $Ce_xPr_{1-x}O_{2.5}$  ( $x=0, 0.2, 0.5, 0.8, 1.0$ ) was prepared by co-precipitation method in alkali media. The corresponding solids obtained after filtration were dried at 110°C and calcined at 500°C for 1 hour. The same formulations were synthesized and calcined at 1000°C for 1 hour as well. The catalysts were characterized by  $N_2$  adsorption-desorption isotherms at -196°C, XRD, TG-MS (under 100 ml/min of inert He atmosphere, with and without pre-treatment at 950°C under 100 ml/min of 5%  $O_2/He$ ),  $H_2$ -TPR and CO-TPR.  $H_2$ -TPR experiments were carried out after pre-treatment at 500°C under 5%  $O_2/He$  for 1 hour.  $H_2$ -TPR experiments were performed heating up to 1000°C at 10°C/min, under 5%  $H_2/Ar$  with an inlet gas flow of 35 ml/min. CO-TPR experiments were performed in a 60 ml/min flow of 5% CO/He, and heating up to 950°C at 10°C/min. Before the CO-TPR experiments, the samples were pretreated with 5%  $O_2/He$  at 500 °C for 1 h and then under a flow of He at the same temperature for 1 h. The outlet of the reactor was connected to a Pfeiffer ThermoStar quadrupole mass spectrometer to continuously monitor the composition of the gas stream.

NO oxidation to  $NO_2$  catalytic tests were performed in a fixed-bed reactor under a 500 ppm  $NO+5\%O_2/N_2$  gas flow (500 ml/min; GHSV 30000  $h^{-1}$ ). Temperature-Programmed NO oxidations were carried out from 25 to 750 °C at 10°C/min. The gas composition was monitored by specific NDIR-UV gas analyzers for NO,  $NO_2$  and  $O_2$ . 80 mg of catalyst were mixed with 300 mg of SiC (to avoid pressure drop) in each test.

Catalytic activity in PROX reaction was carried out in a stepwise manner under isothermal conditions at selected temperatures in the 150-500°C range. Samples were pre-treated under 5%  $O_2/He$ , at 250 °C for 1 hour. CO-PROX experiments were performed with an inlet total gas flow of 100 ml/min, containing 50%  $H_2$ , 1% CO, 1%  $O_2$  and He as balance (GHSV=12,000  $h^{-1}$ ). A gas chromatograph Bruker 450-GC with a thermal conductivity detector is coupled to the reactor for analysis of the reactants and products of CO-PROX. A Molsieve 13X column is used to separate CO and  $O_2$ , and another column of Hayesep is attached to analyze  $CO_2$  and  $H_2O$ . The concentrations of CO,  $O_2$  and  $CO_2$  were calibrated with external standard calibration gas mixtures from Praxair.

### 3. Results and discussion

Figure 1a depicts the  $\text{NO}_2$  formation, obtained from the catalytic oxidation reaction of NO in the presence of  $\text{O}_2$ , for the studied catalysts along with the uncatalyzed reaction. It is worth noting that as the praseodymium content is increased in  $\text{Ce}_x\text{Pr}_{1-x}\text{O}_{2-\delta}$  formulation,  $\text{NO}_2$  production becomes higher, being the maximum  $\text{NO}_2$  production shifted to lower temperatures. There is a remarkable difference between  $\text{CeO}_2$  and  $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ , with an increase in the maximum production of  $\text{NO}_2$  from 24% to 39% when the ceria is doped with only 20 mol% Pr. Pure praseodymia presents the highest  $\text{NO}_2$  production (48% at 375°C), therefore indicating that Pr-based oxides are very active for the NO oxidation to  $\text{NO}_2$ .

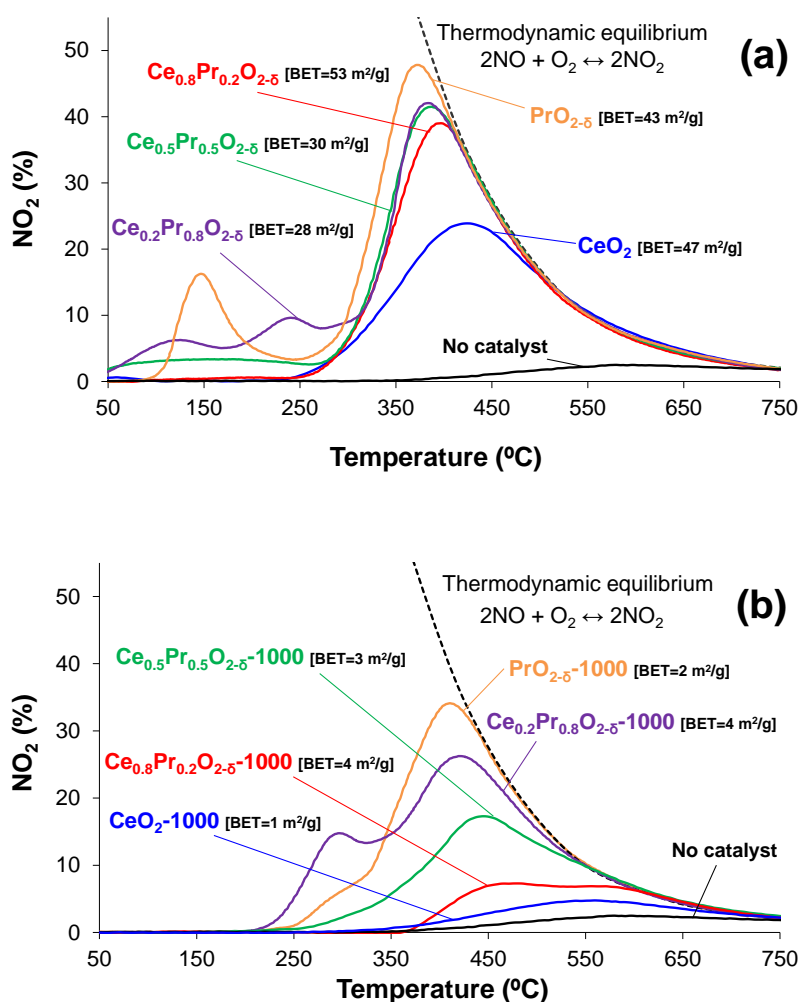


Figure 1. Temperature programmed NO oxidation to  $\text{NO}_2$  for samples calcined at (a) 500°C and (b) 1000°C.

It could be thought that the activity enhancement when CeO<sub>2</sub> is doped with 20 mol% of Pr, Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub>, is related to the BET surface area. However, when pure CeO<sub>2</sub> is doped with 50 mol% and 80 mol% of praseodymium (Ce<sub>0.5</sub>Pr<sub>0.5</sub>O<sub>2-δ</sub> and Ce<sub>0.2</sub>Pr<sub>0.8</sub>O<sub>2-δ</sub>, respectively), the maximum NO<sub>2</sub> production is slightly higher than Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub>, while the former mixed oxides present much lower BET surface areas (30 and 28 m<sup>2</sup>/g, respectively) than Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub>, confirming that the BET surface area is not a determining parameter in the NO<sub>2</sub> production.

In order to verify the excellent behaviour of the Pr-doped ceria in the oxidation reaction of NO to NO<sub>2</sub>, additional samples were prepared, synthesized under identical conditions, but this time calcined at 1000°C for one hour, to minimize the effect of a non-gradual change in the surface area. These samples are named as Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub>-1000. Figure 1b shows a gradual improvement in the catalytic activity when the Pr content increases. Surprisingly, praseodymia calcined at 1000°C, with BET area of 2 m<sup>2</sup>/g, is much more active in the catalytic NO oxidation than ceria calcined at 500°C, revealing that choosing the Pr cation as dopant improves the catalytic properties of the solid, with respect to pure ceria, even minimizing the effects of surface area loss. The satisfactory catalytic activity shown by Ce<sub>0.2</sub>Pr<sub>0.8</sub>O<sub>2-δ</sub> and PrO<sub>2-δ</sub> catalysts calcined at 1000°C was not reported either for pure ceria or other ceria-doped mixed oxides (such as ceria-zirconia), which justifies the choice of Pr as doping cation for Ce-based mixed oxides. These results are supported by the binding energy values of Ce-O bond, which are higher than those of Pr-O [6]. The Ce<sup>3+</sup> ionization energy is 2.22 eV lower than that of Pr<sup>3+</sup> [7]. Because of this, the addition of praseodymium in the ceria network increases the creation of oxygen vacancies and the presence of more labile oxygen species.

To get further insight into the quantification of the oxygen species lability and in an attempt to determine the degree of lattice oxygen release in these materials, TG-MS experiments under inert atmosphere were carried out for all the catalysts calcined at 500°C. All the evolved products were registered. The use of an inert atmosphere is justified, because it is deduced from TPR experiments (discussed below) that the commonly used reducing agents might present different degree of interaction with these mixed oxides' surface sites. In this sense, the catalysts' O<sub>2</sub> evolution profiles were obtained and depicted in Figure 2a (solid lines correspond to fresh catalysts and dotted lines to pre-treated catalysts). Figure 2a provides extremely interesting information, because pure ceria is not able to release oxygen under inert atmosphere up to 950°C,

and both surface and sub-surface oxygen is not labile enough to evolve under these experimental conditions. However,  $O_2$  evolution is observed as a broad band for  $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ . From  $Ce_{0.5}Pr_{0.5}O_{2-\delta}$  composition to  $PrO_{2-\delta}$ , the corresponding peaks become sharper and profiles become more complex, especially for pure  $PrO_{2-\delta}$ , whose multi-modal profile can be related to the surface and bulk praseodymia reduction, and could also be related to phase segregation:  $PrO_2$ ,  $Pr_6O_{11}$  and  $PrO_{1.83}$  (identified by XRD), as discussed in a previous article [8]. It is worth noting the sharp peak appearing at low temperature for  $Ce_{0.2}Pr_{0.8}O_{2-\delta}$ , which could be ascribed to very labile oxygen species, partially responsible of the  $NO$  oxidation to  $NO_2$  at low temperature (Figure 1a).

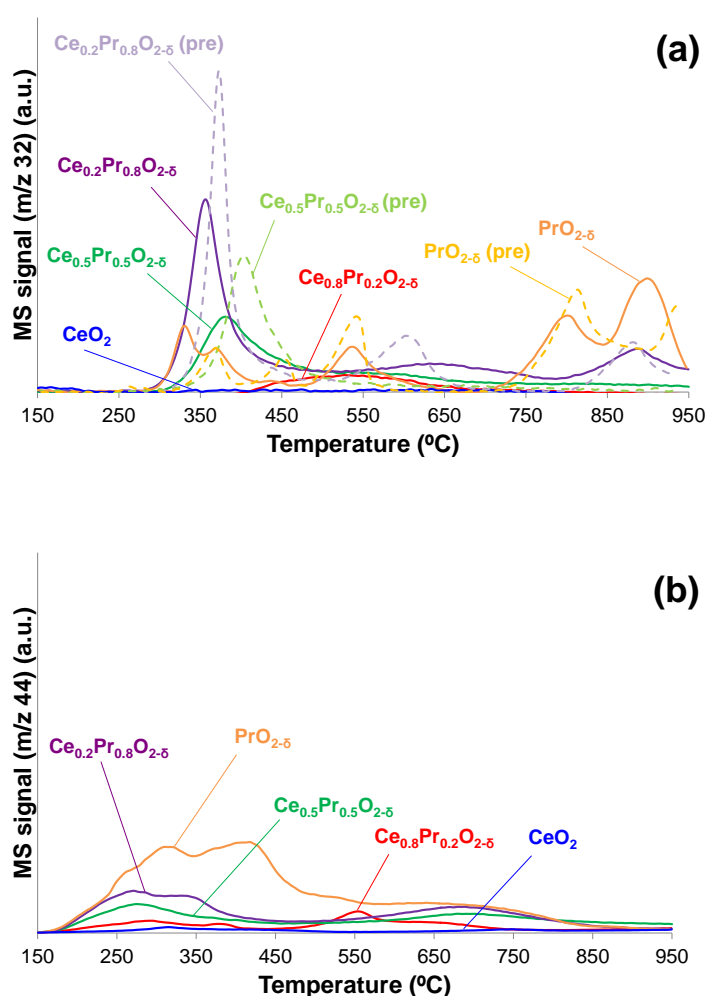


Figure 2. Evolved gases profiles obtained by TG-MS under He (solid lines correspond to fresh catalysts and dotted lines to pre-treated catalysts). (a) Evolved  $O_2$  ( $m/z$  32); and (b) Evolved  $CO_2$  ( $m/z$  44).

In order to investigate the origin of these O<sub>2</sub> emissions, it is important to verify that evolved O<sub>2</sub> is generated by desorption/decomposition of the surface and/or sub-surface oxygen species, and it is not only due to parallel reactions (such as decomposition of carbonates). This fact was verified by conducting additional experiments where samples were pre-treated; they were heated up to 950°C under 5%O<sub>2</sub>/He (thus removing catalysts' surface contamination). Pre-treated CeO<sub>2</sub> presents no signal and Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> signal is similar to its profile without pre-treatment. Results from the other samples reveal that after this treatment, catalysts kept on evolving O<sub>2</sub>, and few differences among O<sub>2</sub> profiles were observed, regarding catalysts without pre-treatment, as seen in Figure 2a.

It is worth mentioning that these ceria-based samples present a high degree of surface contamination, due to the presence of different hydroxyl groups, water and CO<sub>2</sub> adsorbed (not shown for the sake of brevity), as well as carbonates on surface, both of cerium and praseodymium. However, since exhaust gases from vehicles present H<sub>2</sub>O and CO<sub>2</sub>, which is one of the most important applications of these solids, it is interesting to carry out the NO oxidation catalytic reactions without any "cleaning" pre-treatment. As an example, and in order to identify the degree of contamination in the samples, Figure 2b illustrates their CO<sub>2</sub> profiles in TG-MS experiments up to 950°C. Remarkably, the presence of stable carbonates dramatically increases with the Pr content, from pure ceria to pure praseodymia, which decompose in a wide temperature interval (from 170°C to 880°C). It is worthwhile to highlight that these carbonates seem to be, *a priori*, spectators and not inhibitors of the NO oxidation reaction; but nevertheless, this fact might not be extrapolated to other oxidation reactions, as will be discussed below.

CO-PROX reaction was performed with this series of catalysts to check the importance of the molecule's features to be catalytically oxidized. Figure 3a depicts the CO conversion obtained on the basis of the CO<sub>2</sub> produced (not considering the original carbonates). CO conversion reaches the maximum at 450°C over all the Ce-containing oxide catalysts. The highest CO conversion (86.8%) is shown by Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> at 450°C. However, pure PrO<sub>2-δ</sub> exhibits the lowest activity for CO-PROX reaction since the highest CO conversion is only around 45% at 400°C. During CO-PROX process, two parallel and competitive oxidation reactions occur: CO oxidation and H<sub>2</sub> oxidation.

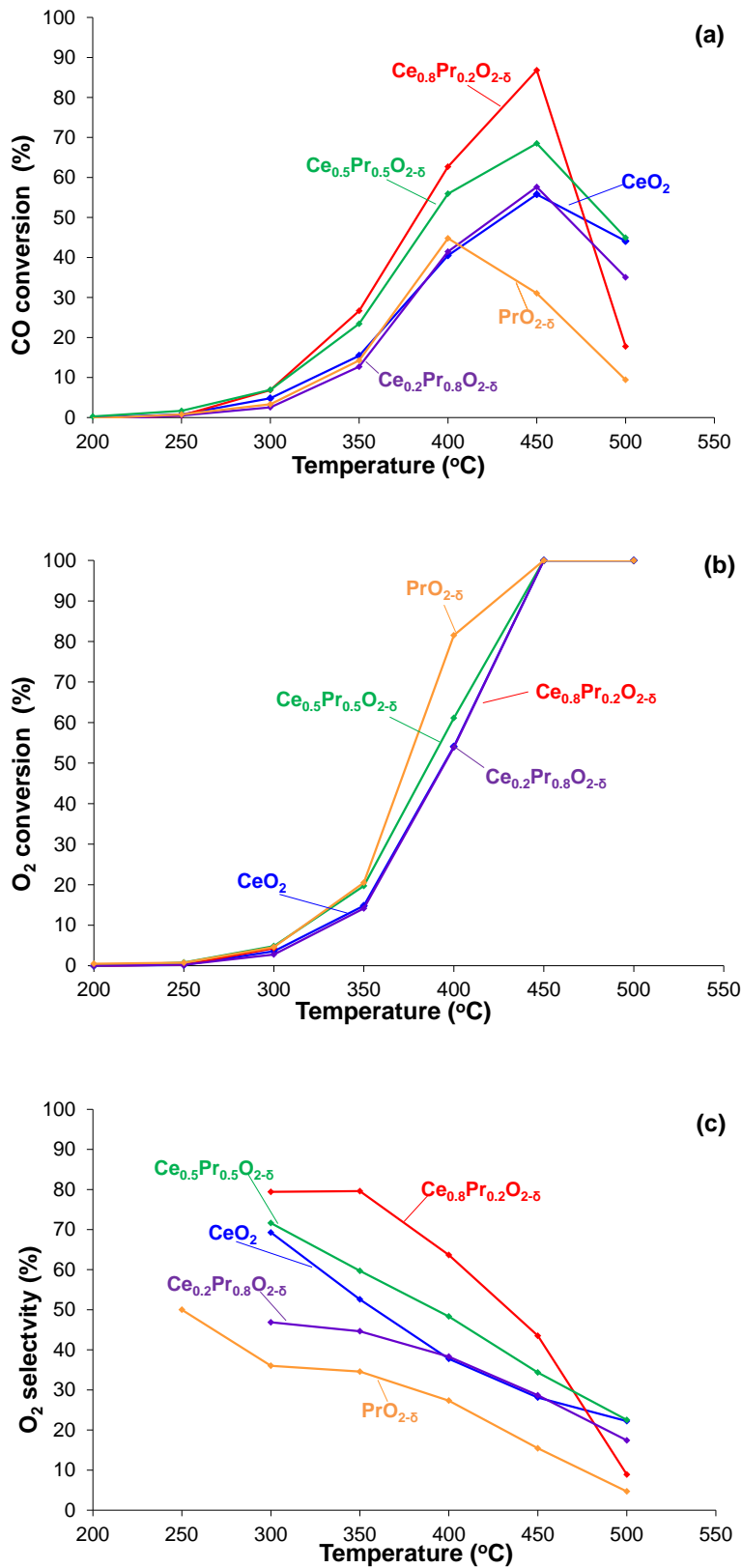


Figure 3. (a) CO conversion, (b) O<sub>2</sub> conversion and (c) O<sub>2</sub> selectivity to CO<sub>2</sub> in CO-PROX reaction for the studied catalysts.



Figure 3b presents O<sub>2</sub> conversion of the catalysts during CO-PROX. It can be observed that O<sub>2</sub> conversion over pure PrO<sub>2-δ</sub> catalyst is the highest at 400°C. Meanwhile its O<sub>2</sub> selectivity to CO<sub>2</sub> is the lowest among all the tested catalysts. This suggests that H<sub>2</sub> oxidation is dominant over pure PrO<sub>2-δ</sub> catalyst. Furthermore, all the Ce-containing catalysts show higher O<sub>2</sub> selectivity to CO<sub>2</sub> than pure PrO<sub>2-δ</sub> sample. The highest O<sub>2</sub> selectivity to CO<sub>2</sub> is reached over Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> which also shows the highest CO conversion. CO oxidation is more favourable than H<sub>2</sub> oxidation over Ce-containing catalysts. The optimized composition for CO-PROX reaction is Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> due to its highest CO conversion and O<sub>2</sub> selectivity to CO<sub>2</sub>.

CO-TPR curves shown in Figure 4 provide some insight into these ideas, revealing that the main reduction peak is slightly moved towards higher temperatures (from 323°C for Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> to 423°C for PrO<sub>2-δ</sub>). The Ce-Pr samples show a certain relationship between CO-TPR profiles and catalytic behaviour towards CO-PROX reaction. Thus, samples with the lowest main peak reduction temperatures, present the highest CO conversions at 450°C.

Figure 5 depicts the H<sub>2</sub>-TPR curves of the Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> catalysts. It can be observed that the reduction temperature decreases with increasing Pr amount in the Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> mixed oxide. This result indicates that the reducibility is remarkably improved with incorporation of larger amounts of Pr. In fact, with gradually increasing the Pr content in the catalysts, the overall hydrogen consumption is also increased. This trend seems to be in accordance with the catalytic activity order reported for the NO oxidation to NO<sub>2</sub> (see Figures 1a and 1b).

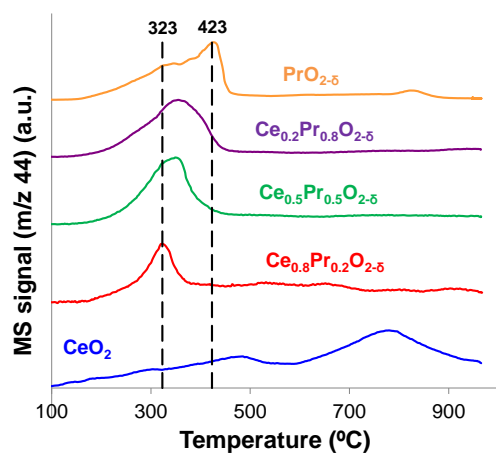


Figure 4. CO-TPR profiles of the Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> catalysts calcined at 500°C.

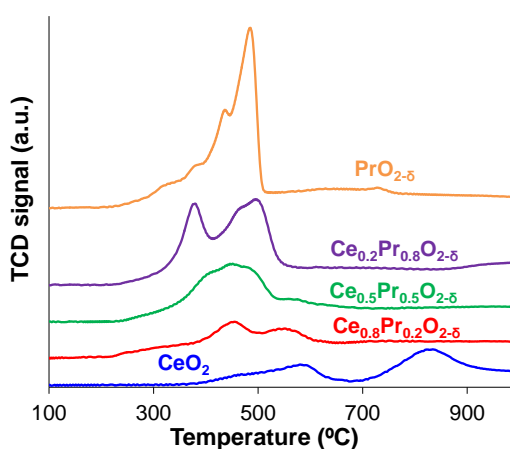


Figure 5. H<sub>2</sub>-TPR profiles of the Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> catalysts calcined at 500°C.

In an attempt to elucidate the origin of these divergences, the differences between conducting TPR experiments under CO and H<sub>2</sub> are discussed below.

It is known from the literature that CO can reduce the surface CeO<sub>2</sub> even at lower temperature compared with H<sub>2</sub>, although it is generally considered that CO is a weaker reducing agent than H<sub>2</sub>. This can be clearly seen by comparison of Figures 4 and 5 (CeO<sub>2</sub> profiles). As reported in the literature, the reason may be that the dissociation of adsorbed H<sub>2</sub> is necessary for the reduction by H<sub>2</sub>, while CO can directly attack the surface oxygen in CeO<sub>2</sub> [9]. However, if the amount of surface carbonates with different degree of stability is high, the CO ability to interact with the surface of the oxides could be affected. This relationship seems very clear for pure praseodymia, because it presents the highest amount of carbonates among the catalysts studied. Regarding the evolved CO<sub>2</sub> profiles on Figure 2b, decomposition peaks of surface carbonates (between 320°C and 430°C) are nearly coincident with the shoulder and main peak observed in CO-TPR for CO consumption (seen in Figure 4 as CO<sub>2</sub> generation). The amount of carbonates on the surface of the oxides plays an important role in CO-PROX reaction. This could be the explanation for the low catalytic activity shown by PrO<sub>2-δ</sub> towards CO-PROX. On other hand, the reducibility order as determined by H<sub>2</sub>-TPR of the catalysts is in accordance with the activity of H<sub>2</sub> oxidation during the CO-PROX process. As discussed in CO-PROX results, PrO<sub>2-δ</sub> exhibits the lowest O<sub>2</sub> selectivity to CO<sub>2</sub> but the highest O<sub>2</sub> selectivity for H<sub>2</sub> oxidation, which means that the rest of O<sub>2</sub> was consumed by H<sub>2</sub> oxidation and H<sub>2</sub> oxidation is dominant during CO-PROX reaction. For Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2-δ</sub> mixed oxides, H<sub>2</sub>-TPR reduction temperature decreases, CO conversion also decreases. At the same time, the O<sub>2</sub> selectivity to CO<sub>2</sub> also decreases, suggesting that H<sub>2</sub> oxidation is more favourable. To summarize, CO oxidation in CO-PROX process follows the same order of CO-TPR, while H<sub>2</sub> oxidation in CO-PROX process is related to the catalysts' reducibility in H<sub>2</sub>-TPR. For this reason, PrO<sub>2-δ</sub> shows the lowest activity for CO oxidation during PROX process, however it is more active for H<sub>2</sub> oxidation and NO oxidation to NO<sub>2</sub>, even after calcination at 1000°C.

Regarding the oxidant molecules' features, NO/NO<sub>2</sub> present a stronger Lewis acid character than CO/CO<sub>2</sub>, so nitrogen oxides could react with basic oxygen sites, displacing surface carbonate species [10]. In this sense, a high amount of surface praseodymium carbonates has minor or no negative influence on the NO oxidation reaction, since the forming nitrates can

displace surface carbonates, and therefore  $\text{PrO}_{2.5}$ , which presents the highest reducibility under  $\text{H}_2$  and the highest  $\text{O}_2$  evolution under He, is the most active sample.

Interestingly,  $\text{PrO}_{2.5}$  and  $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2.5}$  showed a certain NO oxidation activity at the temperatures below  $250^\circ\text{C}$ . It is important to outline that these catalytic tests were conducted with fresh samples (no pretreatments) as explained above. The desorption of surface contamination (carbonates, hydroxyl groups) under the reactive stream can create nascent  $\text{Ln}^{3+}$  centers able to suffer NO attack and promote several reaction routes [10] and these two samples are those with the highest population of carbonate-like species desorbed (from  $150^\circ\text{C}$ ). This fact joined to an easy desorption of their labile oxygen species are tentatively ascribed to be responsible of NO oxidation in such low temperature region.

On the contrary, carbonates generated during PROX reaction (or those which were not decomposed during the pre-treatment at  $250^\circ\text{C}$ ) seem to inhibit the CO preferential oxidation reaction to  $\text{CO}_2$ .

Finally, the  $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2.5}$  sample shows a certain lattice oxygen mobility (evolving  $\text{O}_2$  is observed in TG-MS experiments, while it is not observed for pure ceria) and a low population of carbonates, comparing to the other Pr-containing samples. A combination of both factors make this composition the most active one among those studied for PROX reaction.

#### **4. Conclusions**

In this work, a series of  $\text{Ce}_x\text{Pr}_{1-x}\text{O}_{2.5}$  mixed oxides was prepared by co-precipitation method. These catalysts were characterized and studied for the NO oxidation to  $\text{NO}_2$  and the CO-PROX reactions. The general conclusions that have been drawn are the following:

TG-MS results reveal that pure ceria is not able to release  $\text{O}_2$  under inert atmosphere, but ceria-praseodymia mixed oxides and pure praseodymia present different and complex  $\text{O}_2$  evolution profiles. In addition, the released  $\text{CO}_2$  profiles show that the presence of surface carbonates increases with the Pr content in the catalysts. These carbonates seem not to inhibit the NO oxidation reaction, but the CO-PROX reaction is negatively affected by their presence. The catalytic activity results observed in CO oxidation during PROX process can be related to the CO-TPR trends in reducibility; meanwhile  $\text{H}_2$ -TPR results can be correlated to NO oxidation to

NO<sub>2</sub> trends in activity and H<sub>2</sub> oxidation during PROX reaction. All these results can explain the superior catalytic activity for NO oxidation to NO<sub>2</sub> shown by PrO<sub>2-δ</sub> and its low activity for CO-PROX reaction. On the other hand, Ce<sub>0.8</sub>Pr<sub>0.2</sub>O<sub>2-δ</sub> becomes the most active catalyst for CO-PROX due to the balance of a moderate reducibility under H<sub>2</sub>, a low carbonate population and a measurable O<sub>2</sub> evolution under He.

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