Study by *in situ* electrical conductivity measurements of Ce-Pr mixed oxides catalysts

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Abstract
The semiconductive and redox properties of different Ce\(_{1-x}\)Pr\(_x\)O\(_{2-\delta}\) systems with \(x = 0, 0.2, 0.5, 0.8\) and 1 were investigated by *in situ* electrical conductivity measurements and correlations with their catalytic behavior in the total oxidation of methane and the CO-PROX process were attempted. Thus, the electrical conductivity of the Ce\(_{1-x}\)Pr\(_x\)O\(_{2-\delta}\) oxides was measured as a function of temperature and oxygen partial pressure, and was followed with time during sequential exposure to air and different gaseous mixtures containing CH\(_4\), CO or H\(_2\), in conditions close to those of their catalytic applications. All the solids showed both electronic and ionic conductivities, the total conductivity increasing continuously with the value of \(x\). CeO\(_2\) appeared to be of n-type, while all the Pr-containing materials were p-type semiconductors in air. They kept their semiconductivity type under different gaseous atmospheres, except for Ce\(_{0.8}\)Pr\(_{0.2}\)O\(_{2-\delta}\) mixed oxide which switches from p-type to n-type passing through a NDC-like (Negative Differential Conductivity) state in the presence of CO and H\(_2\). The catalytic behavior of the Ce\(_{1-x}\)Pr\(_x\)O\(_{2-\delta}\) oxides, which function during the catalytic oxidation reactions *via* a

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heterogeneous redox mechanism, was discussed for both processes studied in correlation with the electrical conductivity results.

**Keywords:** Electrical conductivity; Ce-Pr mixed oxides; Catalytic oxidation; Methane total oxidation; CO-PROX reaction; Negative Differential Conductivity.

1. **Introduction**

In the past several years, CeO$_2$-based materials have been extensively studied as heterogeneous catalysts for a large variety of well-established and emerging applications [1, 2], several review papers being dedicated to the understanding of the mechanism of their functioning in catalysis [3-5].

Modification of ceria with various cations is known to improve the stability towards the sintering and also the oxidation activity of the resulting catalysts. This modification leads to changes in redox properties and the creation of oxygen vacancies, both of them improving the oxygen exchange capacity between the gas phase and the catalyst and its oxygen storage capacity. In this sense, considerable attention has been paid to incorporate variable valence cations into the ceria lattice. The oxygen atoms/vacancies attached to reducible elements are mobile and contribute to the oxygen storage/release capacity of the mixed oxides, and, hence, to their oxidation activity. Among the reducible elements, praseodymium is particularly suitable to obtain solid solutions with ceria in determined compositions. The structure of Pr$_6$O$_{11}$ is fluorite type, and the ionic radius of Pr$^{4+}$ (0.096 nm) is close to that of Ce$^{4+}$ (0.097 nm). In the mixed oxide, it can form mixed oxidation states with both Pr$^{3+}$ and Pr$^{4+}$ cations. Furthermore, in ceria-praseodymia solid solutions, both elements can adopt 3+ and 4+ oxidation states, and the anionic vacancies are highly mobile in this system. Thus, the insertion of praseodymium within the fluorite host lattice of CeO$_2$ provides new materials with improved catalytic properties for environmental applications, such as automotive three-way catalysts [6, 7], NO$_x$ trap catalysts [8], N$_2$O decomposition [9, 10], (preferential) CO oxidation [11-13], volatile organic compounds combustion [13-15] and soot removal [16-18]. These studies showed that the Ce$_x$Pr$_{1-x}$O$_{2-δ}$ mixed oxides can undergo more oxygen exchange than pure ceria at lower temperatures and that they are more promising catalysts than other trivalent rare-earth substituted ceria formulations. The
Ce$_{1-x}$Pr$_x$O$_{2-δ}$ mixed oxides exhibit intermediate and close to optimal combination of capacity, stability and reactivity with respect to reversible oxygen evolution/uptake [11], and the establishment of redox properties – catalytic performances relationships in different environmental reactions could be of special interest.

A useful and highly sensitive technique to characterize the electronic and redox properties of oxidation catalysts in correlation with their catalytic performances is the in situ electrical conductivity measurement [19]. This allows to gain insight into the key features of the redox catalysts that determine their catalytic activity in order to better understand the origin of the catalytic effect and the reaction mechanism involved and, consequently, to improve the catalysts on a scientific basis or to rationally design efficient new ones [20, 21]. The CeO$_2$-based materials are semiconducting metal oxides and function in oxidation catalysis via a heterogeneous redox mechanism involving the reduction and re-oxidation of the solid during the catalytic cycle [22]. This behavior can be studied by following the evolution of the electrical conductivity of the oxide as a function of the nature of the gas phase in contact with this [19]. For example, the electrical conductivity of a $p$-type semiconducting oxide increases in the presence of oxygen. Indeed, electrons flow from the valence band of the oxide to the adsorbed oxygen species, new positive holes being created in the solid, according to the following equilibrium:

$$O_{2(gas)} \rightleftharpoons O_{2(ads)}^- + h^+ \rightleftharpoons 2O_{2(ads)}^- + h^+ \rightleftharpoons 2O_{2(ads)}^{2-} + 2h^+ \rightleftharpoons 2O_{O}^0$$  \hspace{1cm} (1)$$

where $h^+$ represents a positive hole and $O_{O}^0$ a lattice oxygen anion of the solid. On the contrary, in the presence of reducing molecules, such as H$_2$, CO or a hydrocarbon, which consume lattice oxygen species with subsequent formation of oxygen vacancies, electrons are released in the valence band of the oxide resulting in a decrease of the positive holes concentration and, hence, of the $p$-type electrical conductivity.

Similarly, the electrical conductivity of an $n$-type semiconducting oxide decreases in the presence of oxygen as the electrons flow from the conduction band of the oxide to the adsorbed oxygen species, according to the following equilibrium:

$$O_{2(gas)} + e' \rightleftharpoons O_{2(ads)}^- + e' \rightleftharpoons 2O_{2(ads)}^- + 2e' \rightleftharpoons 2O_{2(ads)}^{2-} \rightleftharpoons 2O_{O}^e$$  \hspace{1cm} (2)$$

where $e'$ represents a free electron. On the other hand, in the presence of reducing species, which consume surface and lattice oxygen species with subsequent formation of oxygen vacancies,
electrons flow into the conduction band of the oxide leading to an increase of the charge carriers concentration and, hence, of the $n$-type electrical conductivity.

The present study is complementary to the characterization and catalytic performance studies of the Ce-Pr mixed oxides catalysts reported earlier [11, 14] and has been undertaken to investigate their semiconductive and redox properties in correlation with their catalytic behavior by means of in situ electrical conductivity measurements. Thus, DC-electrical conductivity of the Ce-Pr mixed oxides, namely Ce$_{0.8}$Pr$_{0.2}$O$_2$, Ce$_{0.5}$Pr$_{0.5}$O$_2$ and Ce$_{0.2}$Pr$_{0.8}$O$_2$, as well as of pure CeO$_2$ and PrO$_{2-\delta}$ was studied as a function of temperature and oxygen partial pressure, and temporal responses during sequential exposures to air and different gaseous mixtures containing methane, CO or H$_2$, in conditions close to those of their catalytic applications were analyzed. Comparisons between the different Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ systems and correlations between their redox and semiconductive properties and their catalytic behavior in different oxidation reactions have been established.

2. Experimental

2.1. Catalysts preparation and characterization

Both Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ ($x = 0.2, 0.5$ and $0.8$) mixed oxides and CeO$_2$ and PrO$_{2-\delta}$ pure oxides were prepared by the coprecipitation method, as described elsewhere [14]. Thus, ammonia was added drop wise under stirring to aqueous solutions containing the required amounts of Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.99 %) and Pr(NO$_3$)$_3$·6H$_2$O (Sigma Aldrich, 99.9 %) precursors until the complete precipitation (pH $\approx 9$). The obtained precipitate was recovered by filtration, dried at 110 °C for 24 h and then calcined at 500 °C for 1 h in static air. The samples were noted Ce20Pr80, Ce50Pr50, Ce80Pr20, Ce100 and Pr100, respectively.

The crystal structure of the prepared samples was determined by X-ray diffraction. The Ce100 sample presented the typical fluorite structure of ceria while the Pr100 sample consisted of a mixture of Pr$_6$O$_{11}$ (or PrO$_{1.83}$) and PrO$_2$ phases [14]. The Ce-Pr mixed oxides consisted of a main fluorite phase and, although the introduction of Pr cations within the fluorite lattice of ceria was clearly evidenced by Raman spectroscopy, segregated phases of praseodymium oxide with different stoichiometries are present [14]. A detailed physicochemical characterization of these materials has been published elsewhere [14], while the main physicochemical characteristics referred to in the present study are tabulated in Table 1.
2.2. **Electrical conductivity measurements**

The oxide samples were compressed at ca. $2.76 \times 10^7$ Pa using a Carver 4350.L pellet press to ensure good electrical contacts between the catalyst grains. The obtained pellet was placed in a horizontal quartz tube between two platinum electrodes. Flow rates of gases flowing over the sample were controlled by fine needle valves and were measured by capillary flow meters. The temperature was controlled using Pt-Rh thermocouples soldered to the electrodes and, when short-circuited, they were used to determine the electrical conductivity $\sigma$ of the samples, which can be expressed by the formula:

$$\sigma = \frac{1}{R} \times \frac{t}{S}$$  \hspace{1cm} (3)

where $R$ is the electrical resistance and $t/S$ is the geometrical factor of the pellet including the thickness $t$ (ca. 3 mm) and the cross sectional area $S$ of the pellet whose diameter was equal to 13 mm. The electrical resistance was measured with a megaohmmeter (FLUKE 177 Digital Multimeter).

To compare the electrical conductivities of the samples, it is required that the solids have similar textures and surface states. Indeed, the electrical conductivity of semiconducting oxide powders can be written as:

$$\sigma = An$$  \hspace{1cm} (4)

where $n$ is the concentration of the main charge carriers and $A$ is a coefficient of proportionality which includes the mobility of the main charge carriers and the elementary charge of the electron and depends on the compression of the powder and on the number and quality of contact points between particles [19]. Since the samples were compressed at the same pressure and have similar BET surface areas (Table 1), and since the electrical conductivity measurements were standardized, $A$ can be considered similar for all the samples under identical conditions.

The common reference state for $\sigma$ determination has been chosen under air at atmospheric pressure at 475 °C. At this temperature, which is in the range used in the catalytic reactions, most of the ionically adsorbed species such as $\text{H}_3\text{O}^+$, $\text{HO}^-$ which would produce an additional surface conductivity are eliminated. The solid was initially heated from room temperature to the desired temperature at a heating rate of 5 °C/min.
2.3. Catalytic tests

Catalytic activity in the total oxidation of methane reaction was measured at 475 °C in a fixed bed quartz tube down-flow reactor operated at atmospheric pressure using 1 g of catalyst supported by quartz wool. The reaction temperature was increased from room temperature to 475 °C at a rate of 5 °C min⁻¹ under the air flow, and then the reaction mixture consisting of 5 vol. % methane in air was fed into the reactor with a flow rate of 333.33 mL min⁻¹. The reactor feed and outflow gases were analyzed on-line by a Clarus 500 Gas-Chromatograph equipped with a thermal conductivity detector (TCD), using two packed columns in series (a 6 ft Hayesep and a 10 ft molecular sieve 5Å). The conversion was calculated as the amount of methane transformed in the reaction divided by the amount that was fed to the reactor. Complete selectivity to CO₂ and H₂O was always observed. The carbon balance was satisfactory in all runs to within ± 4 %.

Catalytic activity tests in the CO-PROX process were carried out in a stepwise manner under isothermal conditions at selected temperatures in the 150-500 °C range as described in Ref. [11]. The catalyst samples were pretreated into the reactor under 5 % O₂/He, at 250 °C for 1 h. The CO-PROX experiments were performed with an inlet total gas flow of 100 mL min⁻¹, containing 50 % H₂, 1 % CO, 1 % O₂ and He as balance (GHSV = 12,000 h⁻¹). A gas chromatograph Bruker 450-GC with a thermal conductivity detector was coupled to the reactor for analysis of the reactants and reaction products. A molecular sieve 13X column was used to separate CO and O₂, and another column of Hayesep was attached to analyze CO₂ and H₂O. The concentrations of CO, O₂ and CO₂ were calibrated with external standard calibration gas mixtures from Praxair.

3. Results and discussion

3.1. Variations of the electrical conductivity as a function of temperature

The electrical conductivities of the CeO₂ (Ce100), PrO₂₋δ (Pr100) and Ce₁₋ₓPrₓO₂₋δ mixed oxides samples have been measured as a function of temperature under air at atmospheric pressure, in the temperature range from 150 to 500 °C, the variations of lgσ versus reciprocal temperature being presented in Fig. 1. The linear variations observed show that all the oxides behaved as semiconductors whose electrical conductivities vary exponentially with temperature according to the typical activation law:

$$\sigma = \sigma_0 \cdot \exp \left( - \frac{E_s}{RT} \right)$$

(5)
where $\sigma_0$ is the preexponential factor and $E_c$ is the dynamic activation energy of conduction. The change of the slope of the Arrhenius-type plot at ca. 380 °C observed for Ce100 sample suggests a change in the conduction mechanism with temperature. This has already been observed for ceria-based materials [23, 24] and was attributed to changes of either the nature of the defects generating the charge carriers or the mobility of these carriers [23].

The data in Fig. 1 also show that the electrical conductivity within all the temperature range studied increased with increasing the Pr content following the order: Ce100 < Ce80Pr20 < Ce50Pr50 < Ce20Pr80 < Pr100. This behavior has already been observed for Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ mixed oxides with $x \leq 0.5$ [25]. It is noteworthy that, as it can be observed in Fig. 2, the electrical conductivity of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ mixed oxides increases by more than four orders of magnitude with increasing the Pr content up to $x = 0.5$, while it increases within only ca. one order of magnitude for $0.5 < x \leq 1$. This suggests that the effect of Pr on the electrical properties of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ oxides is significantly higher at low Pr contents than at high Pr contents.

Notably, the evolution of the electrical conductivity of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ oxides is in agreement with the trends in reducibility measured by means of H$_2$-TPR experiments. Indeed, with gradually increasing the Pr content in the catalysts, the overall hydrogen consumption is also increased [11].

As $\sigma_0$ values should depend on the density of charge carriers, they were estimated from the intercept of the straight lines in Fig. 1 and are presented in Table 2. The $\sigma_0$ value increases by adding PrO$_2$ to CeO$_2$ and by increasing its content, passing through a maximum for the Ce20Pr80 oxide, then it decreases for pure PrO$_2$ (Pr100 sample). It is noteworthy that maximum values of O$_2$ release, mainly at low temperatures, obtained from TPD under inert atmosphere are observed for Ce20Pr80 oxide [11].

The slopes of the semi-log plots in Fig. 1 enabled the calculation of the $E_c$ values presented in Table 2. It can be observed that the activation energy of conduction varies between 0.56 eV for Ce100 and 0.33 eV for Pr100, irrespective of the Pr content for the CePrO mixed oxides, being close to the $E_c$ values reported in the literature for Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ mixed oxides with $x \leq 0.5$ in the same temperature range [25]. The $E_c$ value observed for CeO$_2$ (Ce100) sample is close to that reported in the literature and measured in the same temperature range [26]. The higher $E_c$ value observed for this sample at high temperature accounts for the ionic conduction mechanism [27], which becomes prevalent over the electronic mechanism at temperatures higher than 380 °C.
Indeed, the \( E_c \) value (0.92 eV) is close to previously reported data for oxygen vacancy migration in ceria [28].

### 3.2. Variations of the electrical conductivity under air as a function of oxygen partial pressure

Oxide materials may exhibit several types of conductivity simultaneously, i.e. \( n-\), \( p-\) and ion-type conductivity, and the prevalent conduction mechanism can be determined from the change of the overall conductivity as a function of the oxygen partial pressure [27]. Fig. 3 shows the variations of \( \sigma \) as a function of the oxygen pressure for \( \text{CeO}_2 \), \( \text{PrO}_{2-\delta} \) and \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) oxides at 475 °C in a log–log plot. It is worth noting that the oxygen pressure was varied in a range which corresponds to the oxygen partial pressure in the catalytic zone. It appears that \( \text{CeO}_2 \) (Ce100 sample) shows a negative slope, \( i.e. \frac{\partial \sigma}{\partial P_{O_2}} < 0 \), suggesting an \( n-\)type behavior, while for \( \text{PrO}_{2-\delta} \) (Pr100 sample) and all \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) oxides positive slopes are observed, \( i.e. \frac{\partial \sigma}{\partial P_{O_2}} > 0 \), suggesting a \( p-\)type behavior.

The slope of the \( \log \sigma - \log P_{O_2} \) plot for pure \( \text{CeO}_2 \) is different from \(-1/4\) or \(-1/6\), which respectively correspond to the existence of singly or doubly ionized oxygen vacancies. This suggests that pure ceria has, as expected [29, 30], both electronic (\( \sigma_n \)) and ionic (\( \sigma_i \)) conduction, the total conductivity being:

\[
\sigma = \sigma_n + \sigma_i \quad (6)
\]

Usually, the electronic conductivity of ceria at high oxygen pressures and high temperatures is expected to be a function of \( P_{O_2}^{-1/6} \) [31, 32], accounting for the existence of doubly ionized oxygen vacancies as main point defects formed according to the following equilibrium written in the Kröger-Vink notation [33]:

\[
\text{O}_0^\circ \leftrightarrow \frac{1}{2}\text{O}_2 + \text{V}_0^{**} + 2e' \quad (7)
\]

where \( \text{O}_0^\circ \), \( \text{V}_0^{**} \) and \( e' \) denote oxygen anions in regular lattice points, doubly ionized oxygen vacancies and quasi-free electrons, respectively.

However, taking into consideration that the electrical conductivity measurements were performed at relatively low temperature, i.e. 475 °C, the formation of singly ionized oxygen vacancies (\( \text{V}_0^* \)) according to the equilibrium:

\[
\text{O}_0^\circ \leftrightarrow \frac{1}{2}\text{O}_2 + \text{V}_0^* + e' \quad (8)
\]
cannot be ignored. If they are considered to be dominant, then $\sigma_n \propto P_{O_2}^{-1/4}$. Indeed, the formation of singly charged and even uncharged oxygen vacancies by defect association between oxygen vacancies and electrons is expected at low temperatures, as already shown for ceria-based materials at 470 °C [28].

In order to confirm the conduction model proposed in Eq. (6) for the Ce100 sample, the total conductivity $\sigma$ was plotted as a function of both $P_{O_2}^{-1/6}$ (Fig. 4a) and $P_{O_2}^{-1/4}$ (Fig. 4b). It can be observed that linear relationships were obtained, with good R$^2$ coefficients in both cases, suggesting that both types of point defects coexist in the Ce100 sample. This confirms the conduction model proposed involving that the electronic conductivity coexists with a lattice oxygen-anion conductivity. The $\sigma_i$ conductivity values at the temperature concerned, i.e. 475 °C, were calculated for the Ce100 sample from the $\gamma$-intercept of the plots in Figs. 4a and 4b and are tabulated in Table 3.

With $\sigma_i$ known, $\sigma_n$ values, i.e. $\sigma_n \propto P_{O_2}^{1/6}$ and $\sigma_n \propto P_{O_2}^{1/4}$, were calculated by subtracting $\sigma_i$ from $\sigma$ according to Eq. (6) and were represented as a function of the oxygen pressure in a log–log plot (Fig. 5a and 5b, respectively). The obtained plots exhibit the expected $-1/6$ and $-1/4$ slopes, respectively. As the R$^2$ coefficients of the plots are quite good, this confirms that both types of oxygen vacancies are present in the $n$-type ceria. Notably, for both $\sigma_n$ dependencies on the oxygen pressure, the $\sigma_i$ value is higher than the electronic conductivity (Table 3), confirming that the lattice oxygen-anion conductivity becomes the main conduction mechanism for Ce100 oxide at temperatures higher than 380 °C, in line with the observed change of the slope of the Arrhenius-type plot in Fig. 1.

The praseodymium oxide PrO$_2$-$\delta$ belongs to a fluorite-related homologous series with the general formula Pr$_n$O$_{2n-2}$ with $n = 7, 9, 10, 11, 12$ and $\infty$, which correspond to the iota, zeta, epsilon, delta, beta and alpha phase, respectively [34]. The stability of each of these phases depends on both the temperature and the oxygen partial pressure, and transition between them occurs rapidly by changing one of these two parameters. Interestingly, the Pr$_6$O$_{11}$ phase ($n = 12$) rather than the $\alpha$-PrO$_2$ mother phase is stable at ambient temperatures in air [34]. It is worth remembering here that our Pr100 sample consists of a mixture of phases evidenced by XRD at room temperature [14]. Detailed electrical conductivity studies of different oxides from this series have already been reported [34-36]. Inaba and Naito [35, 36] showed that the electrical conductivity of
different praseodymium oxides increases with oxygen pressure accounting for a \( p \)-type semiconducting behavior, and found for zeta and alpha phases at 565 and 630 °C, respectively, positive slopes of the \( \log \sigma - \log P_{O_2} \) plots of 0.031 and 0.042, respectively. Within a similar oxygen partial pressure range, the value of the slope for the Pr100 sample at 475 °C was found to be 0.036. The \( p \)-type behavior of praseodymium oxide can be explained considering that Pr ions form a narrow band and the electrical conduction occurs via the hopping mechanism between \( \text{Pr}^{3+} \) and \( \text{Pr}^{4+} \) sites [35]. Moreover, if \( \text{Pr}^{3+} \) is considered a trivalent impurity added to \( \text{PrO}_2 \) to form a substitutional solid solution, then it may be shown that in the intermediate oxygen pressure range a mixed \( p \)-type and ionic conductivity region exist, the \( p \)-type conductivity being a function of \( P_{O_2}^{1/4} \) [29].

In the case of the \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) mixed oxides it has been shown that within a certain high oxygen pressure range, the reduction of \( \text{Pr}^{3+}_{\text{Ce}} \) substitutional defects takes place [37] according to the following equilibrium:

\[
2\text{Pr}^{3+}_{\text{Ce}} + \text{O}_2 \leftrightarrow 2\text{Pr}^{4+}_{\text{Ce}} + \text{V}_{\text{O}^2-}^\ast + 1/2\text{O}_2(g)
\]  

(9)

At low Pr contents, its energy level, which lies within the ceria band gap, remains discrete. As the Pr content increases, the discrete levels overlap forming an impurity band allowing an electronic conductivity by small polaron hopping between two adjacent Pr ions having different valence states, i.e. \( \text{Pr}^{3+} \) (\( \text{Pr}^{3+}_{\text{Ce}} \)) and \( \text{Pr}^{4+} \) (\( \text{Pr}^{4+}_{\text{Ce}} \)) [37, 38]. This corresponds to a \( p \)-type behavior and, hence, an increase of the electrical conductivity with increasing the oxygen pressure is observed. Moreover, a “standard” behavior of the electronic conductivity as a function of the oxygen pressure with +1/4 slope is expected [38, 39]. Indeed, the oxygen pressure dependence of the \( p \)-type electronic conductivity of a \( \text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta} \) sample measured at 800 °C under suppressed flow of ions was shown to exhibit the expected slope of +1/4 [40]. Also, in the case of a ceria – praseodymia single crystal in which the electronic transport process was shown to be dominant over the ionic transport in the high oxygen pressure range, the observed slope was close to +1/p with \( p \geq 4 \) in the temperature range 400 – 800 °C [41]. Taking into consideration that the \( p \)-type electronic conductivity coexists in the polycrystalline \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) oxides with the ionic conductivity [37], the total conductivity is expected to be a function of \( P_{O_2}^{1/p} \) with \( p > 4 \). Moreover, according to Eqn. (6), the ionic conductivity is expected to increase with increasing
the reduction of \( \text{Pr}_{Ce}^+ \) substitutional defects. This is the case of the \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) mixed oxides studied in this work (Fig. 3 and Table 3). However, the fact that segregated phases of praseodymium oxide with different stoichiometries and a significant surface Pr enrichment, mainly at high Pr content, were evidenced in the Ce-Pr mixed oxides by XRD and XPS, respectively [14], suggests that in the Ce50Pr50 and Ce20Pr80 samples the \( \text{PrO}_{2-\delta} \) phases are concentrated on the surface of the particles. Moreover, as the composition limit corresponding to the percolation threshold [42, 43], which in the case of \( \text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \) oxides it seems to correspond to ca. 20 at. % Pr, is largely exceeded, the electrical conductivity of the Ce50Pr50 and Ce20Pr80 samples is governed by the \( \text{PrO}_{2-\delta} \) phases.

Based on the discussion above, the proposed model for the total electrical conductivity of our Pr-containing samples is:

\[
\sigma = \sigma_p + \sigma_i
\]  

(10)

with the electronic conductivity \( \sigma_p \propto P_{O_2}^{1/4} \) and the ionic conductivity \( \sigma_i \) independent of the partial pressure of oxygen. The linear plots of the total conductivity \( \sigma \) as a function of \( P_{O_2}^{1/4} \) with good \( R^2 \) coefficients observed (Fig. 4c) confirm the model proposed. The \( \sigma_i \) conductivity values at the temperature concerned, \( i.e. \) 475 °C, were calculated for the Pr-containing samples from the \( y \)-intercept of the plots in Fig. 4c and are tabulated in Table 3. With \( \sigma_i \) known, \( \sigma_p \) was calculated by subtracting \( \sigma_i \) from \( \sigma \) according to Eq. (10) and was represented as a function of the oxygen pressure in a log–log plot for all the Pr-containing samples (Fig. 5c). The obtained plots with quite good \( R^2 \) coefficients exhibit the expected +1/4 slope, in line with the conductivity model proposed.

The data in Table 3 show that both electronic and ionic conductivities strongly increase when passing from Ce100 to Ce80Pr20 sample. Then the ionic conductivity increases continuously with increasing the Pr content, while the electronic conductivity passes through a slight maximum for Ce20Pr80 sample. Notably, the ionic conductivity at 475 °C is higher than the electronic conductivity for all the samples studied.

It is interesting to note that for the Pr-containing oxides having a \( p \)-type behavior, the slope of the log \( \sigma \) – log \( P_{O_2} \) plot (Fig. 3) increases following the order: Ce80Pr20 (+1/57) \( \ll \) Pr100 (+1/28) \( \ll \) Ce20Pr80 (+1/17) \( \ll \) Ce50Pr50 (+1/10). This suggests that the oxygen exchange
kinetics between the $p$-type solid and the gas phase, which involves the following equilibrium [32]:

$$V^+_O + 1/2O_2 \leftrightarrow O^+_O + 2h^*$$

where $h^*$ indicates an electron hole, increases following the same order: the oxygen exchange kinetics increases by adding ceria to praseodymia and by increasing its content up to 50 % (Ce50Pr50 sample), then it strongly decreases for Ce80Pr20 sample.

3.3. Study of the redox behavior of the catalysts by in situ electrical conductivity measurements under catalytic conditions

For studying the redox behavior of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts under conditions as close as possible to those of catalysis, electrical conductivity measurements were performed at a temperature within the temperature range of different oxidation reactions, i.e. 475 °C, during sequential periods under air, methane-air mixture (simulating a reaction mixture with 5 vol % CH$_4$ in air), and different reducing gases (5 vol %) in nitrogen, i.e. methane, carbon monoxide and hydrogen. The results obtained are displayed in Fig. 6. The solids were heated from room temperature to 475 °C, at a heating rate of 5 °C min$^{-1}$ in air flow at atmospheric pressure.

For the $n$-type Ce100 oxide, it can be observed that the introduction of the methane-air mixture after reaching the steady state under the air flow results in an increased electrical conductivity. Then, air was again introduced over the sample and, after reaching the steady state, a methane-nitrogen mixture was passed over the sample. The electrical conductivity immediately increased abruptly by several orders of magnitude. This behavior corresponds to the $n$-type semiconducting character according to the $n$-type criterion for oxide semiconductors $\partial \sigma / \partial P_{O_2} < 0$ or, considering methane as a reducing gas, $\partial \sigma / \partial P_{CH_4} > 0$. When air was introduced again over the sample, the electrical conductivity decreased immediately and reached a plateau corresponding to a $\sigma$ value identical to the initial value suggesting that the reoxidation of the solid reduced under methane was totally reversible. After reaching again the steady state under air flow, a sequence of CO-nitrogen mixture was introduced over the sample. The electrical conductivity strongly increased reaching a plateau, which confirms the $n$-type character of the Ce100 sample in the presence of CO ($\partial \sigma / \partial P_{CO} > 0$). After a new sequence of air which completely reoxidizes the solid reduced under CO, a sequence of hydrogen-nitrogen mixture was passed over the sample. As expected,
the electrical conductivity strongly increased accounting for the reduction of the solid. Finally, the air sequence was repeated for confirming the reversibility of the phenomena. Indeed, the electrical conductivity decreases and reaches a plateau corresponding to a $\sigma$ value identical to the initial value under air suggesting that the reoxidation of the ceria sample reduced under hydrogen-nitrogen mixture is totally reversible. It is noteworthy that, while under the methane-nitrogen mixture the steady state was reached after ca. 30 min, under both CO-nitrogen and hydrogen-nitrogen mixtures it was reached after more than 50 min. Moreover, the amplitude of the effect is lower under methane than under both CO and hydrogen. These suggest that a deeper reduction of ceria takes place under CO and hydrogen than under methane, which involves not only a surface reduction, but also a bulk phenomenon.

For the $p$-type oxides for which the conductivity of the $\text{PrO}_{2.8}$-type phase prevails, i.e. Pr100, Ce20Pr80 and Ce50Pr50 samples, it can be observed that the introduction of the methane-air mixture after reaching the steady state under the air flow results in a slight decrease of the electrical conductivity. Then, air was again introduced over the samples and, after reaching the steady state, a methane-nitrogen mixture was passed over the samples. The electrical conductivity immediately decreased for all the samples, confirming their $p$-type semiconducting character according to the $p$-type criterion for oxide semiconductors $\partial \sigma / \partial P_{O_2} > 0$ or, considering methane as a reducing gas, $\partial \sigma / \partial P_{CH_4} < 0$. When air was introduced again over the samples, the electrical conductivity increased and reached a plateau corresponding to a $\sigma$ value almost identical to the initial value for all the samples suggesting that the reoxidation of the reduced solids was totally reversible. Then, a sequence of CO-nitrogen mixture was introduced over the samples and the electrical conductivity decreased, as expected, but such slowly that after 50 min. the steady state has not yet been reached. This suggests a slow kinetics of the reduction of these solids with CO. On the other hand, the amplitude of the effect is much higher for Pr100 sample compared to Ce20Pr80 and Ce50Pr50 mixed oxides, suggesting a deeper reduction of the former. After the reoxidation of the solid under a new air sequence, a sequence of hydrogen-nitrogen mixture was passed over the samples. The electrical conductivity immediately decreased abruptly accounting for the reduction of the solids under hydrogen, the amplitude of the effect increasing as follows: Ce50Pr50 < Pr100 < Ce20Pr80.

The Ce80Pr20 sample had a particular behavior during sequential exposures to different gases. Under methane-air and methane-nitrogen mixtures its behavior was similar to other $p$-type Pr-
containing oxides studied, i.e. the electrical conductivity decreased, although the amplitude of the effects is less pronounced, confirming its \( p \)-type character. Under air sequences the electrical conductivity increased accounting for the reoxidation of the reduced solid. When the CO-nitrogen mixture was passed over the sample, the electrical conductivity first slightly decreased accounting for the \( p \)-type semiconducting character of the Ce80Pr20 sample. However, after a couple of minutes, the electrical conductivity passed abruptly in the negative domain, very high negative resistance values being measured during ca. 30 min., which correspond to negative electrical conductivities. In Fig. 6 this period was represented with a dotted line, but the variation in time of the measured electrical resistance of the Ce80Pr20 sample as a function of the nature of the gas phase in contact with the solid is shown in Fig. 7. This corresponds to an NDR-like (Negative Differential Resistance) or NDC-like (Negative Differential Conductivity) behavior, which is a complex electrical phenomenon consisting, in principle, of a high increase of conductivity due to sudden changes in the number or the mobility of the charge carriers in the solid involving various mechanisms [44-46]. It can be associated with structural changes (atomic rearrangements) or electronic changes (quasipermanent change in the occupancy of some electronic states) in the solid at local or bulk level. Usually, the NDR-like behavior takes place under suitable electric fields, but here it is related to the gaseous atmosphere in contact with the semiconducting oxide. After ca. 30 min. of negative values, still under the CO-nitrogen mixture, the electrical conductivity of the Ce80Pr20 sample became positive and reached a plateau, interestingly, at a value higher than that under air. This clearly suggests that the solid switched from \( p \)-type to \( n \)-type behavior passing through the NDR-like state. Then under a new air sequence the electrical conductivity decreased to a plateau corresponding to the steady state in air which is slightly lower compared to the initial plateau under air. On one hand, this confirms the \( n \)-type behavior of the Ce80Pr20 sample under the CO-nitrogen mixture at steady state and, on the other hand, this shows that the reoxidation of the solid reduced with CO is almost completely reversible; some species remain however in the reduced state, probably in the bulk of the solid particles. After this steady state in air, a hydrogen-nitrogen mixture was passed over the sample. The electrical conductivity first slightly decreased confirming that the Ce80Pr20 sample regained its \( p \)-type semiconducting character under air, and then an NDR-like behavior was again observed for ca. 10 min. (see Fig 7) before passing to the \( n \)-type state of the semiconducting oxide, in line with the observed increase of the electrical conductivity under the
reducing gas, i.e. $\partial \sigma / \partial P_{H_2} > 0$. It is noteworthy that under hydrogen the electrical conductivity tends to the steady state at a value significantly higher compared to that under CO suggesting a deeper reduction of the solid in the presence of the former reducing gas. Finally, an air flow was passed over the sample reduced under hydrogen and, as expected, the electrical conductivity decreased rapidly to a plateau corresponding to the steady state in air which is very close to the initial plateau under air confirming the complete reoxidation of the Ce80Pr20 sample and the reversibility of the observed phenomena.

The electrical behavior of the Ce80Pr20 sample under both CO and hydrogen could be understood having in mind the behavior of the $Ce_{1-x}Pr_xO_{2-\delta}$ oxides within a wide range of oxygen pressures, from high to very low, already described in the literature [38, 47]. Thus, as the oxygen pressure is decreased from high to intermediate values, the $Ce_{1-x}Pr_xO_{2-\delta}$ oxide releases oxygen and anionic vacancies are formed with simultaneous reduction of Pr$^{4+}$ to Pr$^{3+}$. This situation corresponds to a mixed ionic – $p$-type conductivity, the latter contribution resulting from small polaron hopping between Pr sites with different valence, as already observed for the Ce80Pr20 sample. When all the Pr$^{4+}$ ions are reduced to Pr$^{3+}$, the $p$-type contribution to the electrical conductivity disappears, the ionic conductivity remaining the unique conduction mechanism. Continuing to decrease the oxygen pressure to low and very low values, the solid continue releasing oxygen with formation of oxygen vacancies and, now, with the simultaneous reduction of Ce$^{4+}$ to Ce$^{3+}$, and it will display a mixed ionic – $n$-type conductivity. In a similar way, when the Ce80Pr20 sample is reduced by CO or hydrogen, it passes from a $p$-type to an $n$-type state involving the successive reduction of both Pr$^{4+}$ to Pr$^{3+}$ and Ce$^{4+}$ to Ce$^{3+}$. Due to the high reducing character of these gases the rate of the reduction process is very high and probably creates an avalanche of charge carriers (oxygen vacancies and electrons) in the solid accounting for the NDR-like behavior observed during the switching process from the $p$-type to the $n$-type state.

It is worth noting that while under CO and hydrogen the reduction of both praseodymium and cerium takes place and the Ce80Pr20 sample has an $n$-type character at steady state, under methane the reduction is limited to praseodymium species and the solid keeps its $p$-type behavior.

In summary, the in situ electrical conductivity measurements during sequential periods under different reducing and oxidizing atmospheres clearly suggest that all the $Ce_{1-x}Pr_xO_{2-\delta}$ oxides
function during the catalytic oxidation via a heterogeneous redox Mars – van Krevelen-type mechanism.

3.4. **Catalytic performance and correlations with the semiconducting properties**

The catalytic performance of the Ce-Pr oxides in two different oxidation reactions, i.e. the total oxidation of methane and the preferential oxidation of CO (CO-PROX), is discussed below in correlation with their electrical and redox properties.

3.4.1. **Methane total oxidation**

Extended studies of Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts in the total oxidation of methane have already been published [13, 15]. Therefore, the Ce-Pr oxides catalysts were tested in the total oxidation of methane in conditions similar to those used for their electrical conductivity measurements, i.e. at 475 °C and atmospheric pressure, with a reaction mixture consisting of 5 % methane in air. The results obtained are depicted in Fig. 8, where a synergetic effect can be observed, the catalytic activity of the Ce-Pr mixed oxides being higher than that of ceria and praseodymia, in line with previously reported results [13]. The methane conversion passes through a maximum as a function of the catalyst composition corresponding to Ce50Pr50 mixed oxide, which was already reported to be the most active Ce-Pr composition in methane combustion [13]. Except for Ce100 which is an n-type oxide, all other catalyst samples are of p-type and keep this behavior in the presence of methane. It is well known [48, 49] that the p-type semiconductivity can be associated to the presence of surface lattice O$^-$ species, i.e. O$_o^*$ species, which can be considered the chemical equivalent of positive holes according to the reaction:

$$O_o^- + h^* \rightleftharpoons O_o^* \quad (15)$$

Taking into consideration that these species are quite active for the oxidation of hydrocarbons [48, 49], this could explain the enhanced catalytic activity of the Pr-containing catalysts compared to CeO$_2$.

The difference $\Delta(lg\sigma)$ between the value of the electrical conductivity under air and that under methane (methane-nitrogen mixture), could be a measure of the availability of the lattice oxygen species in the oxides functioning via a heterogeneous redox mechanism. In the p-type Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ series, the highest $\Delta(lg\sigma)$ value was found for the Ce50Pr50 catalyst, the most active one in methane combustion. Moreover, the oxygen availability expressed as $\Delta(lg\sigma)$ and the catalytic
activity expressed as methane conversion, both of them measured at 475 °C, follow the same trend when plotted as a function of the value of x in the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts (Fig. 9), suggesting that a correlation exists between these two parameters.

At the same time, a good linear correlation can be observed in Fig. 10 between the catalytic activity expressed as the intrinsic rate of methane transformation at 475 °C and the value of the slope of the log $σ$ – log $P_{O_2}$ plot in Fig. 3, which is an indicative of the oxygen exchange kinetics between the $p$-type solid and the gas phase. This clearly suggests that the kinetics of the oxygen exchange with the gas phase is a key factor controlling the methane combustion activity of the $p$-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts.

In summary, p-type Pr-containing catalysts are more active in methane combustion than the n-type CeO$_2$ likely due to the presence of surface lattice O$^-$ species, i.e. O$_o^*$ species, known to be quite active for the oxidation of hydrocarbons. The catalytic activity of the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts depends on both the amount of available oxygen in the solid and the kinetics of the oxygen exchange with the gas phase. The Ce50Pr50 oxide shows the maximum of these two parameters and, hence, was found to be the most active one in this series.

3.4.2. Preferential oxidation of CO in H$_2$ rich stream

The catalytic properties of the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts in the CO-PROX process, which involves two parallel and competitive oxidation reactions (CO oxidation and H$_2$ oxidation), were reported and discussed in detail in Ref. [11]. The main catalytic results relevant for the discussion below are presented in Table 4, including the CO and O$_2$ conversions at 400 and 450 °C as well as the O$_2$ selectivity to CO$_2$. It can be observed that both the CO conversion and the O$_2$ selectivity to CO$_2$ pass through a maximum while the O$_2$ conversion passes through a minimum for the Ce80Pr20 system in the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ series. The semiconductive and redox properties of the Ce80Pr20 mixed oxide show some peculiarities that could account for its particular catalytic behavior in the CO-PROX process. Thus, compared to Ce100, which is of n-type, Ce80Pr20 is of p-type and, hence, accommodates at its surface lattice O$^-$ species known to be highly reactive.

On the other hand, compared to the other p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts in this series, the Ce80Pr20 mixed oxide shows the lowest electrical conductivity within all the temperature range considered (see Fig. 1) and the lowest $σ_0$ value, i.e. density of charge carriers (see Table 2) which could explain its lowest reactivity towards H$_2$ oxidation. Notably, with increasing the electrical
conductivity in the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ series the H$_2$ oxidation reaction becomes more important during the CO-PROX process in line with the increased density of highly reactive surface lattice O$^-$ species. It is also noteworthy that the Ce80Pr20 mixed oxide shows the slowest oxygen exchange kinetics with the gas phase (indicated by the slope of the log $\sigma$ – log P$_O$$_2$ plot in Fig. 3) among the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts. However, no clear correlation can be observed between the slope of the log $\sigma$ – log P$_O$$_2$ plot in Fig. 3 and the catalytic performance in the CO-PROX process. Finally, it is worth noting that the Ce80Pr20 mixed oxide is the only Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalyst that changes its character from p-type to n-type passing through the NDR-like state in the presence of CO and H$_2$ and keeps its n-type behavior at steady state (see Fig. 6) which corresponds to a reduced state involving the reduction of both Pr$^{4+}$ to Pr$^{3+}$ and Ce$^{4+}$ to Ce$^{3+}$. For the other p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts in this series only the reduction of Pr$^{4+}$ to Pr$^{3+}$ takes place under CO and H$_2$. These features could account for both the highest O$_2$ selectivity to CO$_2$ and the lowest O$_2$ conversion observed over Ce80Pr20 catalyst. Moreover, the n-type behavior under the reaction conditions seems to be an important factor favoring the CO-PROX reaction.

4. Conclusion
The electrical conductivity measurements showed that all the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ systems have both electronic and ionic conductivities and their total conductivity increases with the value of $x$. Ce100 (CeO$_2$) has an n-type behavior, while all the Pr-containing oxides, i.e. Pr100 (PrO$_{2-δ}$), Ce20Pr80, Ce50Pr50 and Ce80Pr20, have a p-type behavior in air. They keep their semiconductivity type under different gaseous atmospheres, except for Ce80Pr20 mixed oxide which switches from p-type to n-type passing through a NDR-like (Negative Differential Conductivity) state in the presence of CO and H$_2$. However, they show all a “breathing” redox behavior under sequential oxidative and reductive gaseous atmospheres, which clearly confirms that they function in oxidation catalysis via a heterogeneous redox mechanism.
All the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts were shown to be more active in methane combustion than the n-type CeO$_2$. This is likely due to the fact that the former can accommodate lattice O$^-$ species, i.e. O$^*_O$ species, at their surface which are known to be quite active for the oxidation of hydrocarbons. The catalytic activity of the p-type Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts depends on both the amount of available oxygen in the solid and the kinetics of the oxygen exchange with the gas.
phase. The Ce50Pr50 oxide shows the maximum of these two parameters and, hence, was found to be the most active one in this series.

In the CO-PROX process the Ce80Pr20 oxide showed the best performance in terms of selectivity for CO oxidation compared to H₂ oxidation. This is probably due to the fact that during catalysis the Ce80Pr20 oxide passes from p-type to n-type behavior which corresponds to a reduced state involving the reduction of both Pr⁴⁺ to Pr³⁺ and Ce⁴⁺ to Ce³⁺. For the catalysts with higher Pr contents in the Ce₁₋ₓPrₓO₂₋δ series, for which both p-type electronic and ionic conductivities increase with the Pr content, the H₂ oxidation becomes predominant.

Conflict of interest
There are no conflicts of interest to declare.

References


FIGURES CAPTION

Figure 1. Arrhenius plots for the electrical conductivity $\sigma$ of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts under air between 150 and 500 °C ($\sigma$ in ohm$^{-1}$ cm$^{-1}$).

Figure 2. Variation of $\sigma$ as a function of the Pr content $x$ in the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ oxides ($\sigma$ in ohm$^{-1}$ cm$^{-1}$).

Figure 3. Variation of $\sigma$ as a function of the oxygen pressure for the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts at 475 °C in a log–log plot (P$_{O_2}$ in atm; $\sigma$ in ohm$^{-1}$ cm$^{-1}$).

Figure 4. Total conductivity $\sigma$ versus (a) P$_{O_2}^{1/6}$ and (b) P$_{O_2}^{1/4}$ for the n-type Ce100 sample, and (c) P$_{O_2}^{1/4}$ for the p-type Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ samples at 475 °C (P$_{O_2}$ in atm; $\sigma$ in ohm$^{-1}$ cm$^{-1}$).

Figure 5. Variation of the electronic conductivity as a function of the oxygen pressure at 475 °C in a log–log plot for the different model dependencies on oxygen pressure: (a) $\sigma_n \propto P_{O_2}^{1/6}$ and (b) $\sigma_n \propto P_{O_2}^{1/4}$ for the n-type Ce100 sample, and (c) $\sigma_p \propto P_{O_2}^{1/4}$ for the p-type Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ samples (P$_{O_2}$ in atm; $\sigma_l$ in ohm$^{-1}$ cm$^{-1}$).

Figure 6. Variation of the electrical conductivity during sequential exposures to air, methane-air, methane-nitrogen, CO-nitrogen and H$_2$-nitrogen mixtures for the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts at 475 °C ($\sigma$ in ohm$^{-1}$ cm$^{-1}$).

Figure 7. Variation in time of the measured electrical resistance of the Ce80Pr20 sample as a function of the nature of the gas phase in contact with the solid.

Figure 8. Methane conversion at 475 °C as a function of the composition of the Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts.
**Figure 9.** Methane conversion and oxygen availability expressed as $\Delta(\lg \sigma)$, both of them measured at 475 °C, as a function of the value of $x$ in the p-type Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts.

**Figure 10.** Intrinsic rate of methane transformation at 475 °C as a function of the value of the slope of the log $\sigma$ – log $P_{O_2}$ plot for the p-type Ce$_{1-x}$Pr$_x$O$_{2-\delta}$ catalysts.
### Table 1. Surface area and chemical composition of the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ oxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Ce/Pr atomic ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>nominal</td>
<td>bulk (XRF)</td>
<td>surface (XPS)</td>
</tr>
<tr>
<td>Ce100</td>
<td>47</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce80Pr20</td>
<td>53</td>
<td>4</td>
<td>3.64</td>
<td>1.84</td>
</tr>
<tr>
<td>Ce50Pr50</td>
<td>30</td>
<td>1</td>
<td>0.85</td>
<td>0.66</td>
</tr>
<tr>
<td>Ce20Pr80</td>
<td>28</td>
<td>0.25</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>Pr100</td>
<td>43</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2. Arrhenius parameters for the electrical conductivity of the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ systems.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>E$_c$ (eV)</th>
<th>$\sigma_0$ (Ω$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce100</td>
<td>0.56 (0.92)$^a$</td>
<td>$1.8 \times 10^{-4}$ (3.3 $\times 10^{-2}$)$^a$</td>
</tr>
<tr>
<td>Ce80Pr20</td>
<td>0.38</td>
<td>$5.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ce50Pr50</td>
<td>0.34</td>
<td>$1.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>Ce20Pr80</td>
<td>0.42</td>
<td>1.3</td>
</tr>
<tr>
<td>Pr100</td>
<td>0.33</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$^a$ At temperatures higher than the inflection point of the Arrhenius-type plot.

### Table 3. Total ($\sigma$), electronic ($\sigma_n$ or $\sigma_p$) and ionic ($\sigma_i$) conductivity values for the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ systems under air at atmospheric pressure and 475 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\sigma$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$\sigma_n$ or $\sigma_p$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$\sigma_i$ (Ω$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce100</td>
<td>$2.4 \times 10^{-8}$</td>
<td>$5.7 \times 10^{-9}$</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Ce80Pr20</td>
<td>$2.1 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ce50Pr50</td>
<td>$6.5 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-4}$</td>
<td>$3.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ce20Pr80</td>
<td>$2.4 \times 10^{-3}$</td>
<td>$6.8 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Pr100</td>
<td>$2.9 \times 10^{-3}$</td>
<td>$5.1 \times 10^{-4}$</td>
<td>$2.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Table 4. The catalytic performance of the Ce$_{1-x}$Pr$_x$O$_{2-δ}$ catalysts in the CO-PROX process.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temperature (°C)</th>
<th>CO conversion (%)</th>
<th>O$_2$ conversion (%)</th>
<th>O$_2$ selectivity to CO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce100</td>
<td>400</td>
<td>40.5</td>
<td>54.1</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>55.8</td>
<td>100</td>
<td>28.1</td>
</tr>
<tr>
<td>Ce80Pr20</td>
<td>400</td>
<td>62.7</td>
<td>49.4</td>
<td>63.7</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>86.8</td>
<td>100</td>
<td>43.5</td>
</tr>
<tr>
<td>Ce50Pr50</td>
<td>400</td>
<td>55.9</td>
<td>61.1</td>
<td>48.3</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>68.5</td>
<td>100</td>
<td>34.3</td>
</tr>
<tr>
<td>Ce20Pr80</td>
<td>400</td>
<td>41.5</td>
<td>53.9</td>
<td>38.3</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>57.6</td>
<td>100</td>
<td>28.7</td>
</tr>
<tr>
<td>Pr100</td>
<td>400</td>
<td>44.8</td>
<td>81.5</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>31.0</td>
<td>100</td>
<td>15.4</td>
</tr>
</tbody>
</table>
Figure 1.
Figure 2.
Figure 3.
Figure 4.

\[ R^2 = 0.9969 \]

\[
\begin{array}{cccc}
0.00E+00 & 5.00E-09 & 1.00E-08 & 1.50E-08 \\
2.00E-08 & 2.50E-08 & 3.00E-08 & \\
\end{array}
\]

\[
\begin{array}{cccc}
0 & 0.5 & 1 & 1.5 \\
2 & 2.5 & \\
\end{array}
\]

\[
\begin{array}{cccc}
(PO_2)^{-1/6} (atm^{-1/6}) & \\
\end{array}
\]

\[
\begin{array}{cccc}
\sigma (\text{ohm}^{-1}\text{cm}^{-1}) & \\
\end{array}
\]

\[
\begin{array}{cccc}
0.00E+00 & 0.50E+00 & 1.00E+00 & 1.50E+00 \\
2.00E+00 & 2.50E+00 & 3.00E+00 & \\
\end{array}
\]

(a)
Figure 4 (continued).

\[ R^2 = 0.9945 \]

\[
\begin{array}{cccccc}
0.00E+00 & 5.00E-09 & 1.00E-08 & 1.50E-08 & 2.00E-08 & 2.50E-08 \\
0 & 0.5 & 1 & 1.5 & 2 & 2.5 \\
\end{array}
\]

\( (P_{O2})^{-1/4} \) (atm\(^{-1/4}\)) vs. \( \sigma \) (ohm\(^{-1}\)cm\(^{-1}\))

(b)
Figure 4 (continued).

\[ R^2 = 0.9939 \]
\[ R^2 = 0.9948 \]

\[ \sigma \text{ (ohm}^{-1}\text{cm}^{-1}) \]

\begin{align*}
\text{Pr100} & \quad \text{Ce20Pr80} & \quad \text{Ce50Pr50} & \quad \text{Ce80Pr20}
\end{align*}

(c)
Figure 5.

\[ R^2 = 0.9967 \]

-8.1
-8
-7.9
-7.8
-7.7
-1.6 -1.4 -1.2 -1 -0.8 -0.6

\( \lg P_{O2} \)
\( \lg \sigma_1 \)

Slope: \(-1/6\)
Figure 5 (continued).

\[ R^2 = 0.9942 \]

-8.5
-8.4
-8.3
-8.2
-8.1
-8
-1.6 -1.4 -1.2 -1 -0.8 -0.6

\[ \lg P_{O2} \]
\[ \lg \sigma_1 \]

Slope: -1/4

R\(^2\) = 0.9942

(b)
Figure 5 (continued).

![Graph](image-url)

- $R^2 = 0.9938$
- $R^2 = 0.999$
- $R^2 = 0.9991$
- $R^2 = 0.9959$

- lg $P_{O2}$
- lg $\sigma_1$

- Pr100 - Ce20Pr80 - Ce50Pr50 - Ce80Pr20
Figure 6.
Figure 7.
Figure 8.
Figure 10.

The graph shows the relationship between the slope of the logσ-logP plot and the methane conversion rate (10^{-6} mol m^{-2} s^{-1}). The plot demonstrates a linear trend with data points indicating the correlation.