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Title: Ni/LnOx catalysts (Ln = La, Ce or Pr) for CO2 methanation

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Ni/LnOx catalysts (Ln = La, Ce or Pr) for CO2 methanation


Abstract: The effect of the LnOx support has been studied for Ni-based CO2 methanation catalysts. 10 wt.% nickel catalysts with LaOx, CeO2 and PrOx supports have been prepared, characterized by N2 adsorption, XRD, XRF, TG-MS (N2-TPD and H2-TPR) and XPS, and have been tested for CO2 methanation. The catalytic activity follows the trend Ni/β-CeO2 > Ni/PrOx >> Ni/LaOx, all catalysts being very selective towards CH4 formation. The activity depends both on the nature of the catalytic active sites and on the stability of the surface CO2 and H2O species. Ni/β-CeO2 is the most active catalyst because (i) the Ni2+-ceria interaction leads to the formation of the highest population of active sites for CO2 dissociation, (ii) the reduced Ni0 sites where H2 dissociation takes place are the most electronegative and active, and (iii) the stability of surface CO2 and H2O species is lowest. Ni/LaOx achieves lower activity because of the strong chemisorption of H2O and CO2, which poison the catalyst surface, and because this support is not able to promote the formation of highly active sites for CO2 and H2 dissociation. The behavior of Ni/PrOx is intermediate, being slightly lower to that of Ni/β-CeO2 because the formation of active sites is not so efficient and because the stability of chemisorbed CO2 is slightly higher.

Introduction

CO2 methanation is known as the Sabatier reaction, because it was first reported by Paul Sabatier in the 1910s. This is an exothermic reaction between CO2 and H2 that yields CH4 + H2O.

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165.0 \text{ kJ/mol}
\]

Sabatier reaction (1)

Despite the reaction is known since more than 100 years ago, scientists are paying more attention to this process in the last decade[6-15] because it has been identified as a potential route to valorize CO2 emissions, yielding a valuable fuel. From an environmental point of view, the key aspect of this process is the utilization of H2 obtained from renewable sources, and this type of H2 is expected to be available at low prize in a hypothetical energy scenario where H2 is massively used as energy vector. CH4 has several advantages in comparison to H2 as energy vector. One of the most relevant is that can be liquefied and transported using the facilities already available for natural gas, while storage and transportation of H2 are so far unsolved problems that will require an important economical inversion.

As a proof of concept, Hashimoto et al. [20] successfully built in 1996 a prototype plant at the Institute for Materials Research, at the Tohoku University in Japan, using electrolytic cells working on solar energy for H2O electrolysis and H2 production. This H2 was used for CO2 methanation, and the CH4 obtained was combusted in a reactor with a CO2 capture unit, using this CO2 for further methanation, thus closing the energy cycle without CO2 emissions. Despite the Sabatier reaction is exothermic, it has kinetic restrictions due to the high stability of the reactant gases, and a catalyst is necessary to accelerate the reaction until rates with practical relevance for industrial application. Several active phases have been studied, including ruthenium,[21-28] palladium,[29-31] rhodium,[32-35] and nickel.[36-42] Noble metal catalysts are able to operate at lower temperature than nickel catalysts, but the prize of noble metals is much higher and nickel catalysts are a promising option for mild temperature.

CO2 methanation nickel catalysts have been studied using different supports, and the most studied are alumina,[6, 10, 15, 37, 39-41] pure ceria,[19] ceria-zirconia mixed oxides,[11, 39] silica,[12] titania,[13] and zirconia[38] among others.[43-45] The role of the support in the catalytic activity has been related with the dispersion of nickel, with the influence in the reducibility of the nickel oxide species due to the metal-support interaction and with the CO2 chemisorption capacity.[46] Despite alumina is the most studied support, there are evidences of the higher catalytic activity of nickel catalysts with ceria-based supports.[10, 38] It has been reported that alumina-supported nickel catalysts suffer from severe carbon deposition and poor stability due to the high reaction temperature.[47] This high catalytic activity of Ni/β-CeO2 has motivated us to focus our research on the behavior of different Ni/LnOx catalysts, comparing different LnOx supports and understanding the role of the support in the catalytic performance.

In order to evaluate the catalytic activity of Ni catalysts using lanthanide oxide supports, the goals of the present study have been to prepare, characterize and test the catalytic activity for CO2 methanation of nickel catalysts with LaOx, CeO2 and PrOx supports, paying attention to the main features of the LnOx support affecting the catalytic activity. LaOx and PrOx oxides have been selected to be compared with CeO2 because they have some interesting properties for the Sabatier reaction. LaOx is more basic than CeO2, and therefore is expected to improve CO2 and H2O chemisorption. However, La can hardly accomplish redox cycles while Ce and Pr can do. On the other hand, Ce and Pr chemistry is similar in many aspects, since both elements can adopt 3+ and 4+ oxidation states, but the redox and...
chemisorption properties are slightly different. This set of materials will be useful to identify the importance of the different steps of the reaction mechanisms (chemisorption and redox steps) and the role of the support in the behavior of the nickel catalysts.

Results and Discussion

2.1. Fresh catalysts and supports characterization by N\textsubscript{2} adsorption.

Three catalysts have been prepared and characterized in this study, which are referred to as Ni/CeO\textsubscript{2}, Ni/PrO\textsubscript{x} and Ni/LaO\textsubscript{x}. Details about the preparation procedure are included in the experimental section at the end of this document. Figure 1 shows the N\textsubscript{2} physisorption isotherms of the fresh supports and catalysts, and the specific surface areas are compiled in Table 1.

The specific surface areas are low for all supports and catalysts (≤ 13 m\textsuperscript{2}/g), as expected for lanthanide oxides prepared by calcination of citrates. However, all catalysts present similar surface areas, and this allows comparison of the catalytic results ruling out differences in the specific surface areas. The N\textsubscript{2} physisorption isotherms present very low N\textsubscript{2} adsorption at low relative pressures due to the very low microporosity, and hysteresis loops that suggest the presence of large mesopores or even macroporosity. Meso and macropores could be attributed to the interparticles space, and the absence of micropores suggests that particles have not internal pores. Note that the surface areas of PrO\textsubscript{x} and LaO\textsubscript{x} increase upon nickel loading, and as it will be demonstrated in the next section, this can be attributed to changes in the crystalline phases of the supports after nickel impregnation.

2.2. Fresh catalysts and supports characterization by XRD and XRF.

The nickel percentage on the catalysts was determined by XRF, and the results obtained are included in Table 1. The nickel contents are near the target value of 10 wt. %, as expected.

Figure 2 shows the X-ray diffractograms for the supports and catalysts, and the nature of the crystalline phases is different for each material. The Ni/CeO\textsubscript{2} catalyst shows the characteristic peaks of CeO\textsubscript{2} (JCPDS 00-034-0394) and NiO (JCPDS 01-075-0269), while the bare support only shows the characteristic peaks of CeO\textsubscript{2} (Figure 2a), as expected. Different crystalline parameters were determined from the diffractograms of Figure 2a, which are compiled in Table 2.
The cell parameter of bare CeO$_2$ is 0.5425 nm, and this cell parameter decreases slightly to 0.5415 nm upon NiO loading. Note that these values are quite similar to that reported on the JCPDS database for this material (0.5411 nm). The small contraction of the unit cell after NiO loading could be attributed to the insertion of nickel cations into the ceria lattice, since nickel cations are smaller (0.078 nm for Ni$^{2+}$ and 0.062 nm for Ni$^{3+}$) than Ce$^{4+}$ cations (0.097 nm). The difference between the cell parameters of CeO$_2$ and NiO/PrO$_x$ has been used to estimate, using the Kim’s equation,[46, 47] the amount of Ni$^{2+}$ inserted into the ceria lattice. This equation can be written as follows:

$$\text{CP (Ni$^{2+}$-doped CeO$_2$) = CP (CeO$_2$) - (0.022 \cdot (r_{Ni^{2+}} + r_{Ce^{4+}}) + 0.00015 \cdot (Z_{Ni^{2+}} - Z_{Ce^{4+}}) \cdot X_{Ni})}$$

where CP means cell parameter, r$_{Ni^{2+}}$ and r$_{Ce^{4+}}$ are the cationic radii of Ni$^{2+}$ and Ce$^{4+}$ respectively, Z$_{Ni^{2+}}$ and Z$_{Ce^{4+}}$ are the cationic charges of Ni$^{2+}$ and Ce$^{4+}$ respectively, and X$_{Ni}$ is the fraction of Ni$^{2+}$ inserted into the parent ceria lattice.

These calculations predict that the percentage of Ni$^{2+}$ inserted into the CeO$_2$ lattice in the NiO/PrO$_x$ catalyst amounts to 1.4 %, which is much lower than the total amount of nickel in the catalyst. Therefore, these XRD results indicate that most nickel is not forming a solid solution, but is present as a segregated phase. The crystallite sizes estimated for CeO$_2$, using the Scherrer equation and the (111) plane at $2\theta = 28.5^\circ$, are 20 and 31 nm for the support and catalyst, respectively, and the size of NiO crystallites (estimated with the (200) plane at $2\theta = 43.3^\circ$) is 22 nm, that is, the sizes of CeO$_2$ and NiO crystallites are of the same magnitude order. Note that the size of CeO$_2$ slightly increases upon nickel doping, and this could be due to the promoting effect towards sintering of the Ni$^{2+}$ cations inserted into the ceria lattice.[48]

The diffractograms of the praseodymium samples are included in Figure 2b, and some crystalline parameters determined from these diffractograms are compiled in Table 3.

| Table 3. Crystalline parameters determined from XRD for PrO$_x$ and Ni/PrO$_x$. |
|---|---|---|---|
| Cell parameter Pr$_2$O$_3$ (nm) | Crystallite size of Pr$_2$O$_3$ (nm) |
| PrO$_x$ | 0.5459 | 26 |
| Ni/PrO$_x$ | 0.5462 | 26 |

The bare PrO$_x$ support shows a diffractogram consistent with the presence of the Pr$_2$O$_3$ phase (JCPDS 00-042-1121), and the tiny shoulder in the peak at $2\theta = 47.3^\circ$ suggests the presence of few Pr$_2$O$_3$ (JCPDS 00-024-1006). The Ni/PrO$_x$ catalyst also shows peaks of these two phases, but the formation of the Pr$_2$O$_3$ phase is promoted upon nickel loading. Peaks of NiO are not clearly shown in the Ni/PrO$_x$ diffractogram, and only a very broad band could be assigned to this phase is observed at $2\theta = 28.5^\circ$. The cell parameters of the Pr$_2$O$_3$ phase were estimated to evaluate if Ni$^{2+}$ cations were inserted into the Pr$_2$O$_3$ phase or if well dispersed NiO crystals, with low diffraction capacity, were formed. The cell parameters calculated for the Pr$_2$O$_3$ phase were 0.5459 and 0.5462 nm for the PrO$_x$ and NiO/PrO$_x$ samples, respectively, and these values suggest that Ni$^{2+}$ cations were not inserted into the Pr$_2$O$_3$ phase because there is not cell contraction upon nickel loading. Therefore, it is postulated that small nickel oxide particles are probably spread on the PrO$_x$ support.
The diffractograms of the lanthanum samples (Figure 2c) are more complex than those of ceria and praseodymia. The LaOx support shows diffraction peaks of La₂O₃ (JCPDS 00-005-0602) and La(OH)₃ (JCPDS 00-036-1481), and these phases are partially modified upon nickel loading. The Ni/LaOx catalyst also shows peaks of the La(OH)₃ phase, but not those of La₂O₃, and instead, peaks of La₂O₂(CO₃) (JCPDS 01-084-1963) and La₄Ni₃O₁₀ (JCPDS 01-083-1164) are identified. In this case, NiO peaks are not detected. The formation of lanthanum carbonates after impregnation of lanthana with metal salts was already reported by Bernal et al. [49, 50] and was attributed to the basic character of this oxide. Huanling et al. also reported the formation of La₂O₂(CO₃) on a Ni/La₂O₃ CO₂ methanation catalyst. [44]

In conclusion, the XRD characterization evidences important differences in the interaction between nickel and the LnOx supports. The Ni/CeO₂ catalyst consists of a mixture of NiO and CeO₂ nanoparticles with average crystal size of 22 and 30 nm, respectively, and a few fraction of nickel cations inserted into the CeO₂ lattice. The Ni/PrOₓ catalyst combines a high proportion of the Pr₆O₁₁ phase mixed with a lower proportion PrO₂, and nickel oxide particles are probably dispersed on these phases forming small particles with low crystallinity and without evidences of nickel cations insertion into the PrOₓ lattices. Finally, the Ni/LaOₓ catalyst combines lanthanum hydroxide with partially carbonated oxides, and nickel forms a Ni-La mixed oxide. Evidences of the presence of NiO particles were not obtained from the Ni/LaOₓ diffractogram, but the presence of small nickel oxide particles with low crystallinity cannot be ruled out.

2.3. Fresh catalysts characterization by TG-MS (N₂-TPD and H₂-TPR experiments).

The catalysts were characterized by Temperature Programmed Desorption in N₂ and Reduction in H₂/Ar, and results are included in Figures 3 and 4 respectively. The release of CO₂ (Figure 3a) and H₂O (Figure 3b) under inert gas flow is highest for Ni/LaOₓ, and this in agreement with the presence of La(OH)₃ and La₂O₂(CO₃) observed by XRD (Figure 2c). H₂O is released from Ni/LaOₓ around 350 ºC, and most CO₂ around 750 ºC, and this indicates that carbonate species are more stable than hydroxides.

The release of H₂O from Ni/PrOₓ and Ni/CeO₂ is negligible (Figure 3b), while Ni/LaOₓ shows a H₂O release peak between 300 and 400 ºC. In the same line, CO₂ is mainly emitted by Ni/LaOₓ above 600 ºC, and additionally, very few CO₂ is evolved from all catalysts in the 100-500 ºC range (Figure 3a). In this range of temperatures, the highest amount of CO₂ released comes from Ni/PrOₓ and the lowest from Ni/CeO₂.

As it will be discussed afterwards, the stability of the H₂O and CO₂ species on the catalysts play an important role during the catalytic methanation of CO₂, as CO₂ is one of the reactants and H₂O is one of the reaction products. The reduction of the catalysts in H₂-TPR experiments also provides valuable information to explain their catalytic behavior.

Figure 3. Characterization of fresh catalysts by Temperature Programmed Desorption in a N₂ flow followed by TG-MS. (a) CO₂ profiles (m/z 44 signal) and (b) H₂O profiles (m/z 18 signals).

The Ni/CeO₂ catalyst (Figure 4a) shows a H₂O peak around 370 ºC that can be attributed to the reduction of Ni²⁺ to Ni⁰. Quantitative calculations were performed using the area under the peak and a reference CuO sample, and the consumption of H₂ exactly matches the amount required for 100 % reduction of Ni²⁺ to Ni⁰ (Table 4). This confirms that the amount of Ni on the Ni/CeO₂ catalyst is 10 %, and that probably all nickel is present on the fresh catalyst as Ni²⁺ cations.

Table 4. Estimation from H₂ consumption in H₂-TPR experiments of the percentage of nickel reduced assuming the presence of Ni²⁺ or Ni⁰ cations on the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni²⁺ reduced (%)</th>
<th>Ni⁰ reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/CeO₂</td>
<td>100</td>
<td>66</td>
</tr>
<tr>
<td>Ni/PrOₓ</td>
<td>205</td>
<td>137</td>
</tr>
<tr>
<td>Ni/LaOₓ</td>
<td>192</td>
<td>128</td>
</tr>
<tr>
<td>Ni/LaOₓ*</td>
<td></td>
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</tr>
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</table>

*The amount of H₂O released from this catalyst in the N₂-TPD experiment has been subtracted for these calculations.
 nickel on the catalyst, assuming the presence of NiO\(^{2-}\) and 1.4 times the amount required if Ni\(^{3+}\) is assumed (Table 4). These calculations evidence that Pr\(^{4+}\) cations are also reduced in this wide double peak. Note that XRD suggests the presence of Ni\(^{2+}\) cations, and probably this is the main oxidation state of Ni cations. However, calculations for Ni\(^{3+}\) have been also included to make sure there is a stoichiometric excess of H\(_2\) consumed even if some Ni\(^{3+}\) were present on the sample. Experimental evidences suggest that this is not the case, but it cannot be ruled out. The H\(_2\)-TPR profile of Ni/LaO\(_x\) is shown in Figure 4c, and several H\(_2\)O release peaks are identified. The most intense peak appears at 370 °C, but the release of H\(_2\)O continues until 750 °C with several smaller peaks and shoulders. Considering the conclusions of the XRD characterization, it is postulated that H\(_2\)O released in the lowest temperature peak could be related with the reduction of nickel oxide, and the release at higher temperatures with the reduction of the Ni-La mixed oxide. Note that the release of H\(_2\)O in this case, not only comes from the reduction of the catalyst by H\(_2\), but also from the decomposition of La(OH)\(_3\), as observed in N\(_2\)-TPD experiments (Figure 3b). The consumption of H\(_2\) has been estimated from the Ni/LaO\(_x\) profile in Figure 4c, subtracting the amount of H\(_2\)O released due to La(OH)\(_3\) decomposition, and this amount is two times higher than that required for all nickel reduction assuming the presence of Ni\(^{2+}\) cations, and 1.3 times higher the amount required for Ni\(^{3+}\) reduction (Table 4). It is hard to assume in this case the reduction of La\(^{3+}\) cations, despite the LaO\(_x\) support also shows two important H\(_2\)O peaks in the H\(_2\)-TPR profiles (Figure 4c). Thus, it is tentatively proposed that the additional release of H\(_2\)O might come from the reduction of hydroxyl or oxygen groups that are stable under N\(_2\)-TPD conditions but not in the presence of H\(_2\). The profiles on Figure 4 and calculations on Table 4 allow concluding that total reduction of the cationic nickel species present in all catalysts occurs during the H\(_2\)-TPR experiments, and that, in some cases, the support is also partially reduced together with the nickel reduction. The reduction temperature of nickel is around 370 °C for all catalysts, but it is difficult to report a convincing reducibility trend for the catalysts due to overlapping of different events. In the case of Ni/LaO\(_x\), it must be taken into account that a fraction of nickel is reduced at much higher temperature (until 750 °C) due to the formation of a Ni-La mixed oxide.

2.4. Catalytic methanation of CO\(_2\).

Figure 5 shows catalytic results obtained with the Ni/LnO\(_x\) catalysts, including the conversion of CO\(_2\) (Figure 5a) and the carbon species distribution, H\(_2\) conversion and selectivity to CH\(_4\) and CO (Figure 5b).

The three CO\(_2\) conversion curves are qualitatively similar, increasing with temperature until the thermodynamic equilibrium limits conversion at high temperature. The dashed curve in Figure 5a represents the theoretical maximum conversion at equilibrium with temperature, for the actual feed composition (CO\(_2\)/H\(_2\)/He = 1/4/1,25) and considering in calculations both CO\(_2\) methanation and reverse water gas shift (RWGS, Equation 3) reactions.
\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H = 41.2 \text{ kJ/mol} \quad \text{RWGS (3)} \]

The onset temperature for CO2 consumption is around 250 °C for Ni/CeO2 and Ni/PrOx and 275 °C for Ni/LaOx, and the temperature required for 50% CO2 conversion (T50) is 300, 312 and 365 °C for Ni/CeO2, Ni/PrOx and Ni/LaOx, respectively. These behaviors lead to the following catalytic trend:

\[ \text{Ni/CeO}_2 > \text{Ni/PrOx} >> \text{Ni/LaOx}. \]

Concentrations of H2 and CO2 gases were independently determined by chromatographic analysis, and the H2 conversion (data in Figure 5a) follow the same trend than CO2 conversions (Figure 5a). However, due to the different stoichiometry and selectivity of reactions (1) and (3), the H2 conversions are slightly lower than the corresponding CO2 conversion.

CH4 selectivity was almost 100 % in most experimental conditions, and only few CO was detected at 300 °C and above this temperature mainly for Ni/LaOx (Figure 5b). The balance of carbon between reactants and products of reaction was well closed in all experiments, thus ruling out carbon deposition on the catalysts. This hypothesis was confirmed in a experiment carried out with the Ni/CeO2 catalyst at 350 and 300 °C for 24 h (Figure 1SM). After the reaction at 300 °C, the used catalyst was submitted to a thermogravimetric analysis under 5% O2/He, ruling out carbon deposition on the catalyst during reaction.

Considering the characterizations reported until now, the lowest activity of Ni/LaOx can be attributed to the nature of the nickel species and to the strong interaction of CO2 and H2O with this catalyst. It has been reported that H2 dissociates on reduced nickel sites, and dissociated H atoms further hydrogenate the surface carbon intermediates.\(^{[53]}\) As it was observed by XRD, part of the nickel on the Ni/LaOx catalyst is conforming a Ni-La mixed oxide (LaNi3O10) with poor reducibility (750 °C is required for total reduction in H2-TPR conditions). On the contrary, the reducibility of all nickel species on Ni/CeO2 and Ni/PrOx is much higher, being reduced around 370 °C under H2-TPR conditions. Therefore, it is expected that the formation under reaction conditions of reduced nickel sites suitable for H2 dissociation is easier on Ni/CeO2 and Ni/PrOx than on Ni/LaOx.

Additionally, N2-TPD experiments showed that Ni/LaOx retains CO2 and H2O strongly, while not Ni/CeO2 and Ni/PrOx. Therefore, poisoning of the Ni/LaOx surface by these species is expected under CO2 methanation conditions. In this context, it must be distinguished between the roles of CO2 and H2O in the reaction mechanism. H2O is a reaction product that must be released from the catalyst surface once formed, and the onset temperature for H2O release from Ni/LaOx in N2-TPD conditions is 250 °C (Figure 3b). This is also the onset temperature for CO2 methanation by Ni/LaOx (Figure 5a), that is, it seems that CO2 methanation by Ni/LaOx only starts once the temperature is high enough for the desorption of H2O formed as a reaction product. On the contrary, CO2 is a reactant gas, and there exist different opinions about the reaction pathway for CO2 chemisorption and dissociation.\(^{[53]}\) Two mechanisms have been proposed, which are referred to as associative and dissociative. In the associative mechanism, CO2 is chemisorbed without dissociation, and then is hydrogenated in two consecutive steps removing one oxygen per step. In the dissociative mechanism, the CO2 molecule is chemisorbed dissociatively, providing a surface oxygen atom and a surface carbonyl. It has been proposed for ceria catalysts\(^{[33, 53]}\) that reduced cerium cations (Ce\(^{3+}\)) are the active sites for chemisorption and dissociation of CO2, and for this reason ceria favors the dissociative mechanism. The Ce\(^{3+}\) sites are oxidized to Ce\(^{4+}\) upon CO2 dissociation, and must be reduced again by H2 to close the redox cycle. This 3+/4+ redox cycle described for ceria is expected to occur also on praseodymium, because praseodymium is also able to adopt the 3+ and 4+ oxidation steps. However, lanthanum is not able to get involved in redox cycles because only forms 3+ cations.

The poor reducibility of nickel and the strong interaction of CO2 and H2O with the catalyst explain the lower catalytic activity of Ni/LaOx, but differences between the catalytic behavior of Ni/CeO2 and Ni/PrOx are not easily explained with the characterization results discussed until now, and the fresh and used catalysts were characterized by XPS to get further insight on these differences.

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**Figure 5.** Catalytic methanation of CO2. (a) CO2 conversion and (b) carbon species distribution, H2 conversion and selectivity to CH4 and CO. (Experimental conditions were 16% CO2 + 64% H2 with He balance; 12000 h\(^{-1}\)).
2.5. XPS characterization of the fresh and used catalysts.

The fresh and used catalysts were characterized by XPS, and the binding energy of the electrons was studied in three energy regions corresponding to the Ni2p, O1s and C1s transitions. Proper Ni2p profiles were obtained with Ni/CeO2 and Ni/PrOx, but unfortunately, the La3d transition overlaps in this energy region, and it is not possible to observe information about nickel in the Ni/LaOx catalyst by this technique. XPS characterization in the energy region of La3d transition is included in the supplementary material for the fresh and used Ni/LaOx catalyst (Figure 1SM).

The surface composition of the catalysts has been determined, and Table 4 shows the Ni/Ln atomic ratios. The amount of surface nickel is higher on fresh Ni/CeO2 than on fresh Ni/PrOx, and this is in agreement with the NiO peaks observed by XRD. The Ni/Ln ratio decreases after the catalytic tests for both catalysts, and this could be related with the decoration of the nickel particles with the NiOx support. This decoration has been reported for Ni/CeO2 catalysis under reducing conditions, and has been observed that the decoration process is reversible.[54]

Figure 6 shows the profiles in the Ni2p region. Assignation of bands in the Ni2p spectra is still a matter of debate, but it has been proposed[55-58] that the nature of the nickel species can be inferred from the position of the most intense peak. Auxiliary lines have been plotted in Figure 6 on particular energies reported in the literature for selected nickel species.[54-57] The main band in all spectra of Figure 6 can be deconvoluted in two contributions, suggesting the presence of nickel species of different nature. The position of these bands in the fresh catalysts confirms the presence of cationic species of nickel, probably NiO and Ni(OH)2·H2O, and the presence of reduced nickel on fresh catalysts is ruled out.

The nature of the nickel species changes during the catalytic tests, as deduced from the XPS spectra of the used catalysts (Figure 6b). Part of the nickel species appear also oxidized after the catalytic tests and part are reduced to metal nickel. Considering the H2-TPR characterization (Figure 4), nickel oxides are expected to be fully reduced to metal nickel during the reducing pre-treatment performed before the catalytic tests, and the presence of oxidized nickel species after the catalytic tests must be attributed to the redox process occurring during the methanation reaction, CO2 being the oxidizing gas. It has to be mentioned that partial re-oxidation during atmospheric exposition cannot be ruled out.

One important conclusion from spectra in Figure 6 is that the binding energy of the metal nickel band is lower for Ni/CeO2 than for Ni/PrOx, and this suggests that the interaction of metal nickel with the support is stronger on Ni/PrOx than on Ni/CeO2, in agreement with the XRD characterization. It has been proposed that H2 dissociation takes place on reduced nickel sites,[53] and therefore, it is reasonable to think that the higher negative charge density observed by XPS (Figure 6b) for reduced nickel on Ni/CeO2 with regard to Ni/PrOx, is positive for H2 dissociation. Therefore, it can be postulated that one of the reasons of the higher CO2 methanation activity of Ni/CeO2 with regard to Ni/PrOx is the presence of reduced nickel sites with higher activity for H2 dissociation.

In the previously described dissociative mechanism,[53] CO2 is chemisorbed on the reduced sites of the catalyst providing an oxygen atom and a metal carbonyl, which would explain the presence of cationic species of nickel formed with oxygen coming from CO2. The used Ni/CeO2 catalyst shows the highest concentration of oxidized nickel sites (Figure 6b), which can be related with CO2 dissociation. The higher concentration of active sites for CO2 dissociation could be another argument to explain the highest activity of Ni/CeO2.

Additional information is obtained from the O1s spectra (Figure 7), which can be deconvoluted in three bands. Despite assignation of these bands is not easy, important differences are noticed in the band around 529 eV. This is the band with the lowest binding energy, that is, it belongs to the oxygen species with the highest negative charge density, which are expected to be those with the strongest interaction with metal cations.

![Figure 6. XPS characterization in the energy region of Ni2p transition for (a) fresh catalysts and (b) used catalysts.](image-url)
remarkable for Ni/CeO$_2$ (from 60.2 to 43.3 %). These to 13.7 %) and Ni/LaO$_x$ (from 15.1 to 5.4 %), while not so catalysts, but the decrease is very relevant for Ni/PrO$_x$ (from 47.2 > Ni/LaO$_x$, which is coincident with the catalytic activity trend (see Figure 5). The area of this band decreases after reaction for all catalysts studied, this nickel-support synergy is more efficient for Ni/CeO$_2$ than for the other two oxide supports. Among the catalysts studied, this nickel-support interface. Among the catalysts studied, this nickel-support synergy is more efficient for Ni/CeO$_2$ than for the other two catalysts.

In conclusion, considering the Ni 2p and O 1s spectra, we suggest that Ni/CeO$_2$ combines very electronegnegative reduced nickel sites suitable for H$_2$ dissociation with a Ni$^{2+}$-ceria interface very efficient for CO$_2$ dissociation.

Finally, the XPS spectra were analyzed in the C 1s region, and the spectra for the fresh and used catalysts are compiled in Figure 8.

Three bands are also identified in the deconvoluted C 1s spectra. Assignation of these bands is neither easy, but interesting in formation about the behavior of the catalysts during the methanation tests can be obtained from the band around 289 eV. This band increases for all catalysts during reaction, which is probably related in somehow with CO$_2$ chemisorption or with carbon intermediates. Both for fresh and used catalysts, the area of this band follows the opposite trend (Ni/LaO$_x$ > Ni/PrO$_x$ > Ni/CeO$_2$) than the catalytic activity, that is, the presence of stable carbon species on the catalysts surface is negative for the catalytic activity, probably because these carbon species block active sites and hinder the chemisorption of reactants. This observation is in agreement with the conclusions of the N$_2$-TPD characterization (Figure 3a).

As a summary, the activity for CO$_2$ methanation of the Ni/LnO$_x$ catalysts studied depends both on the nature of the catalytic active sites (Ni$^{2+}$ cations with strong interaction with the support and Ni$^{0}$) and on the stability of the CO$_2$ and H$_2$O surface species, both variables being strongly affected by the LnO$_x$ support. Ni/CeO$_2$ is the best catalyst for CO$_2$ methanation for several reasons: i) the Ni$^{2+}$-ceria interaction leads to the formation of the highest population of active sites for CO$_2$ dissociation, ii) the reduced Ni$^{0}$ sites where H$_2$ dissociation takes place are the most electronegnegative and iii) this catalyst shows the lowest affinity for CO$_2$ and H$_2$O, keeping clean the catalyst surface during the
reaction. On the contrary, Ni/LaOx shows the lower activity because strongly chemisorbs H$_2$O and CO$_2$, and because is not able to favor the formation of highly active sites for CO$_2$ and H$_2$ dissociation. The behavior of Ni/PrOx is slightly lower to that of Ni/CeO$_2$ because the formation of active sites is not so efficient and because the stability of CO$_2$ on surface is slightly higher. Note that both Ce and Pr can adopt the 3+ and 4+ oxidation states, and therefore can participate in the redox processes occurring at the Ni$^{2+}$-support interface during the catalytic tests, while La can only adopt the 3+ state, and therefore, is not expected to participate in these redox processes.

Conclusions

Nickel catalysts with LaO$_x$, CeO$_2$ and PrO$_x$ supports have been prepared, characterized and tested for CO$_2$ methanation, and the main conclusions of the study can be summarized as follows. The nature of the nickel species present on fresh catalysts strongly depends on the support. The Ni/CeO$_2$ catalyst consists of a mixture of NiO and CeO$_2$ nanoparticles with comparable average crystallite sizes (22 and 30 nm, respectively) and a few fraction of nickel cations inserted into the CeO$_2$ lattice. Much smaller nickel oxide particles are dispersed on PrO$_x$, without insertion of nickel cations into the PrO$_x$ lattices, and LaO$_x$ forms Ni-La mixed oxides and probably dispersed nickel oxide nanoparticles are also present on Ni/LaO$_x$. The catalytic activity for CO$_2$ methanation follows the trend Ni/CeO$_2$ (T50=300 ºC) > Ni/PrO$_x$ (T50=312 ºC) >> Ni/LaO$_x$ (T50=365 ºC), all catalysts being very selective towards CH$_4$ formation, and the activity depends both on the nature of the catalytic active sites and on the stability of the surface CO$_2$ and H$_2$O species.

Ni/CeO$_2$ is the most active catalyst because the Ni$^{2+}$-ceria interaction leads to the formation of the highest population of active sites for CO$_2$ dissociation, the reduced Ni$^0$ sites where H$_2$ dissociation takes place are the most electronegative, and shows the lowest stability of surface CO$_2$ and H$_2$O species. The activity of Ni/PrO$_x$ is slightly lower to that of Ni/CeO$_2$ because the formation of active sites is not so efficient and because the stability of chemisorbed H$_2$ is slightly higher.

Ni/LaO$_x$ shows the lowest activity because suffers strong chemisorption of H$_2$O and CO$_2$, poisoning the catalyst surface, and because is not able to promote the formation of highly active sites for CO$_2$ and H$_2$ dissociation.

Experimental Section


Three catalysts have been prepared, which are referred to as Ni/LaO$_x$, Ni/CeO$_2$, and Ni/PrO$_x$. The metal precursors used were La(NO$_3$)$_3$·6H$_2$O (Aldrich; 99.9%), Ce(NO$_3$)$_3$·6H$_2$O (Aldrich; 99%), Pr(NO$_3$)$_3$·6H$_2$O (Aldrich; 99.9%), and Ni(NO$_3$)$_2$·6H$_2$O (Aldrich; 98.5%). The lanthanide oxide supports were prepared dissolving the metal precursors in ethanol (0.476 M) and citric acid was added to force the precipitation of metal citrates. After filtering, the solids were calcined at 600 °C for 6 hours using a heating rate of 1 °C min$^{-1}$. Ni was loaded by excess solvent impregnation using an ethanol solution of the nickel precursor with the required amount of salt to achieve a Ni loading of 10 wt. % on the catalysts. After total evaporation of the solvent, the solid was dried at 80 °C overnight and calcined at 500 °C for 2 hours with a heating rate of 5 °C/min.

3.2. Catalysts characterization.

The porosity of the catalysts was studied by N$_2$ physisorption. N$_2$ isotherms were measured at -196 °C in an automatic volumetric system (Autosorb-6, Quantachrome). The catalysts were outgassed at 150 °C for 2 hours under vacuum before the adsorption.

The reduction of the fresh catalysts was studied by temperature programmed reduction with H$_2$ (H$_2$-TPR) and the accumulation of CO$_2$ and H$_2$O by temperature programmed desorption in N$_2$ (N$_2$-TPD). The experiments were performed in a TG-MS device, with a thermobalance (Mettler Toledo; TGA/SDTA851) coupled to a mass spectrometer (Pfeiffer Vacuum; Thermostat GSD301T). 20 mg of fresh catalysts were heated in 5% H$_2$/Ar (H$_2$-TPR) or pure N$_2$ (N$_2$-TPD) flows (40 ml/min) at 10 °C/min from room temperature until 900 °C without previous pretreatment. A CuO reference sample was used to correlate the area under the H$_2$O peaks in H$_2$-TPR experiments with the moles of H$_2$ consumed, and quantitative calculations have been performed. The m/z 18 (H$_2$O) has been used instead of m/z 2 (H$_2$) to follow the H$_2$-TPR experiments because peaks are better defined.

The surface of the catalysts was characterized by XPS in a K-ALPHA Thermo Scientific device. This device works with Al-Kα radiation (1486.6 eV) and includes a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 μm, at 3 mA × 12 kV. The binding energy scale calculations have been performed. The m/z 18 (H$_2$O) has been used instead of m/z 2 (H$_2$) to follow the H$_2$-TPR experiments because peaks are better defined.

3.3. Catalytic tests.

CO$_2$ methanation tests were performed in a cylindrical fixed-bed reactor (9 mm inside diameter) coupled to a gas chromatograph (Agilent HP7890B). The catalyst was pre-treated at 500 °C for 1 hour under 20%H$_2$/He flow (200 cm$^3$·min$^{-1}$) for nickel oxide reduction, and after cooling to 200 °C in inert gas, the reaction mixture was fed to the reactor, which consists of 16% CO$_2$ + 64% H$_2$ with He balance (total flow 200 mL·min$^{-1}$). The temperature was increased from 200 to 450 °C with a heating rate of 5 °C/min, in steps of 25 °C. Once the steady state was reached at every temperature step, the concentration of reactants and products at the reactor exit is determined by chromatographic analysis. Once the catalytic tests were finished at 450°C, the reaction gas mixture was replaced by inert gas, the reactor was cooled down, the used catalysts were stored without control of the atmosphere, and were finally characterized by XPS.
The experiments were performed at atmospheric pressure with 0.4 grams of catalysts, which were pelletized, grinded and sieved, working with particles size between 300 and 500 μm. The catalyst particles were diluted with quartz particles (1-1.25 mm) up to ca. 1 cm³ of bed, to improve mass and heat transfer. In these conditions, the GHSV was 12000 h⁻¹.

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Keywords: carbon dioxide; methane; nickel catalysts; hydrogenation; ceria; lanthanides

Ni/CeO₂ is the most active Ni/LnOₓ catalyst because (i) the Ni²⁺-ceria interaction leads to the formation of the highest population of active sites for CO₂ dissociation, (ii) the reduced Ni⁰ sites where H₂ dissociation takes place are the most electronegative and active, and (iii) the stability of surface CO₂ and H₂O species is lowest.