

Soft-templated NiO-CeO₂ mixed oxides for biogas upgrading by direct CO₂ methanation

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Abstract

The catalytic performance in the direct CO₂ methanation of a model biogas is investigated on NiO/CeO₂ nanostructured mixed oxides synthesized by the soft-template procedure with different Ni/Ce molar ratios. The samples are thoroughly characterized by means of ICP-AES, XRD, TEM and HR-TEM, N₂ physisorption at -196 °C, and H₂-TPR. They result to be constituted of CeO₂ rounded nanocrystals and of polycrystalline needle-like NiO particles. After a H₂-treatment at 400 °C for 1 h, the surface basic properties and the metal surface area are also assessed using and H₂-pulse chemisorption measurements, respectively. At increasing Ni content the Ni⁰ surface area increases, while the opposite occurs for the number of basic sites. Using a CO₂/CH₄/H₂ feed, at 12000 cm³ g_{cat}⁻¹ h⁻¹, CO₂ conversions in the 83-89 mol% range and methane selectivities > 99.5 mol% are reached at 275 °C and atmospheric pressure, highlighting the very good performances of the investigated catalysts.

Keywords: biogas upgrading; CO₂ methanation; Ni-based catalysts; CeO₂ support.

1. Introduction

Presently, over 85% of the global energy needs are met by the use of fossil fuels [1], the combustion of which is responsible for about 80% of the worldwide CO₂ emissions [2], widely considered the main factor influencing global warming and climate change. Furthermore, considering that conventional energy resources (*i.e.*, oil and gas reserves) are mainly located in politically unstable regions, securing energy supply is a crucial question. Hence, in order to address these critical issues, significant efforts are aimed at efficiently exploiting renewable energy sources such as geothermal, wind, solar, and biomass energy. In this context, biogas, commonly produced by the anaerobic digestion of biodegradable waste and substrates, is widely regarded as one of the most promising sources of renewable energy [3]. Methane (ca. 40-75 vol.%) and carbon dioxide (25-60 vol.%) are the main components of biogas [4], which also contains N₂, O₂, H₂S, and other contaminants in amounts that depend on the different production plants. In 2018 biogas was consumed for almost two thirds in the production of electricity and heat, whereas only about 5% was purified to biomethane [5]. Anyway, the interest towards biogas upgrading for producing high-quality (> 90%) biomethane (also known as renewable natural gas or upgraded biogas) is rapidly growing; in fact, while being carbon-neutral, biomethane is not distinguishable from natural gas and can thus be transported and utilized alike. Biogas upgrading technologies (water or chemical scrubbing, pressure swing adsorption, membrane permeation, cryogenic technology) that involve CO₂ separation without its subsequent recovery and reuse have been reviewed since 2011 [4, 6-8]. However, converting the high amount of CO₂ into CH₄ by the use of renewable hydrogen through the Power-to-Gas (P2G) process would make biogas valorization more attractive. Power-to-Gas joins the power grid to the gas grid, transforming surplus electricity to synthetic biomethane, first producing H₂ *via* water electrolysis and then converting it to synthetic methane through CO₂ hydrogenation [9,10]. Hence, three steps have to be taken into account when considering the whole process of biomethane generation and utilization: (i) CO₂ removal from the biogas stream, (ii) methanation of the recovered CO₂ through the P2G process, and (iii) injection of the synthesized biomethane into the transmission and

distribution networks. However, the direct methanation of CO₂ in the biogas stream would simplify the process, avoiding the use of expensive separation technologies. In recent years, the production of biomethane has been extensively studied, analyzing various aspects (including thermodynamic, technological, economic, and environmental ones) of the possible different scenarios: biogas upgrading with no CO₂ valorization [11-13] and CO₂ methanation by P2G process (i) without or (ii) after biogas upgrading [14-24].

As demonstrated by the numerous comprehensive reviews appeared in the literature over the last decade [25-36], the conversion of CO₂ into methane has been widely investigated on noble (Ru, Rh, Pt, Pd) and non-noble (Ni, Co, Fe, W, Mo) metals supported on a large number of metal oxides (e.g., Al₂O₃, SiO₂, ZrO₂, CeO₂, CeO₂-ZrO₂, TiO₂) synthesized with different methods, also in the presence of promoters. Moreover, the current research about the effects of the feed composition on the performance of the CO₂ methanation catalysts has been very recently reviewed [37], with the aim of identifying which properties the catalysts must have to be efficiently used in the direct methanation of biogas from different sources. It appears that, in spite of the extensive literature available on the CO₂ hydrogenation into methane, only in very few works this reaction has been studied on Ni-based catalysts in the presence of CH₄ in the gaseous feed mixture [38-42]. Supported Ni-based catalysts have been mostly investigated in carbon oxides hydrogenations, due to the low cost, high activity, and high methane selectivity of nickel. Among the various oxide supports, the peculiar features of CeO₂, like oxygen storage capacity, abundant oxygen vacancies, reducibility, and strong metal-support interactions, made this material particularly promising for use in CO₂ catalysis [43].

In the present work, a series of NiO/CeO₂ nanostructured mixed oxides with different Ni/Ce molar ratios have been synthesized by the unconventional soft-template procedure [44]. Several physico-chemical techniques, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), conventional and high resolution (HR) transmission electron microscopy (TEM), N₂ physisorption at -196 °C, temperature-programmed reduction (TPR), were used to characterize their composition, structure, texture, and redox features. The supported nickel

catalysts were obtained by *in situ* reduction of the synthesized mixed oxides. Their surface basic properties were characterized using adsorption microcalorimetry of CO₂. The metal surface area was also determined by means of H₂-pulse chemisorption measurements. The catalytic performance in the direct CO₂ methanation of a model biogas was investigated using a CO₂/CH₄/H₂ feed with molar ratios equal to 1/2/4.

2. Experimental

2.1. Materials

Cetyl-trimethyl-ammonium bromide (CTAB, $\geq 98\%$), Ni(NO₃)₂·6H₂O (99.999%), Ce(NO₃)₃·6H₂O (99%), and NaOH (pellets, 97%) were supplied by Aldrich. Ethanol (96%) was supplied by Fluka. HCl (37%) was provided by Merck. The gaseous feed mixture with known concentration of the components was supplied by SAPIO.

2.2. Synthesis of catalysts

NiO/CeO₂ mixed oxides with Ni/Ce molar ratios in the range 0.5-4.0 mol/mol were synthesized through the soft-template method, where Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O were used as cerium and nickel oxides precursors, cetyl-trimethyl-ammonium bromide as the template, and NaOH as the precipitating agent. The detailed procedure is reported in a previous work [45]. The synthesized samples were named *x*NiCe, where *x* represents the nominal Ni/Ce molar ratio.

2.3. Characterization of catalysts

Ni and Ce contents were determined by means of ICP-AES analyses, performed with a 5110 ICP-OES spectrophotometer (Agilent Technologies). Each sample was dissolved in a H₂O₂ (35 %) – HNO₃ (70 %) mixture (1:1 by volume) and stirred at 80 °C for 2 h; a HCl (37 %) – HNO₃ (70 %) mixture (3:1 by volume) was then added and after 16 h at RT; the solution was finally diluted to the desired volume with Milli-Q water.

The structural features were assessed by XRD using a PANalytical X'Pert PRO diffractometer with a Cu-K α radiation, a secondary monochromator, and a X'celerator detector. The average crystallite sizes were estimated by the Scherrer equation taking into account the Warren correction [46].

Textural analyses were carried out with a Sorptomatic 1990 System (Fisons Instruments), by determining the nitrogen adsorption-desorption isotherms at -196 °C. Before analyses, samples were heated overnight under vacuum up to 250 °C (heating rate, 1 °C min⁻¹). Surface area values were calculated by the BET equation. The pore size distribution (PSD) profiles were determined by applying the BJH method to the isotherm desorption branch.

Transmission electron microscopy (TEM) images were obtained with a JEOL 1400 Plus, equipped with a EDX module for the elemental analysis. A JEOL JEM 2010 UHR microscope, equipped with a Gatan Imaging Filter (GIF) with a 15 eV window and a 794 slow scan CCD camera, was instead used to collect high resolution TEM (HRTEM) images.

Finely ground samples were dispersed in n-octane using an ultrasonic bath. The suspension was then dropped on a copper grid covered with a carbon thin film for the observation.

The redox properties were studied by means of H₂-TPR, by using a TPD/R/O 1100 apparatus (ThermoQuest) equipped with a thermal conductivity detector (TCD). Prior to the experiments, the samples (typically 0.020 g) were pretreated in air (15 cm³ min⁻¹) at 450 °C for 1 h and then cooled under nitrogen (15 cm³ min⁻¹) to the initial analysis temperature. TPR profiles were recorded under flowing H₂ (5 vol% in N₂, flow rate, 30 cm³ min⁻¹) while heating (20 °C min⁻¹) from 40 °C to 950 °C.

CO₂ adsorption microcalorimetric runs were performed using a Tian-Calvet heat-flow microcalorimeter (Setaram), connected to a volumetric vacuum line. Samples (0.100 g, 40-80 mesh), previously reduced under flowing pure H₂ (15 cm³ min⁻¹) at 400 °C for 1 h, were thermally pretreated at 250 °C for 12 h under vacuum (5×10⁻³ Pa). Analyses were carried out at 80 °C by admitting successive doses of the probe gas. The equilibrium pressure relative to each adsorbed amount was

measured by means of a differential pressure gauge (Datameritics) and the thermal effect was recorded. The run was stopped at a final equilibrium pressure of about 160 Pa.

H₂-pulse chemisorption measurements were carried out in a TPD/R/O 1100 apparatus (ThermoQuest). Before analyses, the samples (0.100 g) were reduced under H₂ flow (15 cm³ min⁻¹) at 400 °C for 1 h. Then, Ar (20 cm³ min⁻¹) was used for purging (1 h) and cooling to 50 °C. Pulses of H₂ (5 vol% in Ar) were then admitted into the reactor until the area of the peaks remained constant. The amount of chemisorbed H₂ was calculated assuming a H/Ni stoichiometric factor equal to 1, after calibration of the TCD signal.

2.4. Methanation catalytic tests

Methanation tests were carried out in a tubular ($\phi_{\text{int}} = 0.8$ cm) quartz-glass fixed-bed microreactor, at atmospheric pressure, in a temperature range between 200 and 380 °C, and at a space velocity (*SV*) value of 72000 cm³ h⁻¹ g_{cat}⁻¹. Each temperature was maintained for 2 h and then was increased to the next setpoint with a heating rate of 2 °C min⁻¹. On selected samples, the influence of space velocity was also investigated by performing catalytic tests at 275 °C in the *SV* range 11000-430000 cm³ h⁻¹ g_{cat}⁻¹. Each catalytic run was repeated twice to test the reproducibility of the data.

Prior to the reaction, the catalyst (0.050 g) was pretreated in N₂ (30 cm³ min⁻¹) at 400 °C overnight, subsequently reduced under H₂ flow (15 cm³ min⁻¹) at the same temperature for 1 h, and then cooled in He (30 cm³ min⁻¹) to the desired reaction temperature. The reactant gas mixture was composed of CO₂ (12.9 mol%), CH₄ (25.9 mol%), H₂ (55.2 mol%) and N₂ (6.0 mol%, used as the internal standard). The CO₂/CH₄/H₂ molar ratios of 1/2/4 were chosen to simulate the composition of a model biogas (CH₄, 33 mol%; CO₂, 67 mol%) and to have the stoichiometric amount of hydrogen required for the methanation reaction (H₂/CO₂ = 4 mol/mol).

At each reaction temperature and/or space velocity, on-line gas chromatographic (GC) analyses of the reactor effluent were performed after 1 h on stream (the time required to ensure steady state is

reached), monitoring the catalytic performance during 2 h. An Agilent 6890 GC was used, equipped with a Carboxen 1010 PLOT capillary column and a TCD. Water was removed from the reaction mixture through an ice trap and a molecular sieves trap placed between the reactor outlet and the GC injection valve. The results of the quantitative analysis of the carbon-containing components were used for checking the carbon mass balance and for calculating CO₂ conversion (X_{CO_2}) and products selectivity (S_i) through the following equations, where \dot{n}_i are the molar flow rates.

$$X_{\text{CO}_2} \text{ (mol\%)} = \frac{\left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{in}} - \left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{out}}}{\left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{in}}} \cdot 100$$

$$S_{\text{CH}_4} \text{ (mol\%)} = \frac{\left(\frac{\dot{n}_{\text{CH}_4}}{\dot{n}_{\text{N}_2}}\right)_{\text{out}} - \left(\frac{\dot{n}_{\text{CH}_4}}{\dot{n}_{\text{N}_2}}\right)_{\text{in}}}{\left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{in}} - \left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{out}}} \cdot 100$$

$$S_{\text{CO}} \text{ (mol\%)} = \frac{\left(\frac{\dot{n}_{\text{CO}}}{\dot{n}_{\text{N}_2}}\right)_{\text{out}}}{\left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{in}} - \left(\frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{N}_2}}\right)_{\text{out}}} \cdot 100$$

3. Results and discussion

3.1. Characterization of fresh samples

For all samples, the actual composition is in close agreement with the nominal one, as can be observed from the ICP-AES results reported in Table 1.

XRD patterns of the fresh materials (Figure S1) exhibit the presence of reflections ascribable to NiO (PDF card: 044-1159) and cubic CeO₂ (PDF card: 034-0394). A mean crystallite size of 4.2±0.5 nm and 7.6±0.4 nm was obtained for NiO [200] and [220] reflections, respectively, strongly suggesting a preferential growth of the NiO particles along the [220] crystal planes. As for CeO₂, the crystal size values calculated on the three reflections were similar to each other, the mean value being 3.0±0.3 nm. The Ni/Ce molar ratio did not show any significant influence on the crystallite size of

either NiO or CeO₂. These results are in agreement with those reported and discussed in a previous work for similar samples [45].

N₂ physisorption isotherms are reported in Figure S2 and summarized in Table 1. According to [47], all isotherms can be classified as type IVa, with the presence of a hysteresis loop, typical of mesoporous solids. All the samples are characterized by high surface areas (S_{BET}), in the range 188-206 m² g⁻¹. Both S_{BET} and the pore volume (V_{p}) slightly increase along with the nickel content. From the PSD profiles (Figure S2, insets) it appears that the mean pore diameter (d_{p}) shifts to higher values (from ca. 5 to ca. 8 nm) at increasing Ni amounts.

Table 1. Chemical composition and textural features of the fresh $x\text{NiCe}$ samples.

Sample	Ni/Ce ^(a) (mol/ mol)	Ni content ^(a) (wt%)	S_{BET} ^(b) (m ² g ⁻¹)	V_{p} ^(b) (cm ³ g ⁻¹)
0.5NiCe	0.46	10.7	188	0.24
0.75NiCe	0.72	15.2	190	0.28
1.0NiCe	1.16	23.6	197	0.31
1.5NiCe	1.51	26.7	202	0.35
2.0NiCe	1.94	31.0	197	0.36
3.0NiCe	2.96	37.3	206	0.37
4.0NiCe	3.95	40.8	205	0.39

^(a) determined by ICP-AES; ^(b) determined by N₂ physisorption data.

Transmission electron microscopy characterization was performed on selected samples (0.75NiCe, 3.0NiCe, and 4.0NiCe); 3.0NiCe was also characterized with HR-TEM. Elemental mapping analysis was performed on 0.75NiCe and 3.0NiCe to assess the homogeneity of the mutual dispersion of the two oxides. For all the investigated catalysts, TEM imaging shows large aggregates of small, rounded nanoparticles, with an inter-particle worm-like porosity, as well as the presence of needle-like particles, confirming the preferential growth (Figure 1) highlighted by XRD data. The

amount of the latter particles increases with the increase in NiO content ($0.75\text{NiCe} < 3.0\text{NiCe} < 4.0\text{NiCe}$), suggesting that they are presumably made up of NiO, while the rounded particles are constituted of CeO_2 . From the particle size distribution of the CeO_2 nanoparticles a mean diameter of 4.1 ± 0.8 , 2.9 ± 0.5 nm, and 3.3 ± 0.8 nm has been calculated for 0.75NiCe , 3.0NiCe , and 4.0NiCe , respectively (Figure S3). The particle size distribution of the NiO elongated particles, determined on the 3.0NiCe sample (Figure S4), shows a mean value of 3.7 ± 0.8 nm, following a lognormal distribution, for the shorter dimension and a size range between 30 and 70 nm for the longer one. Despite the intrinsic limits of this type of analysis, related to the high degree of aggregation among the nanoparticles, their small size, and their irregular edges, these data are in good agreement with the crystallite size obtained from XRD measurements for the CeO_2 particles and for the shorter dimension of the NiO particles, suggesting a high crystallinity. As for NiO nanocrystals, besides their elongated shape, a preferential growth along the [220] plane is also confirmed by XRD, as can be observed by the lower width of the [220] peak located at a 2θ value of 62.6° (see Figure S1). The great difference between the longer dimension value of the NiO particles obtained by TEM imaging (30-70 nm) and that obtained from XRD data on [220] peak (7.6 ± 0.4 nm) indicates a polycrystalline nature of the NiO nanoparticles. Combined with the corresponding bright-field TEM image (Figure S5a), the dark-field one (Figure S5b) points out the presence of both small round-like bright spots throughout the large aggregates and elongated bright spots, indicated by arrows, attributable to the crystalline nature of nanoparticles of the two phases, in agreement with XRD data.

HR-TEM imaging on 3.0NiCe (Figure 2) allows observing the presence of the CeO_2 [111] crystal planes in the rounded particles constituting the large aggregates, confirming their crystalline nature; in the case of the needle-like particles, crystal planes were not observed, probably due to a shielding effect from the small CeO_2 nanoparticles. However, the Fast Fourier Transform (FFT) of the HR-TEM images allows highlighting the presence of spots corresponding to [111] NiO lattice planes.

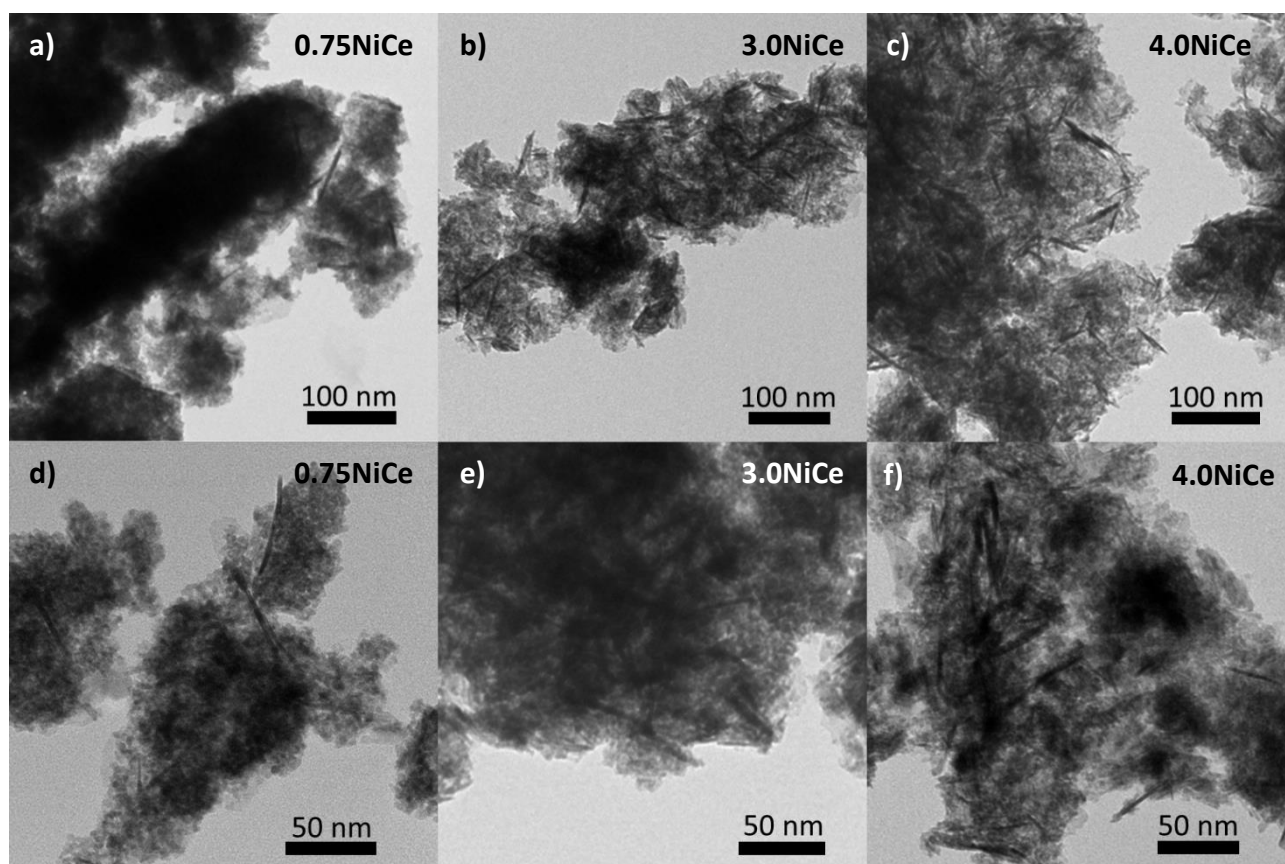


Figure 2. TEM images of 0.75NiCe (a,d), 3.0NiCe (b,e), and 4.0NiCe (c,f).

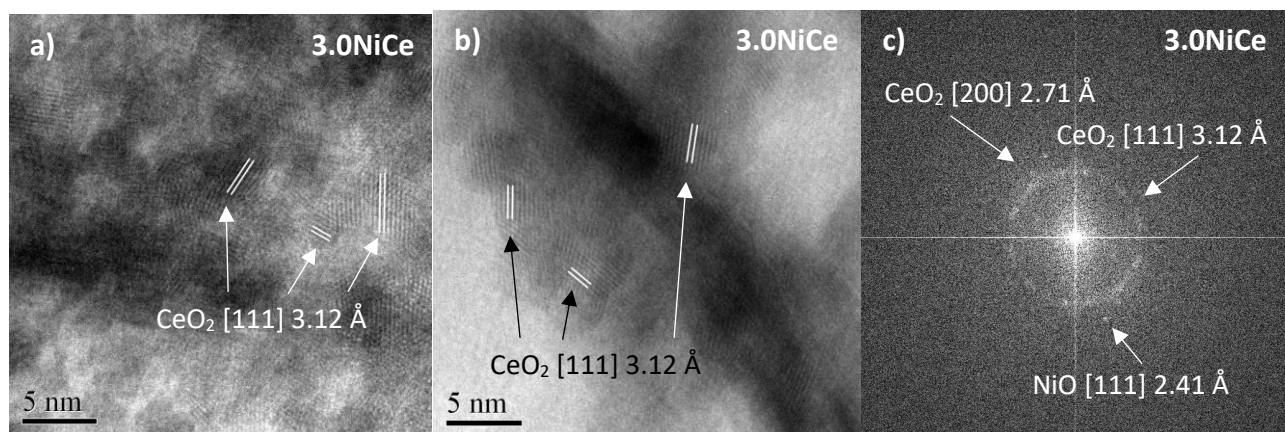


Figure 2. HR-TEM images (a,b) and FFT (c) of the 3.0NiCe sample.

Elemental chemical mapping of Ni, Ce, and O and their linear profile analysis on 0.75NiCe (Figure S6) and 3.0NiCe (Figure S7) confirms an overall homogeneous distribution of the three elements; this is a clear indication of the homogeneous dispersion of the two oxides into each other, which favors the interaction between the two phases.

The H₂-TPR profiles of all the catalysts (Figure S8) show two main signals, the first between 150-380 °C and the second at higher temperatures (up to 750 °C), each one consisting of several overlapping contributions, which clearly indicate the presence of different reducible species. In agreement with previously reported papers [45,48], most of the hydrogen consumed in the high temperature region is ascribed to the reduction of nickel oxide, in the form of bulk-like particles dispersed on the ceria surface (β -peak) and of NiO species strongly interacting with CeO₂ (γ -peak) [49]. However, reduction of CeO₂ can be expected to some extent, as indicated by the high percentages (> 100 %) of H₂ consumed for completely reducing NiO, calculated according to the stoichiometry of the reaction $\text{NiO} + \text{H}_2 \rightarrow \text{Ni}^0 + \text{H}_2\text{O}$ (Table S1). Moreover, it should also be taken into account that, according to the literature [50], hydrogen-spillover processes from the Ni⁰ particles to the oxide support could enhance the reducibility of ceria. Concerning the contribution at low temperature (α -peak), it can be related to the reduction of oxygen species adsorbed on defective sites where Ni and Ce are in close interaction, located both at the NiO/CeO₂ or in the Ni-Ce solid solution [51]. The presence of the α -peak in the TPR profiles of all the samples confirms the intimate contact between the two oxide components, as already suggested by the elemental chemical mapping.

3.2. Characterization of reduced catalysts

CO₂ adsorption properties were studied on selected *x*NiCe catalysts by means of adsorption microcalorimetry. The microcalorimetric results, also compared to those of pure NiO and CeO₂, are reported in Figure S9 and summarized in Table 2. The differential heat of adsorption (Q_{diff}) is plotted as a function of the CO₂ coverage (Figure S9), allowing the assessment of basicity in terms of both concentration and strength distribution of the surface sites. In the evaluation of the basic character, only sites with a $Q_{\text{diff}} \geq 50 \text{ kJ mol}^{-1}$ were taken into account ($n_{\text{B,tot}}$, $\mu\text{mol g}^{-1}$), lower values being ascribed to nonspecific adsorption. Basic sites were roughly divided in weak ($n_{\text{B,w}}$, $50 \leq Q_{\text{diff}} < 90 \text{ kJ mol}^{-1}$), medium-strength ($n_{\text{B,m}}$, $90 \leq Q_{\text{diff}} \leq 150 \text{ kJ mol}^{-1}$), and strong ($n_{\text{B,s}}$, $Q_{\text{diff}} > 150 \text{ kJ mol}^{-1}$) ones. The remarkably higher basicity of 0.5NiCe with respect to pure CeO₂

is mainly due to a manifest increase in the number of medium-strength and strong sites. An analogous trend was previously observed on a similar sample with a Ni/Ce molar ratio of 0.3 and was ascribed to the insertion of nickel in the ceria structure, which enhances the basic character of the NiCe catalysts through the increase in the number of oxygen vacancies [52]. However, the increase in Ni content also leads to the decrease in the number of basic sites responsible for CO₂ adsorption (Table 2).

Table 2. Microcalorimetric results for the x NiCe samples and the pure CeO₂ and NiO oxides after the H₂-pretreatment at 400 °C for 1 h.

Sample	$n_{B,w}$ μmol g ⁻¹	$n_{B,m}$ μmol g ⁻¹	$n_{B,s}$ μmol g ⁻¹	$n_{B,tot}$ μmol g ⁻¹
CeO ₂	78	57	10	145
0.5NiCe	61	191	36	288
1.0NiCe ^(a)	73	88	31	174
1.5NiCe	71	93	20	184
3.0NiCe	56	63	17	136
4.0NiCe ^(a)	46	32	22	100
NiO ^(a)	5	14	-	19

^(a) from ref [52].

The specific surface areas of the Ni⁰ metal particles, expressed per unit mass of catalyst, (A_{met}), are reported in Table 3. Due to the presence of spillover phenomena, responsible for the transfer of atomic hydrogen from the metal to the ceria support [50], the values of the metal surface area and dispersion calculated by H₂ chemisorption techniques could be affected by a significant overestimation. However, even if they cannot be considered as real data, the estimated A_{met} values can be confidently used to compare the ability of the x NiCe catalysts to adsorb and activate H₂. It can

be observed (Figure S10) that A_{met} linearly increases along with the nickel content, suggesting that not remarkable differences exist within the catalyst series in terms of metal dispersion.

Table 2. H₂ chemisorbed amount and specific surface areas of the Ni⁰ metal particles for the *x*NiCe catalysts after H₂-pretreatment at 400 °C.

Sample	H ₂ chemisorbed ($\mu\text{mol g}_{\text{cat}}^{-1}$)	$A_{\text{met}}^{(a)}$ ($\text{m}_{\text{Ni}^0}^2 \text{g}_{\text{cat}}^{-1}$)
0.5NiCe	90	7.0
0.75NiCe	117	9.2
1.0NiCe	156	12.2
1.5NiCe	203	15.9
2.0NiCe	235	18.4
3.0NiCe	247	19.3
4.0NiCe	277	21.7

^(a) automatically computed by the instrument software from the H₂ chemisorbed amount assuming a H/Ni stoichiometric factor equal to 1.

3.3. Characterization of used samples

XRD patterns of the used catalysts are reported in Figure S11. In the case of the 0.5NiCe catalyst, no reflections ascribable to any nickel phase are visible, while a reflection of very low intensity ascribable to the [111] planes of Ni⁰ is observable in the case of 0.75NiCe (PDF Card 04-0850), suggesting that nickel oxide is almost completely reduced after the H₂-pretreatment at 400 °C and very highly dispersed Ni⁰ nanocrystals are formed. The peaks of the Ni⁰ phase become progressively higher in intensity with the increase in nickel content. However, only a limited increase (from ca. 5.7 to ca. 8.7 nm along [111] planes) in the metal nanocrystals size is estimated for Ni/Ce ratios going from 1.0 to 4.0 mol/mol. This indicates that, irrespective of the catalyst composition, nickel retains a

very good dispersion after the H₂-pretreatment, reasonably owing to very effective Ni-Ce interactions and also to a possible positive effect of a small amount of residual nickel oxide [53]. Indeed, the presence of peaks ascribable to the NiO phase for the catalysts with a Ni/Ce molar ratio ≥ 3.0 seems to indicate an incomplete nickel reduction after the H₂-pretreatment, although a partial reoxidation of the surface due to the exposure to air prior XRD measurements cannot be excluded.

TEM imaging performed on 0.75NiCe (Figure S12) and 3.0NiCe (Figure S13) after use shows that the morphology of the large aggregates of spheroidal particles does not show any significant change. However, it is observed that the needle-like NiO particles disappear, indicating a major transformation of NiO into Ni⁰, in agreement with XRD analysis. The absence of elongated crystalline NiO particles is also confirmed by dark-field TEM imaging of the used 0.75NiCe (Figures S12b).

As in the case of the fresh sample, HR-TEM imaging of the 3.0NiCe catalyst after the methanation test only shows the crystal planes associated with CeO₂ (Figures 3a,b) However, the existence of both Ni and NiO is evidenced by the presence of the corresponding [111] planes in the FFT image (Figure 3c).

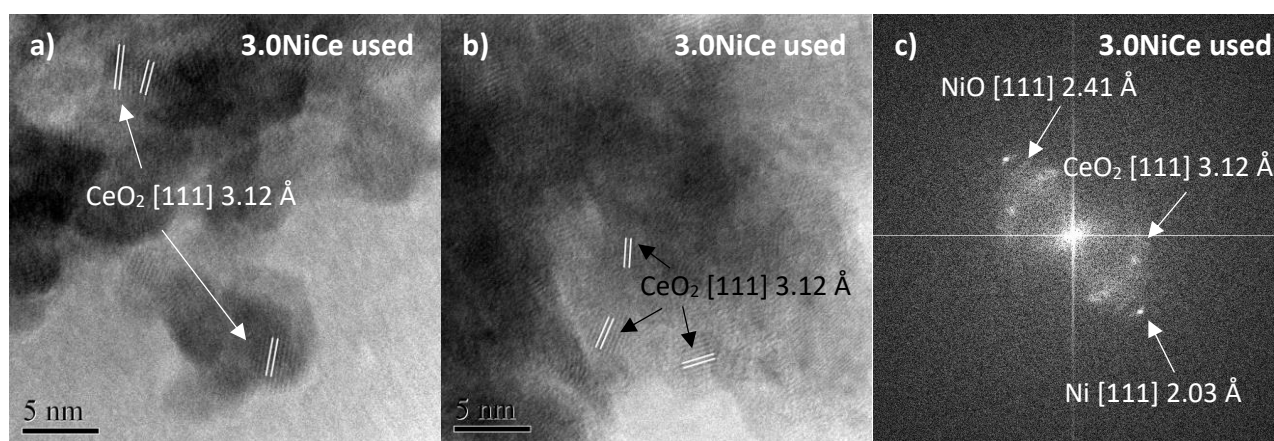
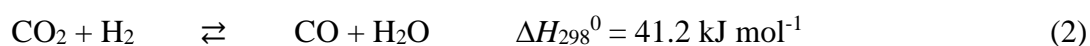
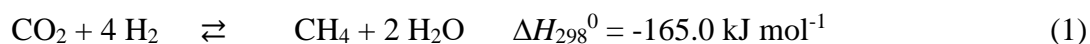


Figure 3. HR-TEM images (a,b) and FFT (c) of 3.0NiCe after the catalytic test.

3.4. Catalytic results

Besides CO₂ hydrogenation, the reverse water gas shift (RWGS) reaction might also occur, being favored at higher temperatures because of its endothermicity. Moreover, methane formation through hydrogenation of the resulting CO could also be possible (Scheme 1).



Scheme 1. Stoichiometric equations for: (1) CO₂ hydrogenation to methane; (2) reverse water gas shift reaction; (3) CO hydrogenation to methane.

Unlike RWGS, the conversion of CO₂ to methane at equilibrium decreases with temperature, due to the exothermic character of the methanation reaction. In the presence of methane in the feed, the equilibrium conversion of CO₂, calculated by means of the total Gibbs free energy minimization method, was found to decrease from ca. 98 mol% to ca. 83 mol% in the range 200-380 °C [41]. Interestingly, such values turned out to be only slightly lower than those calculated through the same theoretical approach in the absence of methane [41,54], indicating that the presence of even high contents of this component has only a little effect on the CO₂ conversion.

The values of CO₂ conversion (X_{CO_2}) as a function of temperature are shown in Figure 4, where the equilibrium conversions are also reported for reference. The catalytic performances were found to be stable within 6 h on stream (Figure S14). Therefore, for each reaction temperature, CO₂ conversions are reported as an average of the values determined throughout 2 h. CO₂ conversion is found to increase with temperature and appears to be lower than the equilibrium value at all the investigated temperatures (Figure 4a). However, the fact that X_{CO_2} at 380 °C is practically the same (80 mol%) for all the catalysts, regardless of their composition, would seem to indicate the achievement of equilibrium conditions although the experimental conversion value is slightly lower

than the theoretical one (83 mol%). Since deactivation phenomena were never observed, possible reactions leading to carbon formation (i.e., methane decomposition or CO disproportionation [41]) can be ruled out. Except for low amounts of carbon monoxide, methane was practically the only reaction product, with selectivity values >99 mol% for all the catalysts up to 350 °C (Figure 4b). The small decrease in S_{CH_4} observed at 380 °C can be ascribed to a slightly higher contribution of the RWGS reaction.

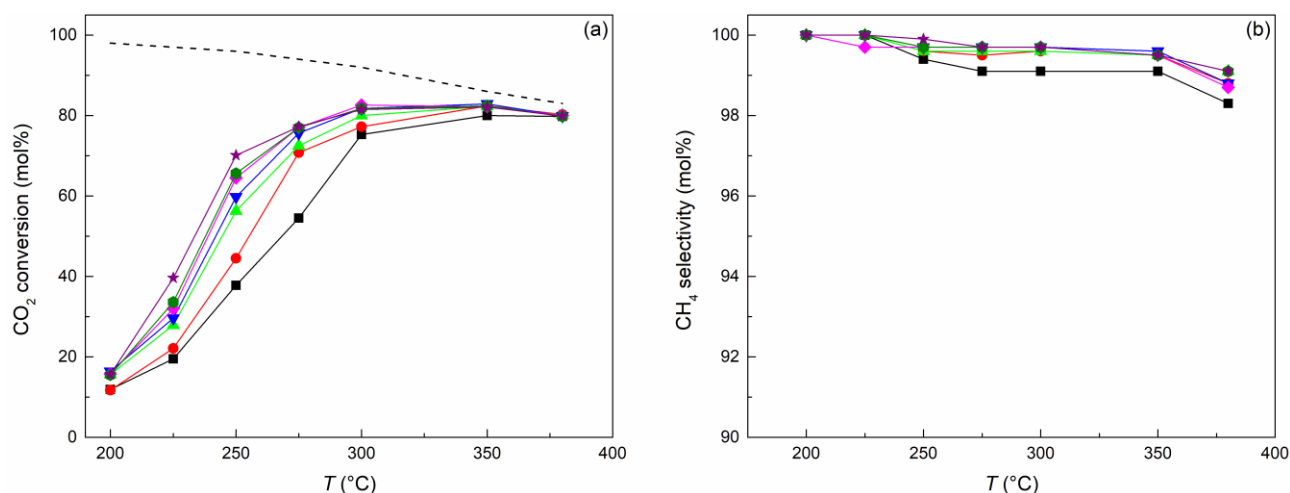


Figure 4. CO₂ conversion (a) and CH₄ selectivity (b) as a function of reaction temperature: (■), 0.5NiCe; (●), 0.75NiCe; (▲), 1.0NiCe; (▼), 1.5NiCe; (◆), 2.0NiCe; (◈), 3.0NiCe; (★), 4.0NiCe. Other reaction conditions: $m_{\text{cat}} = 0.050$ g, CO₂/CH₄/H₂ molar ratios = 1/2/4, $SV = 72000$ cm³ h⁻¹ g_{cat}⁻¹.

In Figure 5, CO₂ conversions are reported as a function of the specific metal surface area. Interestingly, different trends can be observed depending on the reaction temperature. At 200 °C, X_{CO_2} slightly increases from ca. 12 to a constant value of ca. 16 mol% for A_{met} above 10 m²_{Ni0} g_{cat}⁻¹. A continuous increase in conversion from ca. 20 to ca. 40 mol% and from ca. 38 to ca. 70 mol% is instead observed at 225 and 250 °C, respectively, over the whole investigated range of A_{met} . At 275 °C, the conversion increases up to an A_{met} value of ca. 18 m²_{Ni0} g_{cat}⁻¹ (corresponding to the 2.0NiCe

sample) and then stands at 77 mol%. It is noteworthy that the increase in X_{CO_2} is particularly marked between the two catalysts 0.5NiCe (54 mol%) and 0.75NiCe (71 mol%). A further increase in the reaction temperature makes progressively narrower the A_{met} range (and therefore the Ni/Ce molar ratio range) within which X_{CO_2} grows, until a constant value of ca. 80 mol% is achieved at 380 °C for all the catalysts.

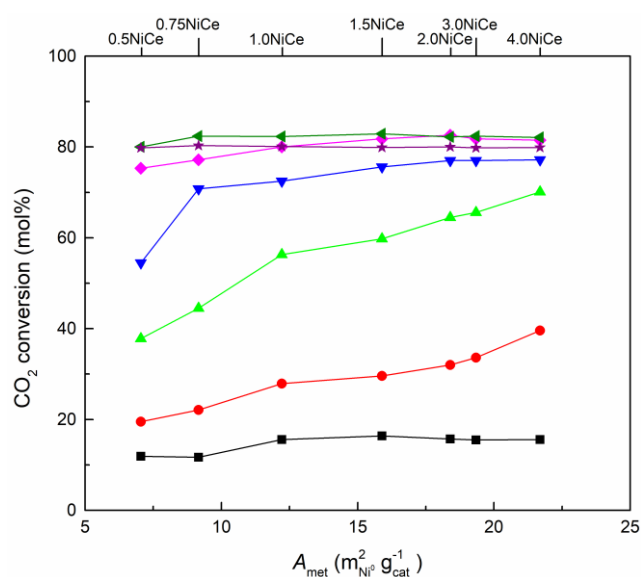


Figure 5. CO_2 conversion as a function of the specific metal surface area at the different investigated temperatures: (■), 200 °C; (●), 225 °C; (▲), 250 °C; (▼), 275 °C; (◆), 300 °C; (◄), 350 °C; (★), 380 °C. Other reaction conditions: $m_{\text{cat}} = 0.050 \text{ g}$, $\text{CO}_2/\text{CH}_4/\text{H}_2$ molar ratios = 1/2/4, $SV = 72000 \text{ cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$.

The observed trends of X_{CO_2} as a function of the specific metal surface area strongly suggest that the concentration of the Ni^0 sites is not the only parameter which affects the catalytic activity. In agreement with Aldana et al. [55], in previous papers dealing with CO_2 methanation [45] and $\text{CO} + \text{CO}_2$ co-methanation [52] on similar soft-templated NiCe catalysts, a reaction pathway was proposed where H_2 is dissociatively adsorbed and activated on Ni^0 sites (formation of H_{ads} species) while CO_2 is mainly activated on the basic sites of ceria, on which it is adsorbed in the form of hydrogen carbonates and carbonates (mono-, bi-, and poly-dentate). Then, the H_{ads} species migrate from the

metal sites through spillover processes [50,56] towards the ceria sites, where methane is formed through the consecutive hydrogenation of the oxygenated intermediates (formates, formaldehyde-type and methoxy species) and finally released to the gaseous phase. It is important to take into account that reaction temperature reasonably affects the rate of each of the steps involved in the catalytic process to a different extent. Anyway, it can be easily guessed that the simultaneous presence of Ni⁰ and basic surface sites in close interaction is crucial to achieve a good catalytic performance. At the lowest investigated temperature (200 °C) more steps are most likely kinetically limited, leading to a low conversion regardless of the catalysts composition. By converse, at the highest temperature (380 °C) all the steps are sufficiently fast to achieve equilibrium whatever the catalyst. The progressive increase in CO₂ conversion along with the specific Ni⁰ surface area observed at 225 and 250 °C seems to indicate that the catalytic activity is mainly governed by the ability of the catalyst to chemisorb and activate H₂. The much less important influence of CO₂ activation is confirmed by the observation that the capacity to adsorb CO₂ decreases passing from 0.5NiCe to 4.0NiCe (Table 2). In the range 275-350 °C, CO₂ conversion as a function of A_{met} initially increases, confirming the major role of H₂ activation in determining the overall rate of the catalytic process. Then it reaches an almost constant value, starting from different A_{met} values depending on the temperatures. Apparently, from that A_{met} value onwards, the further increase in the number of sites capable of activating hydrogen is no longer beneficial. This indicates that the rate of the whole process is governed by other steps.

Catalytic tests in a wide range of space velocities (11000-430000 cm³ h⁻¹ g_{cat}⁻¹) were performed at 275 °C on selected samples (Figure 6). Once again, methane selectivity is always higher than 99 mol%. As expected, CO₂ conversion is found to decrease with the increase in SV. For 0.5NiCe, X_{CO₂} is always lower than that of the other catalysts. Nonetheless, at the lowest SV value its catalytic behavior approaches that of the others, which show practically the same conversion, very close to the equilibrium value.

Such results confirm that the factors that most influence CO₂ conversion change depending on the reaction conditions. At more kinetically unfavored reaction conditions (low temperature or high SV), CO₂ conversion seems to be governed by the ability of the catalyst to activate H₂, which increases along with the nickel content. On the contrary, under more favorable temperature and SV, the reaction is mainly influenced by the rate of some steps of the CO₂ methanation mechanism subsequent to the H₂ activation, that could limit the conversion irrespective to the catalyst composition.

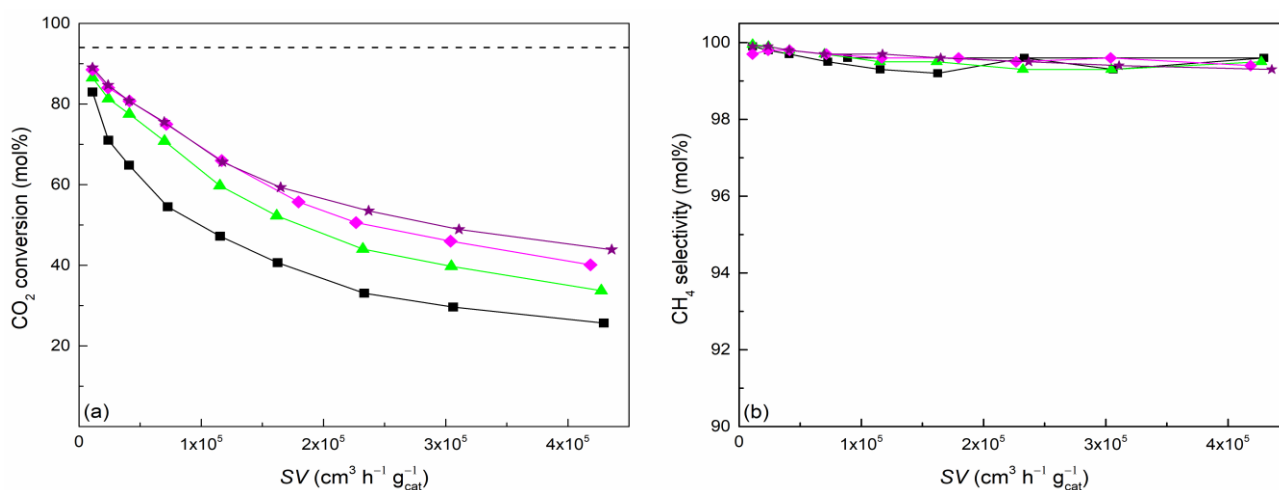


Figure 6. CO₂ conversion as a function of space velocity at 275 °C. (■), 0.5NiCe; (▲), 1.0NiCe; (◆), 2.0NiCe; (★), 4.0NiCe.

In the few papers dealing with the upgrading of biogas by direct CO₂ methanation, the catalytic performance of samples of different nature and composition are studied in a wide range of reaction conditions, in terms of temperature, pressure, and space velocity. Therefore, a clear comparison of the results turns out to be challenging. The catalytic behavior of Ni-based catalysts supported on commercial γ -Al₂O₃ was reported for Ni contents of 20 [38,41] and 40 wt% [41], also in the presence of Ru as the promoter [38]. At 2 bar, 350 °C, 56000 cm³ g_{cat}⁻¹ h⁻¹, CO₂/H₂ = 1/4 mol/mol, CO₂ conversion on the unpromoted catalyst did not exceed 70-72 mol% regardless of the CH₄/CO₂ molar ratio (1/1 or 2/1) in the feed, reaching the value of ca. 81 mol% only in the case of the

20Ni0.5Ru/Al₂O₃ sample. By converse, methane selectivity was always higher than 99 mol% [38]. At a lower *SV* value (30000 cm³ g_{cat}⁻¹ h⁻¹), a conversion of ca. 82 mol% was attained for Al₂O₃-supported catalysts with both 20 and 40 wt% of Ni [41], but with lower values of *S*_{CH₄} (ca. 80 mol%). Similar results were obtained using CeO₂ as the support in the Ni₂₀-CeO₂ catalyst [41]. A Ni-Mg-Al catalyst (20 wt% of Ni) was tested at 400 °C, atmospheric pressure, and 30000 cm³ g_{cat}⁻¹ h⁻¹, varying the CH₄/CO₂ molar ratio from 0.67 to 1.9 [39]: in presence of increasing amounts of methane in the gaseous mixture, *X*_{CO₂} decreased from 67 to 54 mol%, while *S*_{CH₄} remained constant at ca. 98 mol%. The effect of CH₄ content in the feed was also investigated on Ni(15 wt%)/CeO₂-ZrO₂ catalysts promoted with Co [40]: at 350 °C, atmospheric pressure, and 12000 cm³ g_{cat}⁻¹ h⁻¹, CO₂ conversion was found to increase from 72 to 78 mol% at increasing CH₄/CO₂ molar ratios (from 0.26 to 0.88 mol/mol); a very slight increase in *S*_{CH₄} from 97 to 99 mol% was also observed. In another study [42], Ni-based catalysts with a metal content of ca. 10 wt% were prepared by impregnation on porous silica (SP), silica fiber (SF), and a carbon nanotubes-silica fiber composite (CNT-SF). Performing the reaction at 10 bar, 350 °C, CH₄/CO₂ = 1.6/1 mol/mol, and *SV* = 12000 cm³ g_{cat}⁻¹ h⁻¹, the best results were obtained on the Ni/CNT-SF catalyst, which showed *X*_{CO₂} and *S*_{CH₄} values of 86.3 mol% and 97.0 mol%, respectively. A further improvement of the catalytic performance (*X*_{CO₂} and *S*_{CH₄} values of 95 mol% and 98 mol%, respectively, at 24000 cm³ g_{cat}⁻¹ h⁻¹) was found for the Ni-2Mg/SF sample after doping with 2 wt% of Mg [42]. From the comparison of the results from the literature with the present ones (Table 4), some relevant aspects can be highlighted. Noteworthy, at the temperature of 350 °C, atmospheric pressure, and remarkably higher space velocity (72000 cm³ g_{cat}⁻¹ h⁻¹), all the prepared *x*NiCe catalysts are able to achieve CO₂ conversions ≥ 80 mol% and methane selectivity > 99 mol%. Also, such *X*_{CO₂} and *S*_{CH₄} values can be reached by catalysts with Ni/Ce molar ratios ≥ 1.0 even at lower temperatures (300 °C) (Figure 4). By considering the lowest *GHSV* (12000 cm³ g_{cat}⁻¹ h⁻¹) investigated in [40,42], it emerges that, at comparable values (11000 cm³ g_{cat}⁻¹ h⁻¹), the present catalysts allow CO₂ conversions in the 83-89 mol% range to be reached at 275 °C and atmospheric pressure, with selectivity to methane

> 99.5 mol% (Figure 6). Though obtained under milder reaction conditions, more unfavorable from both the thermodynamic (atmospheric pressure) and kinetic (lower temperature) point of view, these results are considerably better than those reported for Ni-Co/Al₂O₃ catalysts at 350 °C [40] and comparable to those showed by the Ni/CNT-SF catalyst at 350 °C and 10 bar [42] (Table 4), proving that *x*NiCe are promising catalysts for biogas upgrading through direct CO₂ methanation.

Table 4. Comparison of the present catalytic results for biomethane upgrading by direct CO₂ methanation with those reported in the literature.

Catalyst	Ni (wt%)	H ₂ :CO ₂ (mol mol ⁻¹)	CH ₄ :CO ₂ (mol mol ⁻¹)	CH ₄ in the feed (vol%)	P (bar)	T (°C)	m _{cat} (g)	SV (cm ³ h ⁻¹ g _{cat} ⁻¹)	X _{CO₂} (mol%)	S _{CH₄} (mol%)	Ref.
20Ni/Al ₂ O ₃	20.0	4:1	1:1	14.3	2	350	0.150	56000	70.8	99.5	[38]
20Ni/Al ₂ O ₃	20.0	4:1	2:1	28.6	2	350	0.150	56000	70.6	99.4	[38]
20Ni0.5Ru/Al ₂ O ₃	20.0	4:1	2:1	28.6	2	350	0.150	56000	ca. 81	ca. 100	[38]
Ni-Mg-Al	20.0	4:1	0.67:1	11.8	1	400	0.500	30000	67	ca. 98	[39]
Ni-Mg-Al	20.0	4:1	1:1	16.7	1	400	0.500	30000	64	ca. 98	[39]
Ni-Mg-Al	20.0	4:1	1.9:1	27.1	1	400	0.500	30000	54	ca. 98	[39]
Ni-Co/CZ	15.7	4:1	0.26:1	5.0	1	350	0.250	12000	72	97.0	[40]
Ni-Co/CZ	15.7	4:1	0.55:1	10.0	1	350	0.250	12000	74	98.0	[40]
Ni-Co/CZ	15.7	4:1	0.88:1	15.0	1	350	0.250	12000	78	99.0	[40]
Ni20-CeO ₂	18.6	4:1	1:1	15.4	2	350	0.200	30000	ca. 82	ca.78	[41]
Ni20-Al ₂ O ₃	19.2	4:1	1:1	15.4	2	350	0.200	30000	ca. 82	ca. 80	[41]
Ni40-Al ₂ O ₃	36.9	4:1	1:1	15.4	2	350	0.200	30000	ca. 82	ca. 80	[41]
Ni/CNT-SF	9.4	4:1	1.6:1	24.2	10	350	0.100	12000	86.3	97.0	[42]
Ni/CNT-SF	9.4	4:1	1.6:1	24.2	10	350	0.100	36000	77.9	> 98	[42]
Ni-2Mg/SF	9.5	4:1	1.6:1	24.2	10	350	0.100	24000	95.0	98.0	[42]
0.5NiCe	10.7	4:1	2:1	25.9	1	350	0.050	72000	80.0	99.5	[this work]
0.75NiCe	15.2	4:1	2:1	25.9	1	350	0.050	72000	82.4	99.5	[this work]
1.0NiCe	23.6	4:1	2:1	25.9	1	350	0.050	72000	82.3	99.5	[this work]
4.0NiCe	40.8	4:1	2:1	25.9	1	350	0.050	72000	82.1	99.5	[this work]

An important aspect that should be taken into account when analyzing the performance of the catalysts to be used for biogas upgrading by the direct CO₂ methanation is related to the strict requirements usually imposed in terms of residual CO₂ and H₂ concentrations, which in turn depend on the speculated end-use of the upgraded biogas. For instance, the residual CO₂ content in biomethane destined for gas grid injection has to be lower than 2.5 mol% in Italy [57] and 2 mol% in

Switzerland [58]. As for hydrogen, the European standard EN 16726 (Annex E – “Hydrogen Admissible Concentrations in natural gas systems”) [59] provides directives on the residual H₂ concentration, pointing out that the proper limits have to be evaluated case by case depending on the possible end-uses. The highest H₂ content generally considered is 2 mol% [13], however various studies have shown that up to 10 mol% of hydrogen can be added to most parts of natural gas systems with no adverse effects [60]. Indeed, Switzerland and Germany regulations indicate limits up to 6 and 10 mol%, respectively [58,61].

From this point of view, it appears that the 89 mol% of CO₂ conversion, obtained with both the 2.0NiCe and 4.0NiCe catalysts, corresponds to residual concentrations of ca. 2.6 mol% and 17 mol% for carbon dioxide and hydrogen, respectively. Such amounts, while resulting very close to the limits imposed for CO₂, are not yet satisfactory with regard to hydrogen. However, considering that the catalytic performance has been studied using a slight excess of hydrogen and relatively mild reaction conditions (atmospheric pressure and 275 °C), it can be reasonably expected that by carrying out the reaction under more favorable conditions, especially in terms of pressure, the final concentration of both CO₂ and H₂ may decrease below the requirements established by current regulations. In addition, it is important to take into account that over the last decade a growing interest has been devoted to the study and development of technological solutions that make possible the safe use of synthetic natural gas blended with hydrogen in concentration up to 30-50 mol%, which would allow important energy and environmental benefits [62-66].

4. Conclusions

A series of NiO/CeO₂ nanostructured mixed oxides with different Ni/Ce molar ratios (from 0.5 to 4.0 mol/mol) was synthesized with high surface areas (between 188 and 206 m² g⁻¹) by the soft-template procedure. After a H₂-pretreatment at 400 °C for 1 h, the catalysts were used in the direct methanation of CO₂ contained in a model biogas. From XRD and TEM results, it was found that the samples were constituted of CeO₂ rounded nanocrystals (3-4 nm in size) and of

polycrystalline elongated NiO particles with dimensions of ca. 4 x 30-70 nm. The close contact between the two oxides was evidenced by EDX results, which showed an overall homogeneous distribution of Ni, Ce, and O. The presence of strong interactions between NiO and CeO₂ was confirmed by the appearance of the α -peak in the H₂-TPR profiles of all the samples. CO₂ adsorption microcalorimetric tests performed on the catalysts after H₂ pretreatment at 400 °C for 1 h showed that the number of basic sites decreases with the increase in Ni content. By converse, the value of the Ni⁰ surface area was found to increase with the same parameter, suggesting that the metal dispersion is comparable within the catalysts series. This is confirmed by XRD patterns of the catalysts after use, from which sizes of Ni⁰ nanocrystals from ca. 5.7 to ca. 8.7 nm were calculated for Ni/Ce ratios in the range 1.0-4.0 mol/mol. CO₂ conversion was found to increase with temperature up to 350 °C, at which $X_{\text{CO}_2} \geq 80$ mol% and $S_{\text{CH}_4} > 99$ mol% were obtained regardless of the catalyst composition. The trend of X_{CO_2} as a function of Ni content, to which the number of sites responsible for either H₂ or CO₂ activation is related, was different depending on the reaction temperature. This indicates that the ability of the catalyst to activate H₂ is not the only parameter which affects the catalytic activity; indeed, at favorable temperature and *SV*, other steps would control the overall reaction rate. The performance of the present catalysts was found to be comparable – if not better – than that reported in the literature for other Ni-based catalysts. Given that a very good methanation activity was obtained even at mild reaction conditions, a remarkable enhancement is expected by a further optimisation of the operating parameters, especially in terms of pressure.

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