



Article CO₂ Methanation Using Multimodal Ni/SiO₂ Catalysts: Effect of Support Modification by MgO, CeO₂, and La₂O₃

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Abstract: Ni/oxide-SiO₂ (oxide: MgO, CeO₂, La₂O₃, 10 wt.% target concentration) catalyst samples were prepared by successive impregnation of silica matrix, first with supplementary oxide, and then with Ni (10 wt.% target concentration). The silica matrix with multimodal pore structure was prepared by solvothermal method. The catalyst samples were structurally characterized by N₂ adsorption-desorption, XRD, SEM/TEM, and functionally evaluated by temperature programmed reduction (TPR), and temperature programmed desorption of hydrogen (H₂-TPD), or carbon dioxide (CO₂-TPD). The addition of MgO and La₂O₃ leads to a better dispersion of Ni on the catalytic surface. Ni/LaSi and Ni/CeSi present a higher proportion of moderate strength basic sites for CO₂ activation compared to Ni/Si, while Ni/MgSi lower. CO₂ methanation was performed in the temperature range of 150–350 °C and at atmospheric pressure, all silica supported Ni catalysts showing good CO₂ conversion and CH₄ selectivity. The best catalytic activity was obtained for Ni/LaSi: CO₂ conversion of 83% and methane selectivity of 98%, at temperatures as low as 250 °C. The used catalysts preserved the multimodal pore structure with approximately the same pore size for the low and medium mesopores. Except for Ni/CeSi, no particle sintering occurs, and no carbon deposition was observed for any of the tested catalysts.

Keywords: silica supported Ni catalysts; CO₂ methanation; multimodal pores catalysts; H₂-TPD; CO₂-TPD for silica supported Ni catalyst

1. Introduction

Efficient CO_2 transformation in useful and value-added compounds is the most promising way of action for the abatement of CO_2 elimination in the environment, and, eventually, for diminishing its negative effects on the climate change. In this regard, the methanation of CO_2 (Sabatier reaction):

 $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H_{298} = -165 \text{ kJ/mol}$

which generates synthetic methane, has re-gained great interest in the last decade [1]. This reaction brings a series of advantages due to the power-to-methane concept, considering both the possibility of hydrogen storage, as well as the utilization of the existing infrastructure for methane transport and utilization. Although thermodynamically favored, the methanation reaction faces significant kinetic limitations, as eight electrons are needed in the reduction process from C^{4+} in CO_2 , to C^{4-} in CH_4 . The development of active catalysts is thus vital for the practical applications of this reaction [2,3].

Traditionally, the most studied catalysts for CO_2 methanation are of metal/support type, with a very large range of metals and supports. Although various metals were studied, only significantly fewer really present the optimum balance between catalytic properties and market availability to make them interesting for practical applications [4–6]. Among them, Ni, although the most studied, seems to be the most promising one, as it optimally



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). combines the good activity and selectivity for methane formation, with its availability and low price [7–9]. Regarding the supports, metal oxides were the most studied, but very interesting results were also reported using porous crystalline frameworks [10], MOFs [11], core–shell structured catalysts [12], or even graphenes [13,14].

Ni catalysts deposited on silica or ordered mesoporous silica (OMS) supports were only relatively recently investigated for CO₂ hydrogenation, but the results reported until now made them very interesting choices as methanation catalysts. Unpromoted silica was tested as support for Ni/SiO₂ [15], Ni@SiO₂ core-shell [16], Ni-SiO₂ microspheres [17], or Ni-MOF derived silica [18]. Some studies reported the results obtained using MCM-41 supported catalysts [19–21], or the comparison of different OMS [22]. The main disadvantage of silica support is its acidic nature, which provides a low interaction with the CO_2 molecule. The solution to overcome this disadvantage is the promotion with basic oxides, which tend to diminish the surface acidity and to improve the interaction with CO_2 . Also, the addition of alkaline-earth or lanthanide oxides to alumina supported catalysts was previously demonstrated to improve the dispersion of Ni [23,24]. There are only a low number of papers dealing with the performances of basic oxide promoted Ni-silica catalysts for CO_2 methanation. These papers report the results obtained by the addition of cerium oxide to Ni-MCM-41 [25], Ni-SBA-16 [26], Ni-microporous silica [27], and Nielectrospinning prepared silica [28], or the addition of lanthanum oxide to Ni/SiO₂ [29], and Ni-SBA-15 [30]. The effect of alkaline earth oxides and more specifically MgO addition to Ni/SiO₂ was reported in two older papers [31,32], while the performances obtained using yttria-magnesia promoted Ni-MCM-41 was very recently published [33].

The aim of this paper was to investigate the effect of MgO, CeO₂, and La₂O₃ addition to Ni/SiO₂ with multimodal pore structure. This porous structure was proved to have a positive effect on the dry reforming of methane [34], and methane cracking [35] by stabilizing the active nanoparticles on the surface, and facilitating the access of reagents to the catalytic active sites. The additional oxides were selected to have different basicity and different ways to get involved in the methanation mechanism. The novelty brought by this paper consists in the combination of multimodal porous silica with basic oxides in order to obtain catalysts with high activity for CO₂ methanation at low temperatures, being known that one disadvantage of Ni catalysts compared to noble metals is the higher temperature required for good conversion.

2. Results

2.1. Characterization Results

The porous structure of the prepared SiO₂ and corresponding Ni/Oxide-SiO₂ catalysts was investigated by means of N_2 adsorption-desorption isotherms (BET method). The type IV(a) isotherm shape with a H5 hysteresis loop is indicative for mesoporous materials with open and partially blocked pores [36]. Upon addition of supplementary oxide, the shape of the isotherms is preserved as illustrated in Figure 1a for the investigated catalysts. Surface area of the as prepared silica is $462.2 \text{ m}^2/\text{g}$, with a corresponding pore volume of $1.24 \text{ cm}^3/\text{g}$ (Table 1). For the mixed oxides supports, as well as for the corresponding Ni catalysts, the surface area and pore volume decrease in the order Ni/Si > Ni/CeSi > Ni/LaSi > Ni/MgSi (see Table 1). In respect to the pore size distribution, Figure 1b reveals a multimodal pore structure of the silica support: (i) small pores with average dimensions around 2.4 nm (around 10 % of the total number), and (ii) larger pores with sizes in the 10–30 nm range. In this latter region, two distinctive pore dimensions are also evidenced, that is 15 nm, and 25 nm average values, respectively. The pore size distribution of Ni/Oxide-SiO₂ materials is preserved to a large extent, with a more pronounced separation of the two pore sizes in the 10–30 nm window, as compared to SiO_2 alone. However, a certain influence of the MgO and La₂O₃ presence upon the pore size distribution can be distinguished: (i) some of the smallest pores collapsed, this being reflected by the broadening of the pores size distribution in this area (2.2–4.4 nm); (ii) the pores with intermediate size remained



approximately unchanged (15 nm); and (iii) the dimension of larger pores decreased for Ni/MgSi, and significantly increased for Ni/LaSi.

Figure 1. (a) N₂ adsorption–desorption isotherms, and (b) pore size distribution for the Ni/Oxide-SiO₂ catalysts.

Sample	S _{BET} (m²/g)	V _p (cm ³ /g)	D _m (nm)	d _{Ni (XRD)} (nm)	d _{Ni (TEM)} (nm)
SiO ₂	462.2	1.24	2.3; 14; 24	-	-
Ni/Si	357.3	0.99	2.4; 14; 24	16.1	13
Mg-Si	239.0	0.88	2.4-4.4; 16; 24	-	-
Ni/MgSi	216.1	0.70	2.4-4.4; 14; 20	6.8	7
Ce-Si	396.0	1.10	2.2; 16; 24	-	-
Ni/CeSi	329.3	0.90	2.3; 16; 24	15.5	13
La-Si	307.3	0.93	2.4-4.4; 16; 32	-	-
Ni/LaSi	296.2	0.78	2.3–4.4; 14; 36	5.8	7–8

Table 1. Textural properties of the samples.

 S_{BET} —total BET surface area; V_p —total pore volume calculated using Dollimore Heal model (p/p₀ = 0.95); D_m—pore size; d_{Ni (XRD)}—Ni crystallite size estimated form XRD data; d_{Ni (TEM)}—Ni nanoparticle size estimated from TEM analysis.

XRD analysis was used to evaluate the composition and crystallinity of the oxidesilica supports, as well as the size of Ni crystallites. The as-synthesized SiO_2 reveals an amorphous structure, with its typical large diffraction peak centered around 22° (Figure 2) (JCPDS 89-3435). Upon addition of the second oxide, except for CeO₂-SiO₂, the XRD patterns of the Oxide-SiO₂ supports do not show distinctive diffraction peaks corresponding to the additional oxide. This might be an indication of either very good dispersion of the second oxide on silica, or its prevalence in a rather amorphous phase. In the case of the CeO₂-SiO₂ XRD pattern, the broad peak corresponding to SiO₂ is very low, in comparison to the sharp and high reflexions generated by the more crystalized ceria: $CeO_2(111)$ at 28.5°, CeO₂(200) at 33.2°, CeO₂(220) at 47.4°, and CeO₂(311) at 56.7° [37,38] (JCPDS 43-1002). A partial coverage of SiO₂ by crystalline CeO₂ cannot be excluded. Upon reduction at 600 °C in H₂, all Ni based catalysts reveal diffraction lines corresponding to metallic Ni: Ni(111) at 44.5°, and Ni(200) at 51.8° (JCPDS 65-0380). For Ni/CeSi the XRD pattern reveals the presence of silica, CeO₂ and metallic Ni. For the lanthana containing catalyst, the "noisy" aspect of the XRD pattern at low 20 angles suggests the presence of poorly crystalized La_2O_3 (JCPDS 065-3185), but also the possible presence of poorly crystalized $La(OH)_3$ (JCPDS 13-1481) and carbonated lanthana La₂O₂CO₃ (JCPDS 37-0804), which both present important reflexions in this 20 range. In case of Ni/MgSi, except for the specific reflexions of SiO₂ and Ni, three additional peaks can be observed at 37.1°, 43.1° and 63.1°. These reflexions can be attributed to NiO (JCPDS 89-7390), but the presence of NiO-MgO mixed

phase (JCPDS 24-0712) cannot be excluded. The XRD patterns of all other Ni based catalysts do not reveal the presence of any remanent NiO, proving thus the complete reduction. The incomplete reduction of NiO in Ni/MgSi is attributed to the higher interaction of NiO with the support constituents (MgO and SiO₂), leading thus to a lower reducibility of NiO. The very good dispersion of MgO and La₂O₃ on the silica surface was previously reported for silica [29,31], as well as for ordered mesoporous silica [30,33] supported catalysts.



Figure 2. XRD patterns of the Ni/Oxide-SiO₂ catalysts—(•) peak corresponds to SiO₂; (o) peaks correspond to CeO₂; (\blacklozenge) peaks correspond to Ni.

Ni crystallite size was estimated by means of Scherrer's equation, using the Ni(200) peak situated at 51.8° (see Table 1). Ni crystallite sizes of 15.2 nm were obtained for Ni/Si, while catalysts with additional oxide reveal smaller Ni crystallites. It should be noted, however, that the decrease of crystallite size is quite small for the Ni/CeSi catalyst (14.2 nm), while the other two materials show crystallite dimensions around 6.2 nm. These data suggest a much better dispersion of Ni particles on the mixed oxides support for the magnesia and lanthana containing catalysts.

TEM images of Ni/Si revealed a non-ordered mesoporous structure, with irregularly shaped pores, which is maintained for the supplementary oxides containing catalysts, as well. By analyzing the TEM images of silica supported catalysts, a good dispersion of relatively uniform shaped and sized Ni nanoparticles (Ni NPs) is observed for each catalyst prepared in this work. EDX mapping revealed that MgO and $La \neg_2O_3$ are very well dispersed on the catalysts' surface, the Mg distribution for example, being very similar to that of Si and O. CeO₂ is evidenced as small islands of 20–30 nm, uniformly distributed on the catalyst surface. These results are in good agreement with the XRD patterns presented above, where the only additional oxide clearly present in the diffractograms is CeO₂. Ni NPs present a narrow size distribution (Figure 3), the average size (Table 1) being also in accordance with the Ni crystallite size determined from XRD. It is important to notice that the catalytic materials for which very high dispersion of the additional oxide is observed (Ni/MgSi and Ni/LaSi) also present an important decrease of Ni NPs size compared to the Ni/Si catalyst.



Figure 3. TEM images and EDX mapping of silica supported Ni catalysts.

The reducibility of the supported NiO nanoparticles upon treatment in hydrogen is a valuable indicator of the strength of the NiO–support interaction and, at the same time, provides information about the metal–support interaction in the reduced catalysts. As NiO reduction is a one-step process, the multiple peaks observed in the TPR profiles (Figure 4) are generated by the differences in the NiO interaction with the support. For silica supported nickel catalysts, previous publications identified a temperature threshold of 450 °C: the reduction peaks situated below this temperature indicate the presence of NiO NPs in low interaction with the support, while the peaks situated at higher temperatures correspond to the reduction of NiO strongly bonded to the silica support [28]. For NiO/Si,

the TPR profiles (Figure 4) show the existence of NiO NPs with two different strengths of interaction with the support: low bonded NPs which correspond to the reduction peak situated at 360 °C, while the lower and broader peak situated at 500–550 °C corresponds to NiO NPs in strong interaction with the support. The addition of CeO_2 does not significantly change the reducibility of catalysts precursors, the difference being the lower proportion of strongly bonded NiO NPs, which are also reduced at a slightly lower temperature: 475 °C compared to 500 °C. Opposite to NiO/Si, NiO/LaSi and NiO/MgSi which contain only irreducible oxides alongside NiO, in case of NiO/CeSi the reduction of ceria can also occur during TPR measurements. Thus, the smaller peak situated at 210 °C was previously attributed either to the reduction of adsorbed oxygen species [26], or to the surface reduction of ceria [39]. A small reduction peak can be observed at high temperature (750 °C), and was attributed to the reduction of Ce^{4+} to Ce^{3+} [26]. The reduction of ceria species alongside with NiO is reflected in the larger amount of consumed hydrogen in H₂-TPR experiments, as compared to the rest of the catalysts (Table 2). Thus, for the ceria containing catalyst prepared in this work, the interaction of NiO with the CeO₂-SiO₂ support is similar to the interaction with SiO₂. This observation is in good correlation with the XRD and TEM results, which evidenced Ni crystallites/nanoparticles of similar size as the ones from Ni/Si catalysts, which are situated on materials with very similar surface area and pore size distribution. A similar effect of CeO₂ addition to electrospinning prepared silica [28], and SBA-15 [40] supported Ni catalyst was previously reported, while for Ni-CeO₂-MCM-41 [25], and Ni-CeO₂-SBA-16 [26] the reducibility is lowered by the presence of ceria. The addition of La₂O₃ and MgO, instead, drastically changes the TPR profile, proving the significant changes in the NiO interaction with MgO-SiO₂ and La₂O₃- SiO_2 , compared to the bare SiO_2 . For NiO/LaSi, the reduction peak situated at 550 °C for Ni/Si is slightly shifted to 600 °C, but the proportion of hard reducible NiO is significantly higher than in Ni/Si. This is an indication of the presence of higher proportion of strongly bonded Ni NPs in Ni/LaSi compared to Ni/Si. In other words, the La₂O₃-SiO₂ support better interacts with NiO NPs, this being reflected in smaller Ni NPs in the reduced catalyst, as revealed by the TEM images. A similar effect of Ni NPs dispersion and stabilization on the surface was observed on lanthana containing Ni-SBA-15 catalyst [30]. In the case of Ni/MgSi, there are also two types of NiO, but their reducibility is much lower than for Ni/Si, the main reduction peaks being situated at 600 °C, and 850 °C. This very hard reducible NiO remained unreduced in Ni/MgSi as evidenced by XRD analysis (Figure 2). The peak situated at 600 °C is given by the reduction of Ni²⁺ from sub-surface layer of NiO-MgO solid solution, while the peak situated at 825 °C might be given by the reduction of Ni²⁺ in the MgO matrix, indicating a more intimate interaction between MgO and NiO, or the existence of NiMgO₂ [41-43]. The important decrease of catalyst reducibility upon MgO addition to Ni/oxide catalyst due to the difficulty of reduction of Ni^{2+} species in intimate contact/chemical combinations with MgO is well documented [24,32,43,44].



Figure 4. TPR profiles of the Ni/Oxide-SiO₂ catalysts.

Catalyst	n _{H2} (µmol/g _{cat})	Q _{H2} (µmol/g _{cat})	N _{Ni surf} /g _{cat} (×10 ¹⁸)	D _{Ni} (%)	T _{50%} (°C)
Ni/Si	895	4.6	5.5	0.6	275
Ni/MgSi	913	17.6	21	2	268
Ni/CeSi	1213	4.1	5	0.5	275
Ni/LaSi	1057	29.1	35	3.5	235

Table 2. Active metallic centers for hydrogen chemisorption and catalytic activity results.

 n_{H2} —quantity of consumed hydrogen in H_2 -TPR experiments; Q_{H2} —quantity of desorbed hydrogen corresponding to type-I peaks in H_2 -TPD experiments; $N_{Ni surf} / g_{cat} (\times 10^{18})$ —number of Ni active centers for hydrogen adsorption per gram of catalyst; D_{Ni} —nickel dispersion calculated from the quantity of desorbed hydrogen in the type-I region; $T_{50\%}$ —temperature of 50% CO₂ conversion in TPRea experiments.

The degree of NiO-support interaction, reflected in the reducibility of nickel oxide, is not only influenced by the crystallites/nanoparticles size, but also by the NPs position on the mesoporous silica support. Analyzing the data provided by porosity measurements, XRD experiments, TEM images interpretation and TPR analysis, it was concluded that the hard-reducible NPs are most probably located inside the medium sized mesopores (14 nm), benefiting thus from the stabilizing effect of pore confinement. The NPs with lower interaction with the support are situated in the larger pores and/or on the grain surface. Ni/LaSi and Ni/MgSi are expected to have a significant proportion of Ni NPs inside the medium size mesopores. This observation is supported by: (i) the higher proportion of strongly bonded Ni NPs as revealed by H₂-TPR for both Ni/LaSi and Ni/MgSi; (ii) the Ni NPs size is significantly lower than the pore size (Table 1), in contrast to Ni/Si for which the dimensions of the Ni NPs and of the support pores are more similar; and (iii) the lower surface area of these two catalysts compared to Ni/Si. This lower value of surface area is given by the presence of mesopores partially filled with Ni NPs, which are small enough to not produce the pore blockage. The observed H5 hysteresis loop also supports this affirmation [36].

The strength of catalytic active sites for H_2 adsorption was studied by H_2 -TPD. For all four catalysts studied in this work, a clear separation of two types of hydrogen desorption peaks was observed: those situated under 400 °C and denoted as type I, and those situated at temperatures higher than 400 $^{\circ}$ C and denoted as type II (Figure 5). Type I peaks are generated by the desorption of hydrogen originated from metallic sites, while type II peaks correspond to the desorption of hydrogen from the support by reverse spillover [45]. In the type I region of the spectra, one main desorption peak situated at 90 °C can be observed for Ni/Si, usually attributed to the removal of H_2 weakly chemisorbed to the surface. For the rest of the catalysts, two desorption peaks can be observed in this region, suggesting the presence of two types of hydrogen adsorption centers having different capacities to activate and bond hydrogen. For Ni/CeSi, the first peak is situated at 90 °C, similar to Ni/Si, and the second one at 210 °C. For Ni/MgSi, the first TPD peak is shifted to higher temperatures, that is 110 °C, while the position of the broad second peak is not significantly changed. For Ni/LaSi, the position of the first peak is further shifted to 130 °C, while the second peak appears at 190 °C. Based on the position of the desorption peaks it can be stated that the strength of catalytic active sites for hydrogen adsorption and activation decreases in the order: Ni/LaSi > Ni/MgSi > Ni/CeSi \approx Ni/Si. The quantity of desorbed hydrogen from type I catalytic sites (Table 2) is approximately the same for Ni/Si and Ni/CeSi, but increases dramatically for Ni/MgSi, and especially for Ni/LaSi. Ni dispersion, calculated from the quantity of desorbed hydrogen in the type I region, follows the same pattern, being approximately five times larger for Ni/LaSi compared to Ni/Si. The presence of both MgO and La_2O_3 on the catalyst support plays a significant role in enhancing the catalyst's capacity to activate hydrogen by increasing the number of catalytic active sites. This information is in good correlation with XRD/TEM results, which both evidenced much lower crystallite/nanoparticles in Ni/LaSi, but also with H2-TPR results which suggested a higher proportion of Ni NPs stabilized on the surface by strong interaction with the support. It is interesting to note that the presence of the second oxide significantly increases

the intensity of the peaks in the type II region of the spectra, indicating the tendency of these materials to host strongly bonded hydrogen, either on support, or on sub surface layers. The reaction temperatures employed in this study are lower than those necessary to activate this type of hydrogen.



Figure 5. H₂-TPD profiles of the Ni/Oxide-SiO₂ catalysts.

 CO_2 -TPD was used to assess the strength of active centers for CO_2 adsorption, and the influence of the additional oxide on the carbon dioxide activation in the reaction. Being a weak Lewis acid molecule, the adsorption of CO_2 is favored by the existence of basic sites, either on the support, or on the metal-support interface. For Ni deposited on acidic supports, the CO₂ adsorption on (O-terminated) Ni metallic sites, or unreduced NiO was also considered, motivated by the low capacity of these supports to adsorb CO_2 [46]. Most authors agree to classify the strength of basic sites from the catalysts' surface in correlation to the desorption temperatures, as follows: (i) weak sites corresponding to the desorption peaks situated below 200-250 °C; (ii) medium basic sites for the CO2 desorbed between 250 °C and 550–600 °C; (iii) and strong basic sites for the peaks situated above 600 °C [46,47]. Low, moderate and strong basic sites correspond to surface OH⁻, Lewis acid-base pairs, and low coordination surface O^{2-} , respectively [48]. Although the mechanism of CO_2 transformation to methane essentially depends on the catalyst composition, and is still open to debate for some materials, it is generally accepted that CO_2 conversion depends on the presence and quantity of medium basic sites. The CO_2 weakly physisorbed could be insufficiently activated for the reaction, while the CO_2 chemically adsorbed to the strong sites do not participate in the reaction. For the silica supported materials prepared in this work there is a clear delimitation of the three types of basic sites, while the presence of supplementary oxides significantly influences their proportion (Figure 6). For Ni/MgSi, a significant increase of weak adsorption centers is observed, suggesting that MgO creates additional weak basic centers on the catalyst, but the proportion of medium basic sites is significantly decreased compared to Ni/Si. For Ni/CeSi, an enhancement of weak and weak-medium adsorption is observed, but also the appearance of a supplementary desorption peak situated in the medium to strong region (527 °C) was noticed. An enhancement of weak and medium basic sites for the ceria containing material was reported for Ni-CeO₂(10%)-SBA-16, attributed to the CO₂ species adsorbed over Ce^{3+} sites, and was considered to play an important role in the methanation reaction mechanism [26]. For Ni/LaSi an important increase of both weak and moderate basic sites compared to all other materials prepared in this work was observed. This enhanced CO_2 adsorption was previously attributed to the formation of lanthanum oxycarbonate ($La_2O_2CO_3$), and formate species [30]. Low concentrations of CO (one order of magnitude lower than for CO_2) were also detected, proving the existence of low proportion of dissociative CO₂ adsorption for all four investigated catalysts. CO desorption peaks are situated around 450–500 °C, their intensity in case of catalysts containing additional oxide being much lower than for Ni/Si.



Figure 6. CO₂-TPD profiles of the Ni/Oxide-SiO₂ catalysts.

2.2. Catalytic Activity Tests

All four silica supported materials prepared and characterized in this work were evaluated as catalysts for low temperature CO_2 methanation using the temperature programmed reaction technique (TPRea), in the temperature window of 30–350 °C (2 °C/min), and at atmospheric pressure. Silica support was also tested, and no significant CO_2 conversion was obtained in the studied temperature interval. The composition of the dried effluent gases was: CO_2 , H_2 , CH_4 , and CO. The first two are unreacted reagents, while the last ones are the products of the methanation reaction and of the reverse water gas shift reaction (RWGS), respectively.

Up to 150 °C, very low CO₂ conversion was observed for all catalysts (Figure 7). Above 200 °C the CO₂ conversion sharply increased, reaching values higher than 90% at 350 °C. At temperatures above 300 °C, no important differences between catalysts were observed, except for Ni/LaSi. Under these conditions, the reaction is controlled by temperature, and the catalysts' properties which make the difference at lower temperature are no longer important. The addition of CeO₂ brought no improvement to the catalytic activity, while the addition of MgO only slightly improved the CO₂ conversion in the 200 $^{\circ}$ C–300 $^{\circ}$ C temperature range. Lanthana containing catalyst instead, performed remarkably well in the methanation of CO₂, both CO₂ conversion and CH₄ selectivity being significantly improved, especially at low temperatures. For this material, 50% conversion is reached at 235 °C, while for Ni/Si $T_{50\%}$ = 275 °C, and for Ni/MgSi it is 268 °C. CO₂ conversion of 95% is obtained for Ni/LaSi at temperatures as low as 300 °C. For comparison, Ni/Al₂O₃ tested in identical conditions reached 50% CO₂ conversion at 345 °C [49]. In terms of CH₄ selectivity, the addition of MgO and CeO₂ to the Ni/Si catalyst brought some advantages at low temperatures. For example, at 240 °C, methane selectivity is 61.2% for Ni/Si, while 65.5% for Ni/CeSi, and 70% for Ni/MgSi. Above 300 °C instead, methane selectivity presents similar values for all three catalysts, being~91% at 300 °C, and 96% at 350 °C. For Ni/LaSi, CH₄ selectivity is significantly improved compared to Ni/Si, reaching 89% at 240 °C, and 97% at 350 °C. In order to evaluate the performance of silica supported catalysts investigated in this work in relation with other supported Ni catalysts, a comparative analysis was made with Ni/Al₂O₃ and Ni/MIL-101-Al₂O₃ which were tested in identical reaction conditions [49]. In respect to both CO_2 conversion and methane selectivity, the results described in this work are better than those previously published for alumina

supported catalysts. For example, in the case of Ni/Al₂O₃, 50% CO₂ conversion was reached at 345 °C, while for Ni/MIL-101-Al₂O₃ at 302 °C. Regarding methane selectivity at 350 °C, 72% was obtained for Ni/Al₂O₃, and 94% for Ni/MIL-101-Al₂O₃, compared to more than 95% for silica supported catalysts used in this work. However, comparison with other silica supported Ni catalysts tested in the methanation of CO₂ is difficult to be done due to the differences in testing conditions, as well as the different concentrations of Ni and/or additional oxide. For example, similar~60% CO₂ conversion at 250 °C was reported for Ni/La₂O₃-SBA-15 (10 wt.% Ni) [30], but the reaction conditions used in this case are so different (nH₂/nCO₂ = 4:1, C_{CO2} = 18%, 1 MPa, 6000 mL·h⁻¹·g⁻¹) that a comparison with our results is not relevant.



Figure 7. CO₂ conversion and CH₄ selectivity for silica supported Ni catalysts in TPRea experiments (0.1 g catalyst, temperature rate 2 °C/min, p = 1 atm, total gas flow 31 mL/min, $C_{CO2} = 6.6\%$, CO_2 :H₂ = 1:5.2; GHSV = 4650 h⁻¹) (left: CO₂ conversion rate; right: CH₄ conversion rate).

When comparing the behavior of silica and promoted silica supported Ni catalysts for CO₂ methanation, one must consider and analyze the two processes involved in the catalytic reaction: (i) the dissociative H_2 adsorption on the Ni active sites, and (b) the adsorption of CO_2 on the basic sites. In this study, the catalyst with best performances for CO₂ methanation was Ni/LaSi. This remarkable activity is due to the good structural characteristics of the catalyst (low Ni NPs size, very good dispersion of both La₂O₃ and Ni) which provide a high number of Ni active sites for hydrogen activation (Table 2), but also to the enhanced proportion of weak-medium basic sites compared to all other catalysts used in this work (Figure 6). Thus, for Ni/LaSi catalyst, both H₂ activation and CO₂ adsorption are considerably enhanced. Additionally, for Ni/LaSi employed in this study, the high improvement in catalytic activity is also due to the multimodal porous structure of this material. This helps: (i) to better stabilize the Ni NPs inside the medium size mesopores (as shown in the characterization section), and (ii) to guide the reagent molecules to the catalytic centers by the "tunnel effect" provided by the larger pores. These former types of pores are with one third larger for Ni/LaSi compared to the other materials in this work, facilitating thus the gas transport through the catalyst grain. Three studies related to CO₂ methanation over lanthana promoted silica supported nickel catalysts were recently reported [29–31], two of them presenting also the lanthana involvement in the CO₂ methanation mechanism (Ni-La₂O₃-SiO₂ [29], and Ni-La₂O₃-SBA-15 [30]). A similar improvement of the catalytic performances for the lanthana containing catalysts compared to the unpromoted ones were observed in these studies, but a direct comparison of the results reported in these papers with the ones obtained in this work is difficult due to the differences in the composition and employed reaction conditions for both catalysts.

Ni/MgSi presents equally good structural characteristics as Ni/LaSi: Ni NPs of similar small size as Ni/LaSi, most probably placed inside the medium size mesopores, and very good dispersion of MgO, but its catalytic activity still is much lower than that of Ni/LaSi, being actually only slightly better than Ni/Si. This can be explained by the hard-reducible nature of this material, which leads to the existence of Ni in unreduced form in the final catalyst. This fact is reflected in the number of active sites for hydrogen activation, which, although significantly larger than for Ni/Si, is still low compared to Ni/LaSi (Table 2). Regarding the activation of CO_2 for the reaction, CO_2 -TPD profile for Ni/MgSi showed the lowest proportion of moderate basic sites in the catalyst series employed in this study. The positive effect of higher number of active sites for hydrogen activation is negatively balanced by the low proportion of medium sites for CO_2 activation. The performances of this material emphasize the need for an optimum catalyst composition, which can provide the best equilibrium between the two processes of the catalytic reaction.

Surprising results were obtained for Ni/CeSi compared to Ni/Si, for which only a slight improvement in CH₄ selectivity was noticed, and no influence on the conversion of CO₂ was observed. This can be explained by taking into account the catalyst's structure. In contrast to magnesia and lanthana containing catalysts prepared in this work following the same procedure, Ni/CeSi catalyst presents very few structural enhancements compared to Ni/Si. No improvement in Ni NPs size or dispersion were obtained, and the number of Ni catalytic active sites is very similar to Ni/Si. This fact is reflected in a very similar behavior of these two catalysts for hydrogen adsorption. CeO₂ is not as well dispersed on the silica surface as MgO or La₂O₃, and the involvement of ceria in the catalytic process by creating oxygen vacancies on the surface to effectively activate CO₂ for the reaction is dependent on the ceria dispersion. The size distribution of Ni NPs suggests that a significant proportion of NPs are probably placed in larger mesopores, or on the grain surface, being thus less stabilized on the surface. The slight improvement in methane selectivity can be due to the ceria activity for the water gas shift (WGS) reaction, and subsequent inhibition of the reverse water gas shift (RWGS) reaction (CO₂+H₂→CO+H₂O) [50].

This behavior of Ni/CeSi is opposite to the results recently reported for CO₂ methanation using Ni-CeO₂-SiO₂ [28], Ni-CeO₂-MCM-41 [25], and Ni-CeO₂-SBA-16 [26], for which the ceria containing catalysts presented significantly better results than the Ni/silica counterparts, especially at low temperatures. Analyzing the mentioned reported results, it was obvious that in all cases the presence of ceria brought significant better structural characteristics accompanied by enhanced capacity to adsorb hydrogen, and by more medium basic sites for CO₂ activation. It was concluded that the method used in this work is not suitable for the preparation of Ni-CeO₂-SiO₂ materials with improved structural and functional properties for CO₂ methanation. The results obtained in this study for Ni/CeSi emphasize the importance of optimum correlation between catalyst composition, selected preparation method, and catalysts' structural and functional properties.

All four materials studied in this work were tested under steady state conditions, for 6 h time on stream (TOS), at 250 °C, and at atmospheric pressure (Figure 8). The low reaction temperature was selected in order to have the proper conditions to study the catalyst influence, but also to demonstrate the very good performances of Ni/LaSi for low temperature CO₂ methanation. As expected, the catalytic activity of the studied materials followed the same trend as in TPRea runs: Ni/LaSi > Ni/MgSi > Ni/CeSi > Ni/Si. In stability tests, the differences in catalytic performances (both CO₂ conversion and CH₄ selectivity) between Ni/Si, Ni/CeSi, and Ni/MgSi are more pronounced than those corresponding to the TPRea runs, most probably due to the fact that under steady state conditions, catalysts show their complete working potential. No obvious deactivation is observed for the catalysts which contain additional basic oxide. In the case of the Ni/Si catalyst, a slight decrease of conversion from 29% to 25% was registered after 6 h TOS.



Figure 8. CO₂ conversion and CH₄ selectivity for silica supported Ni catalysts in stability tests at 250 °C (0.1 g catalyst, 1 atm, total gas flow 31 mL/min, $C_{CO2} = 6.6\%$, CO_2 :H₂ = 1:5.2; GHSV = 4650 h⁻¹).

It is important to notice the very good performances of Ni/LaSi at low temperature: CO_2 conversion is more than 80%, and methane is the only reaction product (methane selectivity more than 98%).

The catalysts used in stability tests for CO_2 methanation were characterized to assess the modifications of catalysts' structure in the tested conditions, and to check the possible carbon deposition on the catalyst surface.

The XRD patterns of used catalysts (Figure 9a) present the same characteristic reflexions as for the fresh materials (as described in Characterization Section 2.1). Ni XRD peaks were used to estimate the Ni crystallites size (Table 3). Only a slight increase was observed for Ni/Si and Ni/MgSi catalysts, while an important increase of Ni crystallites was obtained for Ni/CeSi (approximately 33% larger crystallites for used catalysts compared to fresh ones). A very good stability of the Ni crystallite size was observed for Ni/LaSi, for which the estimated values of Ni crystallites in the fresh and used catalyst are the same. These observations confirm the assumptions made for the confinement of Ni NPs inside the porous structure: for Ni/LaSi, the embedment of NPs inside the medium mesopores leads to their stability against agglomeration and sintering during the catalytic process, while for Ni/CeSi the placement of NPs predominantly on the catalyst grain cannot avoid their agglomeration. For Ni/Si and Ni/MgSi, for which the Ni NPs are situated both inside and outside the medium mesopores, a partial agglomeration and sintering was observed. No carbon deposition could be observed in the XRD patterns of the used catalysts, considering that characteristic diffraction lines of Si and C are superposed, corroborated with possible low intensity C diffraction peaks.

Table 3. The characteristics of catalysts used in the CO₂ methanation reaction (6 h TOS).

Catalyst	S_{BET} (m ² /g)	D _m (nm)	d _{Ni (XRD)} (nm)
Ni/Si	300	2–5; 13; 22	18.3
Ni/MgSi	138.8	5.4; 12; 20	9.7
Ni/CeSi	248.6	2-8; 19; 46	22.7
Ni/LaSi	176.5	2–5; 19; 53	5.5

S_{BET}—total BET surface area; D_m—pore size; d_{Ni} (XRD)—Ni crystallite size estimated form XRD data.



Figure 9. (a) XRD patterns of the Ni/Oxide-SiO₂ catalysts used in CO₂ methanation stability tests at 250 °C; (\blacklozenge) peaks correspond to Ni; (\bullet) peak corresponds to SiO₂; (o) peaks correspond to CeO₂; (**b**) pore size distribution for used catalysts.

TGA measurements were carried out for the used catalysts in order to assess the mass loss associated with the oxidation of deposited carbon on the catalysts' surface. For all catalysts, except for the desorption of water and other adsorbed gases which appear at temperatures lower than 100 °C, no other mass loss was observed. Due to the fact that the oxidation of Ni produces a low mass gain in the same temperature region in which the carbon oxidation would occur, a possible mass loss produced by the oxidation of small amounts of deposited carbon cannot be observed in TGA. To further investigate the possible carbon deposition on used catalysts, the corresponding TEM images were analyzed. No carbon deposits, either as fibers (wires), or as amorphous carbon were observed. In conclusion, for the catalysts tested in this work no observable carbon deposition occurs.

Total surface area and pore size distribution of silica supported catalysts after stability tests at 250 °C in CO₂ methanation were calculated from N₂ adsorption-desorption isotherms. The shape of the isotherms corresponding to the used catalysts is very similar to the fresh ones, suggesting the preservation of the catalysts' porous structure. For all catalysts, the multimodal porous structure is maintained (Table 3 and Figure 9b). In the case of used Ni/Si and Ni/MgSi, the pore size remained relatively unchanged, but the proportion of larger pores increased. Instead, for the used Ni/CeSi and Ni/LaSi, the pore size distribution is changed. While the medium mesopores sizes are in the same region as in the fresh catalysts, the larger pores present a much broader distribution and a shift towards higher values. This can be due to the collapsing of the walls of some larger pores during the stability tests. However, it is important to notice that the general multimodal porosity of the samples is maintained even after catalysts testing.

3. Materials and Methods

3.1. Chemicals and Gases

All chemicals were obtained from commercial suppliers (as indicated in the next section) and were used as received, without additional purification. Used gasses were 5.0 purity and were purchased from Linde Gaz Romania (Cluj Napoca, Romania).

3.2. Synthesis of Ni/Oxide-SiO₂ Multimodal Catalysts

Synthesis of multimodal SiO₂ was performed by means of a solvothermal method, as follows: tetraethyl orthosilicate (TEOS, VWR Chemicals, Fontenay-sous-Bois, France) was precipitated at room temperature with an ammonium solution in the presence of cetyltrimethylammonium bromide (CTAB, VWR Chemicals, Fontenay-sous-Bois, France). The formed gel was maturated at 40 °C for 24 h, and then treated solvothermally at 100 °C

in an autoclave. The obtained solid was further washed and dried at room temperature, followed by calcination in two steps: at 550 °C for 4 h (temperature rate of 5 °C/min), and 1000 °C for 2 h.

Support modification by MgO, CeO₂, and La₂O₃ (10wt.%) was achieved by the wet impregnation method using the appropriate amounts of aqueous solutions of the corresponding nitrate salts (Merck, Darmstadt, Germany), followed by calcination under Ar flow, at 500 °C for 3 h.

Ni/Oxide-SiO₂ catalysts were obtained by the wet impregnation of the MgO-SiO₂, CeO₂-SiO₂, and La₂O₃-SiO₂ supports with the appropriate amount of Ni(NO₃)₂ aqueous solution (Merck, Darmstadt, Germany), in order to obtain a 10wt.% Ni loading. Samples were dried overnight at room temperature, then 2 h at 100 °C, calcined at 500 °C in Ar flow for 3 h, then reduced under H₂ flow at 600 °C for 4 h. The catalysts were denoted as Ni/xSi where x stands for additional oxide; for example Ni/CeSi means Ni/CeO₂-SiO₂.

3.3. Characterization of Catalysts

X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 Advanced Diffractometer (Billerica, MA, USA) working at 40 kV and 40 mA, and equipped with a Ge monochromator to obtain CuK α 1 radiation. Diffractograms were recorded in the angle range $2\theta = 1-85^{\circ}$, with a scan rate of 0.01° /s. Determination of specific surface area was performed following the standard BET procedure by N₂ adsorption–desorption at $-196 \,^{\circ}$ C (Sorptomatic 1990, Thermo Electron, Milan, Italy). Before N₂ adsorption, each sample was degassed under vacuum at 200 $^{\circ}$ C, for 4 h. Thermogravimetric analysis (TGA) was carried out in air flow (100 mL/min) using a temperature rate of 10 $^{\circ}$ C/min in the temperature window of 25–1000 $^{\circ}$ C (SDT Q600, TA Instruments, New Castle, DE, USA). Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and energy dispersive X–ray (EDX) analysis were performed on a HITACHI HD-2700 STEM microscope (Hitachi, Tokyo, Japan) operating at 200 kV. Catalyst samples were grounded manually by mortar and pistil, and then homogeneously dispersed by sonication (5 min) in ethanol before image acquisition.

Temperature programmed reduction (TPR) was performed with a TPDRO 1100 Series instrument (Thermo Scientific, Milan, Italy), equipped with a TCD detector. Approximately 0.05 g of NiO/Oxide-SiO₂ catalyst precursor was placed in the quartz tube reactor (10 mm i.d.), cleaned with Ar for 30 min, at 30 °C, and then heated up to 1100 °C (10 °C/min), using 10.7 vol.% H₂ in Ar (20 mL/min).

Temperature programmed desorption of either H₂ (H₂-TPD) or CO₂ (CO₂-TPD) were carried out by means of the same instrument as for the TPR runs. In case of H₂-TPD analyses, catalyst samples of 0.1 g were subjected to the following sequence of pretreatment steps: (i) in-situ reduction at 550 °C of the previously reduced catalyst, in 20 mL/min $(H_2 + Ar)$ mixture (10.7 vol.% H_2) for 90 min; (ii) cleaning and cooling to 30 °C under Ar flow for 30 min; (iii) chemisorption of H₂ at 30 °C until saturation (60 min) using the same 10.7 vol.% H₂ in Ar gas mixture (20 mL/min); (iv) cleaning under Ar flow at 30 °C, for 30 min, in order to remove the remaining H₂ in the reactor space. H₂-TPD profiles were recorded using the incorporated TCD detector, under Ar flow (20 mL/min) with a temperature rate of 10 °C/min from room temperature to 1100 °C. For CO₂-TPD runs, the pretreatment of catalyst samples (0.1 g) was performed similar to the H₂-TPD experiments, except for step (i), the in-situ reduction step was performed at 300 °C for the previously reduced catalyst, for 30 min (similar to the in-situ reduction performed prior to catalytic activity tests), and (iii), the CO₂ chemisorption step, in which a gas mixture of 10.5 vol.% CO₂ in Ar (20 mL/min) was adsorbed at 30 °C. CO₂-TPD profiles were recorded using the incorporated TCD detector, as well as a coupled quadrupole MS (QMS, Pfeiffer Vacuum, Asslar, Germany), under Ar flow (20 mL/min) with a temperature rate of 10 °C/min, up to 1100 °C.

3.4. Catalytic Activity Tests

The catalytic performance of the Ni/Oxide-SiO₂ samples in the methanation of CO₂ was evaluated by temperature programmed reaction runs (TPRea) in the temperature window of 30–350 $^{\circ}$ C (2 $^{\circ}$ C/min), as well as stability tests performed at 250 $^{\circ}$ C for 6 h. Reaction runs were performed under plug flow conditions, at 4650 h^{-1} GHSV, using a feed of 31 mL/min, consisting in 6.6% CO₂, 34.5% H₂, and Ar as balance gas (CO₂:H₂ = 1:5.2). Catalyst samples of 0.1 g diluted with 0.05 g of SiO_2 were placed in the quartz tube reactor (i.d. 10 mm) of the TPDRO 1100 Series equipment, while effluent gases (reaction products and unreacted components) were continuously monitored by means of the coupled MS (mass numbers 2, 15, 18, 28, and 44 corresponding to H₂, CH₄, H₂O, CO, and CO_2 , respectively). In order to avoid interference with other components, in case of methane, mass number 15 was chosen instead of 16 [51], while signal for mass number 28 was corrected in order to remove the contribution of mass number 44. The output MS signals for the species of interest were used to calculate the conversion of CO_2 and the selectivity in CH_4 (the rest being CO), considering that the intensity of the signals is proportional to the concentration of the species in the mixture. The following relationships were used for the evaluation of catalytic parameters:

$$CO_{2} \text{ conversion}: X_{CO2} = \left(1 - \frac{I_{CO2}^{out}}{I_{CO2}^{out} + I_{CH4}^{out} + I_{CO}^{out}}\right) \times 100, \ (\%)$$
(1)

CH₄ yield :
$$Y_{CH4} = \frac{I_{CH4}^{out}}{I_{CO2}^{out} + I_{CH4}^{out} + I_{CO}^{out}} \times 100, (\%)$$
 (2)

CH₄ selectivity :
$$S_{CH4} = \frac{Y_{CH4}}{X_{CO2}} \times 100$$
, (%) (3)

4. Conclusions

Ni/Oxide-SiO₂ (oxide: MgO, CeO₂, La₂O₃) catalyst samples were prepared by successive impregnation of silica matrix, in order to first deposit the supplementary oxide, and then Ni. The characterization techniques revealed the similar multimodal porous structure of all catalysts, the amorphous nature of silica and the existence of Ni in metallic state. The addition of MgO and La_2O_3 leads to better dispersion of Ni on the catalysts surface, reflected in significantly increased number of active sites for H₂ activation. Ni/LaSi and Ni/CeSi present a larger proportion of moderate strength basic sites for CO₂ activation compared to Ni/Si, while Ni/MgSi lower. CO2 methanation was performed in the temperature range of 30–350 °C, and at atmospheric pressure. The best catalytic activity was obtained for Ni/LaSi: CO₂ conversion of 83%, and methane selectivity of 98% at temperatures as low as 250 °C. This very good catalytic performance is related to its improved capacity to activate both hydrogen and carbon dioxide, but also to the combined effect of Ni nanoparticles stabilization inside the medium sized mesopores, and the facilitated access of reagents to active centers due to the large mesopores. The used catalysts preserved the multimodal pore structure with approximately the same pore size for the low and medium mesopores. Except for Ni/CeSi, no particle sintering occurs and no carbon deposition was observed for any of the tested catalysts.

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