

# Characterization of Ni/SiO<sub>2</sub> and Ni/Li-SiO<sub>2</sub> catalysts for methane dry reforming

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## Abstract

In this study, catalysts based on nickel (15 wt.% Ni) supported on SiO<sub>2</sub> and silica modified by Li addition (0.1 and 1 wt.% Li) were characterized for their application in dry reforming with carbon dioxide. Catalysts were characterized by using hydrogen chemisorption, H<sub>2</sub>-TPR, XRD, DRIFTS and dry reforming reaction tests. The effect of the Li loading on the catalyst structure, the catalytic activity, stability and the deactivation rate by carbon formation are reported. The Li addition on the SiO<sub>2</sub> support increases noticeably the resistance to deactivation by carbon deposition.

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**Keywords:** Nickel catalysts; Lithium addition; Catalyst characterization; Methane dry reforming

## 1. Introduction

The natural gas reforming by means of dry reforming has achieved recently great importance as a way of hydrogen production through synthesis gas attainment. The methane dry reforming (DR) is an important route in the use of biomass as renewable energy source for biogas conversion (60% CH<sub>4</sub> and 40% CO<sub>2</sub>) to synthesis gas. Supported Ni catalysts constitute materials habitually used for these reactions since they are active and of low cost. The most important difficulties presented by the Ni catalysts commercially used in the natural gas reforming is the high carbon formation rate and the sintering of the metallic phase which produces a low stability in time. For this reason, several studies were performed to improve the performance and the useful lifetime of Ni catalysts [1–4]. The stability of Ni catalysts has been

improved by means of the addition of basic supports and promoters. Recent works have found that the alkali addition (Na, K, Li) modifies the Ni active phase inhibiting the activity and the deactivation by carbon formation [5–7]. In particular, Ito et al. [8] have reported catalysts of Ni doped with Li that present very good performance for its potential application to fuel-cell reactor (molten carbonate fuel cell, MCFC) to produce synthesis gas from methane and carbon dioxide. The conventional nickel electrode catalysts without lithium show rapid deactivation, but the catalyst modified by lithium presents good performance in the MCFC reactor. Studies performed in our laboratory showed that the addition of alkaline metals to Ni/SiO<sub>2</sub> catalysts [9] inhibited the carbon deposition weakly affecting the catalytic activity for the methane reforming with CO<sub>2</sub>. For this reason, the aim of this work is to know the behavior of Ni/SiO<sub>2</sub> catalysts exposed to “dry reforming” when the support is modified by the addition of variable Li amounts and also to evaluate the effect of this addition on the catalyst structure.

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## 2. Experimental

The modified supports were prepared by impregnation of the silica (Si) (Kali-Chemie AF 125) with aqueous solution of lithium nitrate (Panreac) at concentrations of 0.1 and 1 wt.% Li (SiLi0.1 and SiLi1). The nickel catalyst was prepared by incipient wetness technique with an aqueous solution of nickel nitrate adjusted to obtain catalyst with 15 wt.% Ni content. After each impregnation step, solids were oven dried at 120 °C and calcined at 500 °C for 4 h.

Catalysts were characterized by H<sub>2</sub> chemisorption, temperature programmed reduction (TPR), X-ray diffraction (XRD), catalytic and stability tests in dry reforming (DR) and infrared spectroscopy (IR).

The experimental equipment used in catalytic tests was described in a previous paper [10]. Catalysts were tested in order to estimate their activity and selectivity for the methane dry reforming (DR). The reaction was carried out at atmospheric pressure, feed flow of 130 cm<sup>3</sup> min<sup>-1</sup>, reaction temperatures within the range of 600–700 °C, composition of the feed mixture: N<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub> = 6/1/1. Prior to reaction, catalysts were reduced in hydrogen stream at 700 °C for 2 h. The catalyst weight was 0.050 g and the grain size between 0.12 and 0.15 mm. The stability test was carried out at constant temperature (700 °C), for 50 h in DR reaction. The stability was evaluated in terms of the activity coefficient  $a_{\text{CH}_4}$ , which represents the ratio between the consumption rate of CH<sub>4</sub> at time  $t$  h in reaction and the initial consumption rate. The feed and effluent of reactor were analyzed in a Shimadzu GC-8A gas chromatograph with a TCD detector connected on line to the reactor via gas sampling valve. The separation of H<sub>2</sub>, CH<sub>4</sub> and CO was performed on a column containing 5A Molecular Sieve, whereas CO<sub>2</sub> was analyzed on a column containing Porapak Q, at 40 °C.

The BET surface and pore volume distribution were measured by nitrogen adsorption at -77 K using an Accusorb 2100E Micromeritics analyzer. Samples were outgassed at 100 °C for 12 h before adsorption.

TPR experiments were carried out in a conventional equipment (Quantachrome Corporation, Quantasorb QS JR-2), with samples of 0.02 g heated from room temperature to 1000 °C at a rate of 10° min<sup>-1</sup> using a 5% (v/v) H<sub>2</sub>/Ar gas flow at a rate of 22 cm<sup>3</sup> min<sup>-1</sup>.

Metallic surface areas were measured by hydrogen adsorption using the dynamic pulse method with a Pulse

Chemisorb 2700 Micromeritics. The Ni surface area was determined assuming Ni/H = 1 and 6.33Å<sup>2</sup> for the area occupied per nickel atom.

A Philips PW 1740 X-ray diffractometer with Cu Kα radiation was used to identify the crystalline phases of catalysts in the range  $2\theta = 20\text{--}80^\circ$  and with scan speed of 0.02° min<sup>-1</sup>.

The amount of carbonaceous deposits was analyzed by temperature-programmed oxidation (TPO). Experiments were carried out in a Shimadzu TGA-50H under air stream (20 cm<sup>3</sup> min<sup>-1</sup>) by increasing the temperature from 25 to 800 °C at a heating rate of 10° min<sup>-1</sup>.

Tests of carbon deposition from methane were performed with a CH<sub>4</sub>/He: 1/1 flow at 50 cm<sup>3</sup> min<sup>-1</sup> at 500 °C.

DRIFTS spectra were obtained in the same conditions as in previous works [11,12] in a Fourier transform Nicolet 5DXC instrument (4000–400 cm<sup>-1</sup>) in the diffuse reflectance mode. The sample was placed in powdered form in the sample holder. The resolution was 2 cm<sup>-1</sup>, and a satisfactory signal-to-noise ratio was obtained by accumulating 200 scans. Samples were heated in flowing N<sub>2</sub> at 500 °C for 2 h and then cooled to room temperature, and a spectrum was collected. Samples were subsequently heated at 500 °C for 2 h under hydrogen flow, and after the reduction treatment, samples were flushed with N<sub>2</sub>. The samples were then cooled down to room temperature in flowing N<sub>2</sub>, and a new spectrum was collected.

Infrared spectroscopy studies of carbon monoxide adsorption were performed after the reduction treatment. A CO stream was diluted with helium. The spectrum of CO was directly computed from spectra recorded before CO adsorption and after flushing out with excess N<sub>2</sub>.

## 3. Results and discussion

### 3.1. Morphological properties

Table 1 summarizes morphological properties of catalysts under study (BET surface area and pore volumes), taking properties of pure SiO<sub>2</sub> as reference. Values of BET surface and pore volumes reveal that the addition of 1% Li to the silica produces significant textural changes in the support. Pereira and Martin [13] related the silica sintering with the formation of superficial silicates in Ni/SiO<sub>2</sub> catalysts promoted by alkali.

Table 1  
Characterization of the studied catalysts

Catalysts	Li (wt.%)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$S_{\text{Ni}}$ (m <sup>2</sup> g <sub>Ni</sub> <sup>-1</sup> )
SiO <sub>2</sub>	0	283	0.85	–
NiSi	0	209	0.51	34
NiSiLi0.1	0.1	215	0.55	14
NiSiLi1	1	83	0.35	4

BET surface area, metallic surface and pore volumes.

Results of  $H_2$  chemisorption shown in Table 1 indicate that the Ni base catalyst is characterized by a higher chemisorption capacity and metallic surface. The Li addition reduces the adsorption capacity, which indicates a decrease of the superficial metallic area ( $S_{Ni}$ ) that could be related to changes in the Ni dispersion with respect to NiSi catalyst. For NiSiLi0.1, when comparing with the NiSi catalyst, a 60% decrease appears in the  $S_{Ni}$  value while in the NiSiLi1,  $S_{Ni}$  decreases 88% if compared with NiSi. It is probable that apart from the fact that in NiLi catalysts there are changes in the metallic particle dispersion, also the decrease in the adsorption of  $H_2$  may be due to the presence of Ni particles decorated by the alkaline element as it has been reported by other authors [14–17].

### 3.2. Infrared spectroscopy

As it was demonstrated in previous works [11,12], DRIFTS spectra in inert atmosphere of catalysts previously reduced in hydrogen atmosphere at 500 °C indicate that lithium interacts with the support modifying its characteristic bands, particularly for the catalyst modified with 1 wt.% Li. The Li introduction produces a decrease of the band intensity corresponding to OH groups at 3700  $cm^{-1}$  (this spectrum part is not presented) attributed to the formation of O–Li groups due to slightly acid OH groups [13].

Fig. 1 shows that between 2200 and 1500  $cm^{-1}$  there exists an important attenuation of the signal for the NiSiLi0.1 sample and the complete disappearance of the

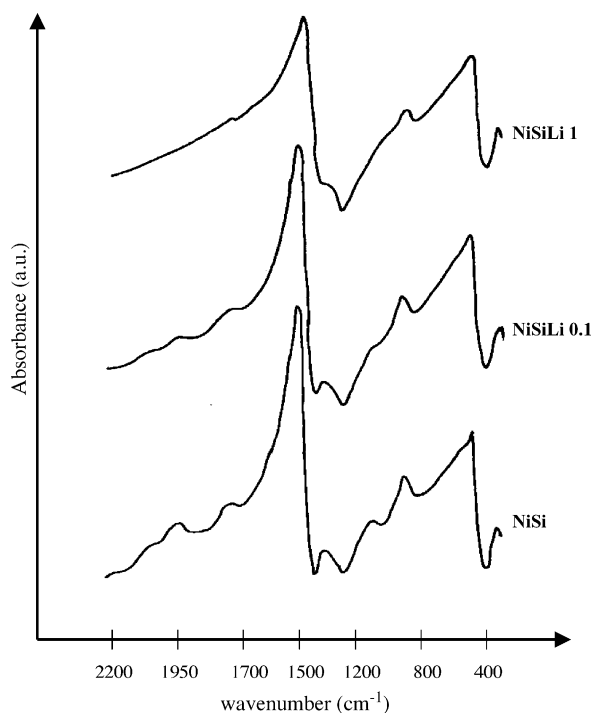


Fig. 1. DRIFTS spectra of NiSi, NiSiLi 0.1 and NiSiLi 1 catalysts after 1 h reduction at 700 °C, recorded at room temperature.

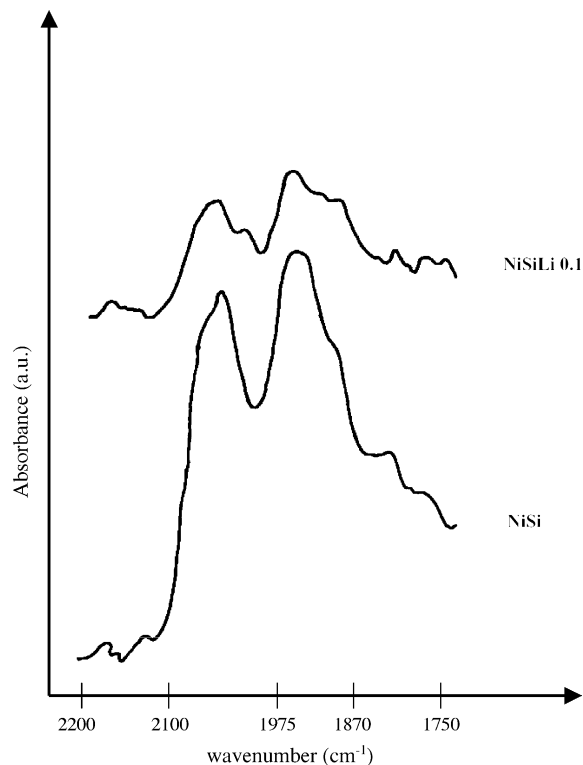


Fig. 2. DRIFTS spectra of NiSi and NiSiLi 0.1 catalysts after admission of CO and following outgassing for 15 min at room temperature.

NiSiLi1 sample from the silica characteristic bands, confirming the hypothesis that lithium modifies the silica structure. The absorption band, peaking at 1360  $cm^{-1}$ , has been ascribed to transverse (TO) and longitudinal (LO) optical modes of the silica support [18].

Fig. 2 shows CO infrared spectra irreversibly adsorbed at 25 °C for NiSi and NiSiLi0.1 samples. For the NiSi base catalyst the following characteristic bands are observed: at 2080  $cm^{-1}$  a band attributed to sub-carbonyl species ( $Ni(CO)_x$ ,  $x = 2$  or 3), CO adsorbed linearly at  $Ni^{2+}$  (2040  $cm^{-1}$ ) and a bridged CO species [19]. For the NiSiLi0.1 sample a decrease in the relative intensities of chemisorbed CO is seen without noticing a modification in the position of the adsorption bands, in agreement with the decrease of the metallic surface. The shoulder appearing around 1920  $cm^{-1}$  in the NiSiLi0.1 catalyst may be explained in terms of an increased electronic density of Ni given by the interaction with the lithium. The frequency shift of the stretching vibration of CO is mainly due to the influence of the support (modified by lithium) on the constant force of the CO–Ni bond [20]. Similar results were obtained in platinum catalysts supported in zeolites modified by Cs and Li [21].

The spectrum of the NiSiLi1 catalyst could not be obtained due to its low CO adsorption capacity. The total inhibition of this lithium doped catalysts suggests that the surface is blocked for CO adsorption, some authors propose that  $Li^+$  ions interact with the NiO lattice during air

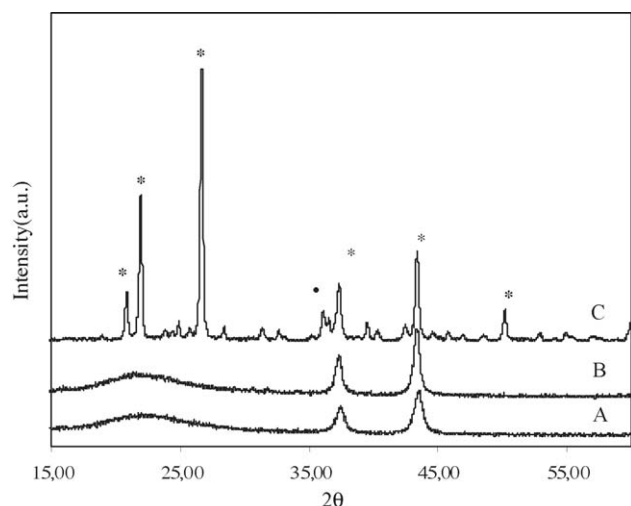


Fig. 3. XRD diffraction patterns; (A) NiSiO<sub>2</sub> fresh catalysts Calcined at 450 °C (NiSi); (B) Ni-Li/SiO<sub>2</sub> fresh catalyst calcined at 450 °C (NiSiLi1); (C) Ni-Li/SiO<sub>2</sub> spent catalyst, reaction temperature 700 °C (NiSiLi1); (\*) correspond to Li<sub>2</sub>SiO<sub>3</sub> from PCPDFWIN 88-1535; correspond to Ni<sub>2</sub>SiO<sub>4</sub> from PCPDFWIN 83-2071; correspond to NiO from PCPDFWIN 78-0643.

calcinations, giving rise to the formation of a Li–Ni–O mixed phase. Thus, Li<sup>+</sup> and NiO form Li<sub>x</sub>Ni<sub>(1-x)</sub>O solid solution [22].

This result could indicate that nickel properties that remain exposed have not been modified by lithium effect.

### 3.3. X-ray diffraction

The characterization of fresh catalysts by XRD does not allow to find differences among them. This can be observed in diffractograms A and B of Fig. 3 where the two characteristic peaks assigned to NiO and to SiO<sub>2</sub> are identified. As regards XRD of post-reaction catalysts (NiSi, NiSiLi0.1 and NiSiLi1), the only diagram that presented differences compared with the fresh sample was the NiSiLi1 (diffractogram C), in which not only the NiO was observed, but also LiSiO<sub>3</sub> and Ni<sub>2</sub>SiO<sub>4</sub> species were detected in agreement with literature. This fact demonstrates the formation of lithium and nickel metasilicates when temperatures are higher than 650 °C [23,24].

### 3.4. Temperature programmed reduction (H<sub>2</sub>-TPR)

The reducibility of catalysts was characterized by TPR experiments. Fig. 4 shows TPR profiles of different samples. The NiSi catalyst presents two reduction peaks with maximums at 470 and 670 °C. The first of them at 470 °C is found in the zone assigned by literature to NiO species of low interaction with the support. The signal at 670 °C is attributed to a nickel oxide interacting chemically with the support as cited by some authors [25,26]. It is well known that compounds of strong interaction with the support, as it is observed in the NiSi base catalyst, provide high resistance to sintering and higher metallic dispersion in

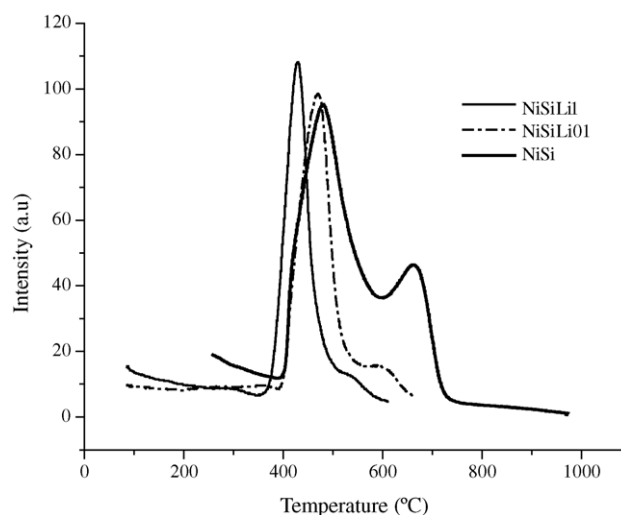


Fig. 4. Temperature programmed reduction (TPR) profiles for NiSi, NiSiLi0.1 and NiSiLi1 catalysts. For the conditions, see the text.

the catalyst [27,28]. This is in agreement with values of the metallic area shown in Table 1.

In catalysts modified by Li, a shift of the reduction signals to lower temperature values is observed. This would indicate an increase in the Ni reducibility and that the same metallic species are maintained qualitatively as in the NiSi base catalyst. Table 2 shows the H<sub>2</sub> consumption of the NiSi base catalyst and of the catalysts promoted by Li for the signals at different temperatures. With the Li addition, a decrease in H<sub>2</sub> consumption at low temperature is observed (Peak 1) but changes are more evident in the peak at high temperature (Peak 2). This would indicate that the Li presence inhibits the interaction Ni-support.

Then, reduction tests were carried out in the samples of catalysts by using post reaction DR (700 °C). Reduction profiles obtained for NiSi and NiSiLi0.1 samples did not undergo changes if compared with the fresh samples, but differences were well marked for the NiSiLi1 catalyst. Table 3 shows that while the maximum temperature of Peak 1 is not different, the peak distribution is inverted with a considerable increase of Peak 2 in relation to Peak 1 (the total area is constant). The increase of Peak 2 suggests the formation of a species of strong interaction under reaction conditions.

So far, results obtained by TPR, XRD and DRIFTS techniques indicate that in catalysts modified by lithium

Table 2  
Temperature programmed reduction (TPR) results for NiSi, NiSiLi0.1 and NiSiLi1 catalysts

Catalyst	Temperature (°C)		H <sub>2</sub> consumption (a.u.)	
	Peak 1	Peak 2	Peak 1	Peak 2
NiSi	479	665	11828	5705
NiSiLi0.1	471	603	6845	1730
NiSiLi1	427	541	5822	n.d.

For the conditions, see the text.

Table 3  
Temperature programmed reduction (TPR) results for NiSiLi1

Catalyst	Temperature (°C)		H <sub>2</sub> consumption (a.u.)	
	Peak 1	Peak 2	Peak 1	Peak 2
NiSiLi1 (fresh)	427	541	5822	n.d.
NiSiLi1 (spent)	436	620	1376	4721

Fresh and spent catalyst (post reaction DR).

addition, Li<sub>2</sub>SiO<sub>3</sub> in the support and two metallic species (NiO of low interaction and Ni<sub>2</sub>SiO<sub>4</sub> of high interaction with the support) are present.

### 3.5. Catalytic performances

The catalytic behavior of these materials in methane reforming with CO<sub>2</sub> (DR) at 700 °C is compared in Figs. 5 and 6. In these figures CO<sub>2</sub> and CH<sub>4</sub> conversion as a function of reaction time are represented. The NiSi base catalyst (Fig. 5) presents the highest conversion values, noticing that CO<sub>2</sub> conversion starts with 77% and falls up to a value of 61% after 50 reaction hours. The methane conversion decreases in the same period of time from 68 to 46%, which produces a H<sub>2</sub>/CO ratio approximately constant and equal to 1 as it is shown in Table 4. The addition of 0.1% Li (Fig. 6) causes a marked conversion decrease in correspondence with the variation presented by these catalysts on their metallic surface.

Table 4 shows data of the reaction rate expressed as CH<sub>4</sub> molecule per time unity by Ni atom. In order to minimize heat transport effects, the supported Ni catalysts were diluted with α-Al<sub>2</sub>O<sub>3</sub> (1:10). Interphase and intraparticle diffusional resistances were strictly limited under these conditions. We observe that the reaction rate values (molecular CH<sub>4</sub>/at Ni s<sup>-1</sup>) increase for catalysts promoted by Li with respect to the NiSi base catalyst. This means that the reforming activity expressed by active site of Ni is higher than catalysts modified by Li.

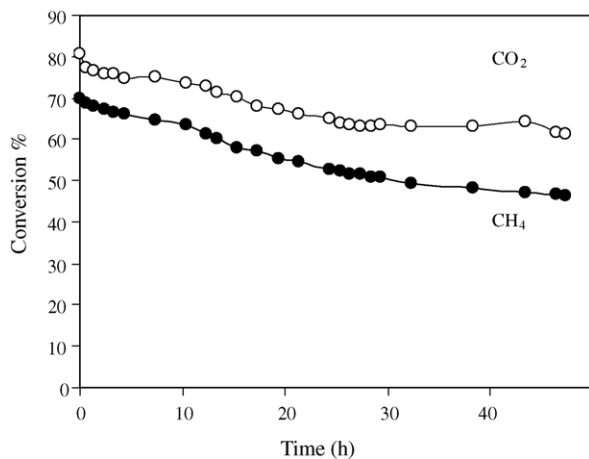


Fig. 5. Results of the catalytic activity of NiSi catalyst at 700 °C. For the conditions see the text (CO<sub>2</sub> conversion ○, CH<sub>4</sub> conversion ●).

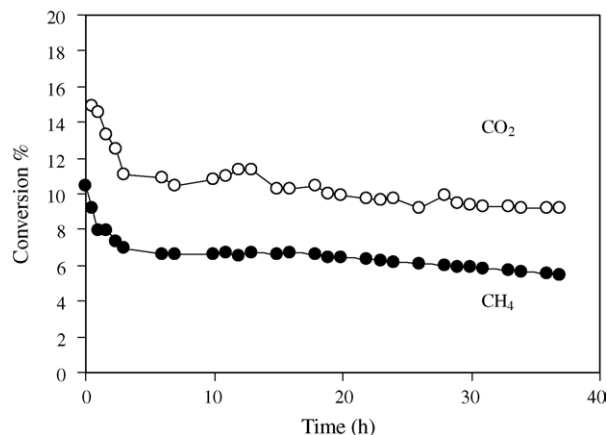


Fig. 6. Results of the catalytic activity of NiSiLi0.1 catalyst at 700 °C. For the conditions see the text (CO<sub>2</sub> conversion ○, CH<sub>4</sub> conversion ●).

In the same table it is observed that the selectivity to CO is lower in catalysts modified by Li than in the NiSi base catalyst. As it was reported by Pereira and Martin [13], the lithium addition systematically produces the formation of carbon dioxide and consequently it is expected that the increase in Li content inhibits the selectivity to CO and leads to a higher selectivity to CO<sub>2</sub>. This is common for alkaline promoters due to the relative basicity of this modifier. Consequently, the CO<sub>2</sub> increase would contribute to carbon gasification according to the inverse of the Boudouard reaction ( $C + CO_2 \rightarrow 2CO$ ).

The temperature effect within the range of 600–700 °C on the activity of NiSi and NiSiLi0.1 was determined by means of Arrhenius equation, thus indicating an apparent activation energy value of 40 kJ mol<sup>-1</sup> for the NiSi catalyst and a value of 53 kJ mol<sup>-1</sup> for the NiSiLi0.1 sample. Since the difference estimated between these apparent activation energy values is not so marked, it is possible to infer that there would not be changes in the reaction mechanism.

With respect to stability tests, Fig. 7 shows results of the evolution of the activity coefficient  $a_{CH_4}$  as a function of the

Table 4

Reaction rate [molecular CH<sub>4</sub>/at.Ni.s<sup>-1</sup>], H<sub>2</sub>/CO ratio and selectivity of CO (S CO (%) = [CO<sub>out</sub>/(CO<sub>2 in</sub> + CH<sub>4 in</sub>) × 100]) for dry reforming of methane for the studied catalysts

Catalysts	T (°C)	Reaction rate (molecular CH <sub>4</sub> /at Ni s <sup>-1</sup> )	Ratio	
			H <sub>2</sub> /CO	S CO%
NiSi	600	5	1.0	90
	650	7	1.0	96
	700	9	1.0	96
NiSiLi0.1	600	14	0.8	73
	650	19	1.0	93
	700	21	1.1	98
NiSiLi1	600	12	0.7	36
	650	20	0.9	76
	700	26	1.0	93

Feed flow composition N<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub> (6:1:1). The catalyst weight was 0.050 g and the grain size between 0.12 and 0.15 mm.

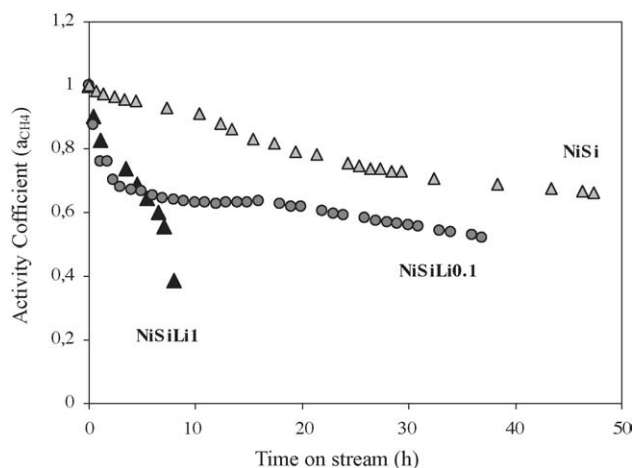


Fig. 7. Stability test of the catalysts at 700 °C ( $\Delta$ , NiSi,  $\circ$ , NiSiLi0.1 and  $\blacktriangle$  NiSiLi1).

hours in reaction at 700 °C. The NiSiLi1 catalyst suffers a strong deactivation in less than 10 h reaction while NiSiLi0.1 and NiSi catalysts present higher stability throughout time at equal temperature.

### 3.6. Thermogravimetric analysis

By analyzing post-test stability samples by thermogravimetric techniques so as to determine the carbon content by oxidation at programmed temperature (TPO), it was possible to observe that the NiSi catalyst presents an important carbon content (6 wt.%) while catalysts with Li do not contain practically carbonous deposits (Table 5). It is known that the carbon formation whisker type on Ni catalysts needs a minimum ensemble of 7 Ni atoms formed by particles of larger size than 5 nm and must fulfill with a C/Ni<sup>s</sup> ratio between 10 and 20 [29]. Probably, lithium avoids the minimum ensemble necessary for this development of filaments. Since TPO results from the post reaction samples we can conclude that the carbon deposition doesn't cause the deactivation for the NiSiLi1 catalyst (Fig. 7). With respect to sintering, although it was not evaluated in the present work, other bibliographic sources demonstrate that the morphological changes and deactivation mechanism of alkali-promoted Ni/SiO<sub>2</sub> in CO hydrogenation indicate that the alkali ions, at least when the atomic ratio Alkali/Ni does not exceed 0.15, prevent nickel sintering [30]. The role of alkali ions would be to reduce the mobility of subcarbonyl species Ni(CO)<sub>x</sub>, therefore slowing down the sintering process.

Table 5  
Carbon content (wt.%) on NiSi, NiSiLi0.1 and NiSiLi1 catalysts after 50 h of DR reaction

Catalysts	Carbon content (wt.%)
NiSi	6.17
NiSiLi0.1	0.03
NiSiLi1	0.03

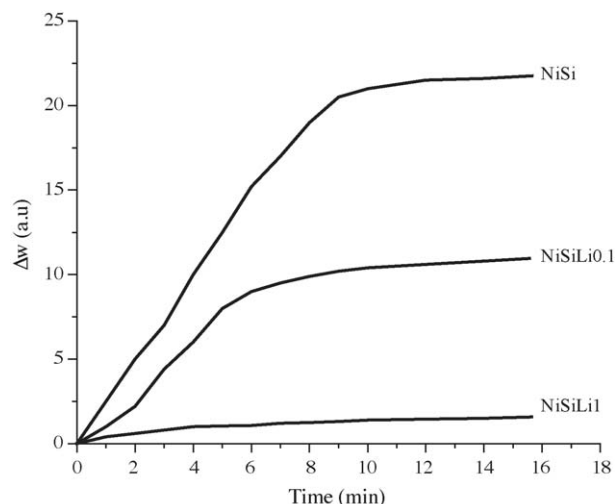


Fig. 8. Rate of carbon deposition for NiSi, NiSiLi0.1 and NiSiLi1 catalysts. Feed composition He/CH<sub>4</sub> 1:1, temperature 500 °C.

In our case, the NiSiLi1 catalyst overcomes this ratio (alkali/Ni = 0.5), and for this reason the sintering contribution is not discarded. This fact together with the evidence of superficial Ni loss by Ni<sub>2</sub>SiO<sub>4</sub> formation (Fig. 3) would be the responsible for the observed deactivation.

Since the CH<sub>4</sub> decomposition constitutes a possible route of carbon deposition in reaction conditions of dry reforming, in this study the deposition rate from methane was determined at 500 °C. Results of Fig. 8 indicate that the Li addition produces a lower deposition rate. For NiSiLi1 the deposition is practically null, but for NiSiLi0.1 the initial rate and the total deposited carbon content is reduced to almost 50% if it is compared with the NiSi base catalyst. This effect, added to the CO<sub>2</sub> presence in the reaction medium and the capacity of alkaline modifiers of favoring the gasification of carbonous deposits, would contribute to inhibit the deactivation by carbon deposition during dry reforming in catalysts promoted by Li.

## 4. Conclusions

The main conclusions of the present work can be summarized as follows:

- The Li introduction in Ni/SiO<sub>2</sub> catalysts generates morphological and textural alterations of the support. The Ni/SiO<sub>2</sub> catalyst is characterized by a higher capacity of chemisorption and metallic surface. This could indicate, as some authors state, that in catalysts with lithium the alkaline element could be placed decorating nickel particles, making difficult the adsorption process.
- Results of TPR, XRD and DRIFTS tests for catalysts with lithium confirm the Li<sub>2</sub>SiO<sub>3</sub> presence in the support and the existence of two metallic species; NiO of low interaction and Ni<sub>2</sub>SiO<sub>4</sub> of high interaction with the support.

- The NiSiLi1 catalyst presents a marked activity decrease with respect to the NiSi base system, in correspondence with the variation presented by this catalyst on its metallic surface.
- In reaction conditions, it was observed that NiSiLi1 presented the lowest catalytic stability, which would be the consequence of Ni superficial loss by formation of Ni<sub>2</sub>SiO<sub>4</sub> species, as it was demonstrated by the TPR and XRD of post-reaction catalyst.
- Since the difference between apparent activation energy values estimated for all catalysts is not significant, it is inferred that there is no change in the reaction mechanism due to lithium presence.
- The NiSiLi0.1 catalyst has good specific activity and stability for dry reforming (DR), mainly evaluating the decrease in carbon deposition. This smaller carbon deposition from methane together with the capacity of favoring the gasification of carbonous deposits from CO<sub>2</sub> present in the dry reforming reaction would contribute to inhibit the deactivation by carbon deposition.

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