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Influence of calcium content in Ni/CaO/γ-Al_2O_3 catalysts for CO_2-reforming of methane

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Abstract

In order to improve the thermal stability and carbon-deposition resistance of the Ni/γ-Al_2O_3 during the reforming of methane with carbon dioxide, the catalyst was modified by adding an alkaline earth (CaO). The catalysts were prepared by successive impregnation of Ni and Ca on alumina, varying the impregnation order. It was found that calcium decreases the sintering resistance of the support and blocks the small pores, especially when it is added above the nickel. It has also been reported that calcium competes with nickel in the interaction with the support, favoring the formation of nickel species being more easily reducible, when it is added first. In catalytic tests, it has been showed that, in low quantities, calcium increases the catalytic conversion, probably due to attraction effects between CaO and CO_2, while in high quantities, calcium decreases the catalytic activity, this effect being associated with the increase in electron density of the catalyst.

Keywords: CO_2-reforming of methane; Ni/γ-Al_2O_3; Calcium; Electrostatic attraction

1. Introduction

The CO_2-reforming of methane consists in the reaction of methane with carbon dioxide to produce hydrogen and carbon monoxide.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2,$$
$$\Delta H_{800\,^{\circ}C} = 62.2\,\mathrm{kcal/mol}$$

Owing to the 1:1 ratio of the products, this reaction has a potentially important role in industry, together with the steam-reforming reaction, in the generation of syngas with a more appropriate ratio for various reactions, such as methanol synthesis and Fisher–Tropsh synthesis, etc. This reaction also has environmental implications because both methane and carbon dioxide are greenhouse gases.

Several catalysts have already been studied, the transition metals of group VIII–B being the most active ones. Among these are the noble metals Rh, Pt, Ru and Ir and non-noble Ni [1–3]. Due to its availability and price, nickel is seen as the most suitable catalyst for the reaction [2]. However, under the conditions used, this reaction leads to a fast deactivation of this catalyst, mainly by the deposition of carbon at the active sites. Thus, there is great industrial interest in the development of stabilized nickel catalyst, usually by the addition of promoters that act on the reaction mechanism or simply on the adsorption of the reactants. Several ceramic supports for the metal have already been studied, showing that MgO offers resistance to deactivation by coke, while Al_2O_3, which achieves high rates of conversion, offers lower stability to coking [3–6].

It is showed here that calcium acts as a good nickel catalyst promoter in the reforming of methane,

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improving the coking stability by increasing electron density of the nickel and so decreasing its methane-dehydrogenating power [7–9]. Despite this, few studies have been done on the influence of the content of this promoter on catalysis of such reactions.

The work reported in this paper was an investigation of the effects of adding Ca and of the order of addition of Ca and Ni on the performance and stability of nickel catalysts supported on alumina for reforming of methane with carbon dioxide.

2. Experimental

Samples of catalysts with 8% (w/w) Ni have been prepared by successive impregnation of aqueous nickel nitrate (Aldrich Chemical Co.) and calcium nitrate (Analyticals Carlo Erba) solutions in a rota-evaporator, with solvent excess, over γ-alumina (Degussa) of 35–60 mesh granulation, at 60 °C until total evaporation of solvent. The order of nitrates addition was altered so as to obtain two series of catalysts with similar compositions, but different nickel and calcium distributions on the support. The samples were calcined under synthetic air flow at 550 °C for 5 h after each impregnation and at 750 °C for 5 h at the end of the process.

The Ni and Ca contents were determined by atomic adsorption spectrophotometry after the digestion of the catalysts in hydrofluoric and nitric acids. The specific surface area was determined by physical adsorption of nitrogen (BET), and the total volume and the pore average radius by nitrogen condensation and adsorption (Quantachrome Nova 2100). Temperature-programmed reduction (Micromeritics chemissorb 2705) were carried out to verify the interaction between the metallic phase of nickel and the support.

The catalytic tests were carried out in a fixed bed microreactor, with 100 mg of each sample at 650 °C in flows of 80 ml/min of each reactant (methane and carbon dioxide) at an absolute pressure of 1.0 bar. The reaction products were analyzed by gas chromatography (Varian 3300 with DCT). The samples were reduced in situ, at 800 °C for 3 h, under a flow of 40 ml/min of pure hydrogen.

Temperature-programmed desorption of carbon dioxide (TPD-CO_2) was used to find the influence of calcium on CO_2 adsorption at the catalyst surface. Each sample was activated at 300 °C in a stream of He. The adsorption of CO_2 was done in a pure CO_2 stream, and unadsorbed CO_2 was purged in a He stream. The analysis was carried out by heating the samples at 10 °C/min and in the He stream.

3. Results and discussion

Fig. 1 shows a decrease in the specific surface area of catalysts with calcium content increase, as a consequence of the reduced sintering resistance of the support caused by the presence of this ion. In the set of samples where calcium was added after nickel, the specific surface area is always smaller than in the set with the order reversed, due to the covering and blocking of catalyst pores by calcium oxide particles. This effect is less pronounced in the samples where calcium was added before nickel, because, in this case, calcium interacts with the support and becomes dispersed as calcium aluminate, with a smaller formation of agglomerates [10]. However, it is not completely avoided, as seen in Fig. 2, where the average pores radius increases with the rising of calcium content in both sample groups, owing to the fact that this blocking occurs preferentially in small pores. Here, it is observed once again that this deleterious effect is larger in samples where calcium is added over nickel (the porous average radius is larger), as a consequence of a greater deposition of CaO over the support. These effects, together, result in a decrease in the total pore volume of the catalyst.

Analysis of temperature-programmed reduction, as shown in Figs. 3 and 4, shows the influence of calcium ion on the interaction between nickel and the support.

When deposited on alumina, nickel tends to form basically two compounds, by different interactions with the support: nickel oxide and nickel aluminate. The segregated oxide, which requires little of energy for reduction, exhibits a weak interation with the support, being simply deposited on the catalyst surface, and it is easily reducible at temperatures above 350 °C. On the other hand, the aluminate phase results from a strong interaction between nickel and support, as it is a surface compound, and so the nickel is located in the support structure. Thus, the reduction

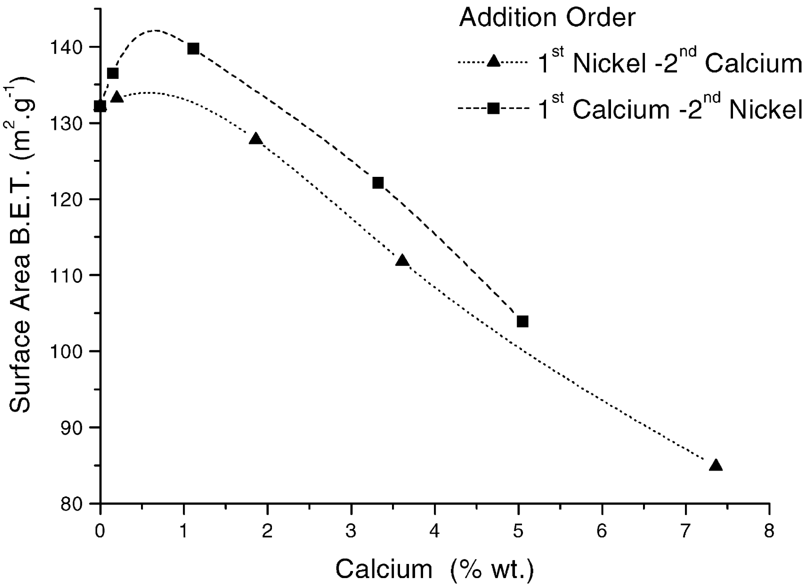

Fig. 1. Change in surface area BET with amount of calcium.

of this compound is more difficult and occurs at high temperatures [4].

From the results of temperature-programmed reduction of samples with addition of nickel before calcium, presented in Fig. 3, it can be seen that the predominant phase is that in which a strong interaction occurs between Ni and alumina, probably in the form of nickel aluminate. With this addition order, calcium does not exert a strong influence on the interaction between nickel and support, but only it is deposited in the pores in the agglomerate form, as has already been discussed. However, in samples

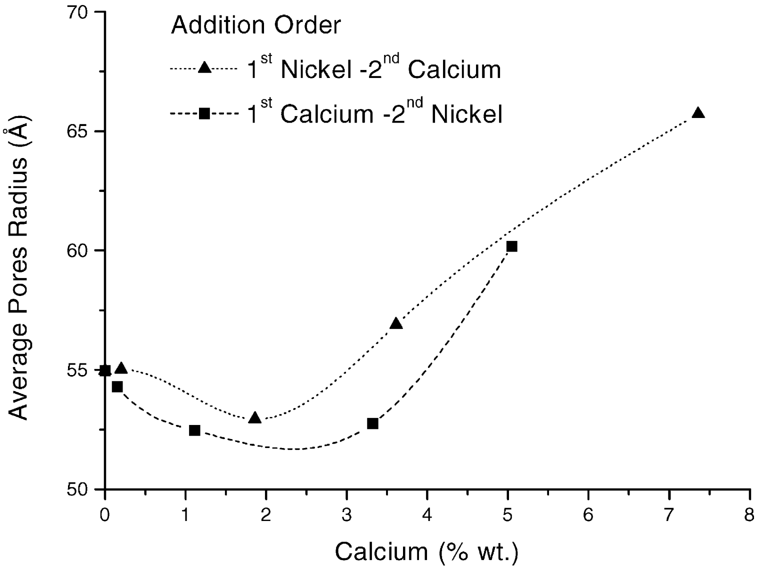

Fig. 2. Change in average pores radius with amount of calcium.

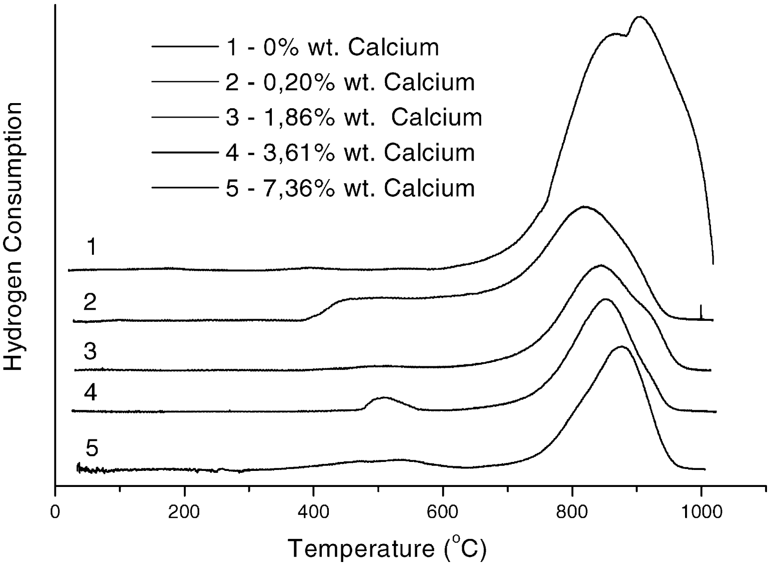

Fig. 3. Temperature-programmed reduction profiles of samples with addition order 1Ni2Ca.

with calcium contents over 3% (w/w) nickel compounds with a weaker interaction with the support are observed, reducing around 500 °C. This happens by nickel oxide segregation due to the great quantity of calcium on catalyst surface, which may form calcium aluminate.

It can be observed in Fig. 4 that, when calcium is added to the support before the active metal, the formation of nickel species with low interaction with the support is favored, due to the competition between nickel and calcium for interaction with alumina, this effect being evident in the sample with the biggest

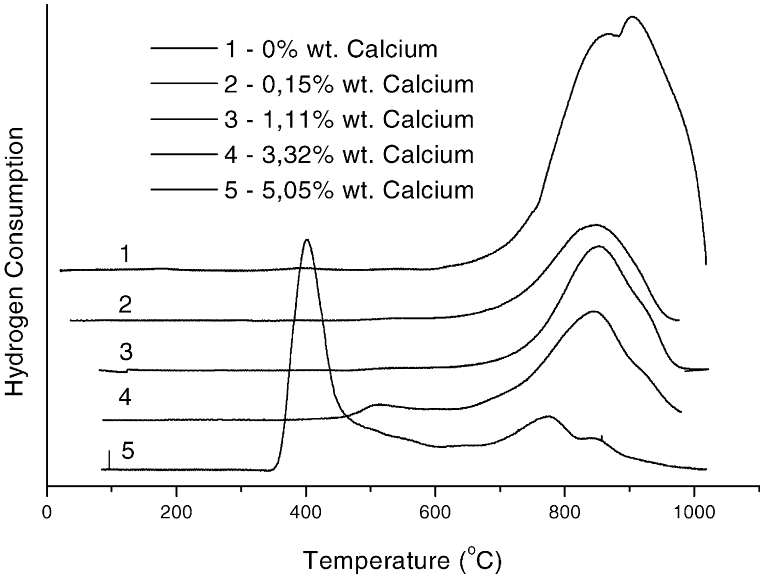

Fig. 4. Temperature-programmed reduction profiles of samples with addition order 1Ca2Ni.

calcium content (5.05%). Calcium will tend to form calcium aluminate, reducing the possibility of subsequent formation of nickel aluminate. The later will remain on the support as oxide agglomerate, which is reducible at lower temperatures. The formation of aluminate is intimately bound up with the phase of alumina present, as it involves migration of positive ions into the structure. Evidence for this can be seen in the literature, where it has been shown that aluminate formation, possible in the presence of γ-Al_2O_3 presence, practically does not occur with α-Al_2O_3, due to the difference in stability between these allotropic phases [3].

The degree of reduction (quantity of reduced nickel as a proportion of the total quantity present in the catalyst) also exhibits interesting features, as illustrated in Fig. 5. It strongly decreases with the addition of calcium to the catalyst, which may be associated with the specific area loss and the consequent decrease of the exposure of the nickel atoms exposition to reducing gas. However, it was found that, for the samples in which calcium was incorporated before nickel, the reduction level started to increase, from 1% Ca, more intensely than for the ones prepared in the reverse order. This is because, when calcium associates with the support in the form of calcium aluminate, the nickel compound will tend to form more easily reducible species. Conversely, when Ni is incorporated before calcium, the latter will tend to form big CaO agglomerates which may cover Ni^{2+} sites which are already more stable than in the first set of samples, making more difficult the reduction process.

Figs. 6 and 7 show that with both the direct and the reversed order of addition, the presence of calcium tends to raise the level of methane conversion into products up to a certain concentration of this ion in the catalyst, beyond which the conversion falls dramatically. When the calcium is added before the nickel, small Ca contents show a remarkable influence on the conversion values, as shown in Fig. 6. Thus, the addition of 0.15% calcium already takes the conversion value to the maximum level obtained for this sample.

For the catalysts prepared by the direct addition method (Fig. 7), calcium also promotes increased conversion rates, but in a less pronounced way than in the samples in which the metals were added in reverse order, with maximum rates obtained with a Ca concentration around 3.61%. At high calcium contents, the methane conversion drops to lower rates than those observed in the unpromoted sample.

Figs. 8 and 9 illustrate the variation of CO_2 and methane conversion after 20 h of reaction in relation to calcium content, for both orders of nickel and calcium addition. Two distinct patterns of conversions can be

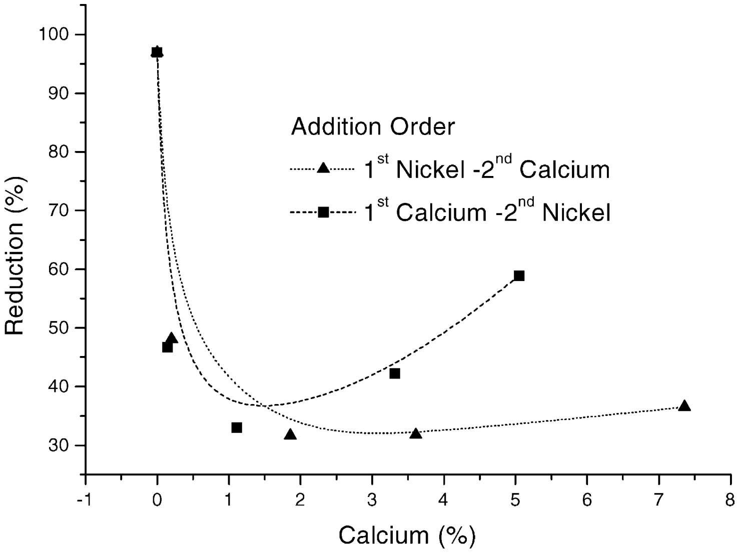

Fig. 5. Change in reduction degree with amount of calcium.

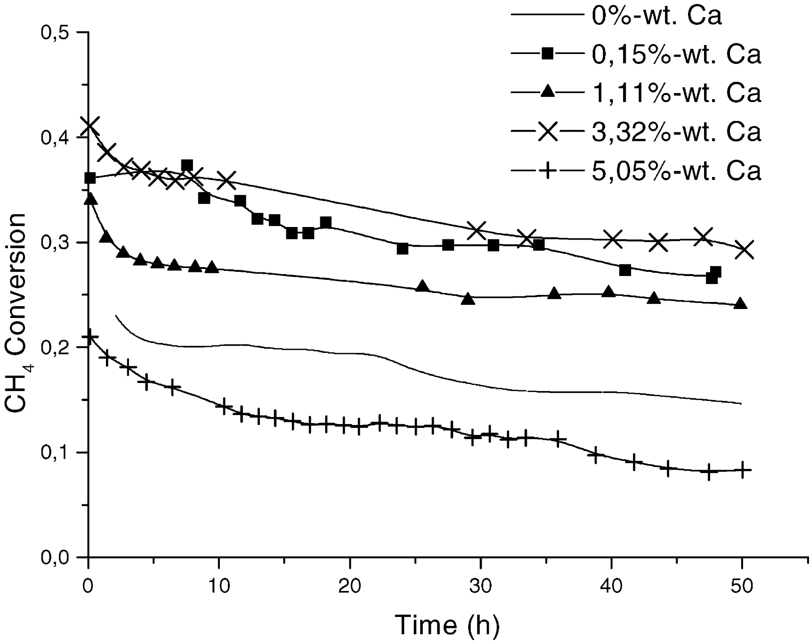

Fig. 6. Total methane conversion of 1Ca2Ni samples.

seen. At lower contents, the methane conversion is higher than that of carbon dioxide, an effect that inverts as the calcium content increases. This behavior is common to the two sets of samples, however, in the direct order of addition, it is less pronounced.

This behavior can be explained by the simplified mechanism of reaction [1]:

Step 1 : $CH_4 \rightarrow C + 2H_2$

Step 2 : $CO_2 + C \rightarrow 2CO$

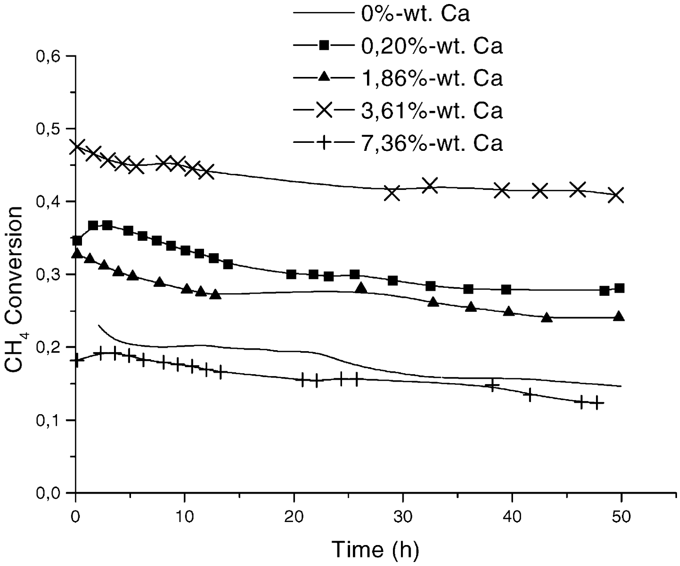

Fig. 7. Total methane conversion of 1Ni2Ca samples.

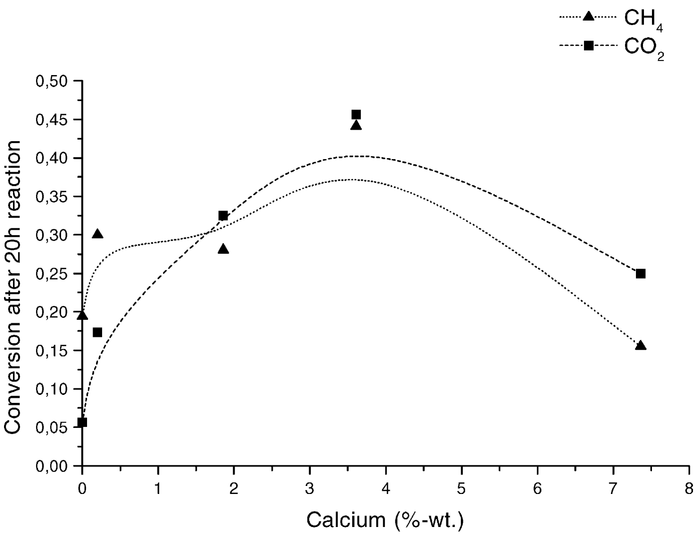

Fig. 8. Change in total methane and carbon dioxide conversion after 20 h reaction with amount of calcium of 1Ni2Ca.

When the removal of carbon in Step 2 is not simultaneous with its generation in Step 1, it accumulates over the catalyst active sites and this is the main cause of deactivation of this nickel catalyst [10]. This phenomenon can be verified in the samples where the methane conversion is higher than that of CO_2.

Calcium, by forming the aluminate or oxide, increases the ionic density, favoring the adsorption of CO_2, which is a polar molecule, on the alumina surface, through the attractions both between the Ca^{2+} of calcium oxide or aluminate and the negative pole O of carbon dioxide, and between O^{2-} of the oxide or calcium aluminate and the positive pole C of carbon dioxide [10]. This phenomenon can be observed for lower Ca contents in Figs. 8 and 9, through the increased conversion of CO_2 and, consequently, of

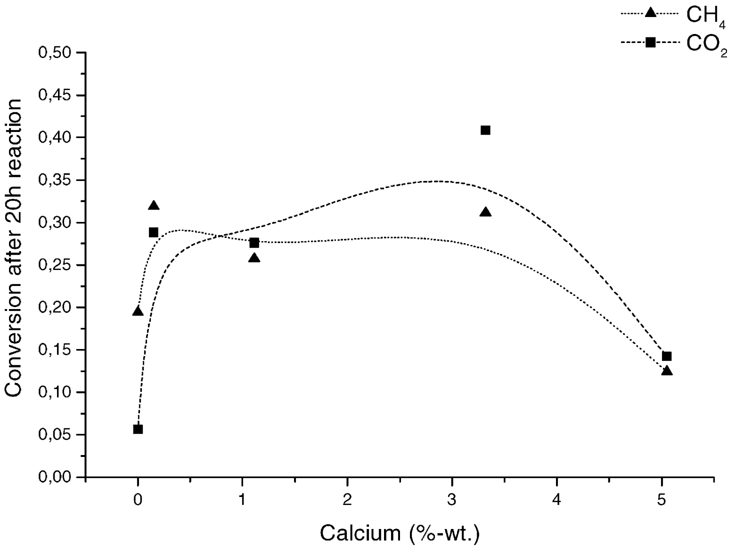

Fig. 9. Change in total methane and carbon dioxide conversion after 20 h reaction with amount of calcium of 1Ca2Ni.

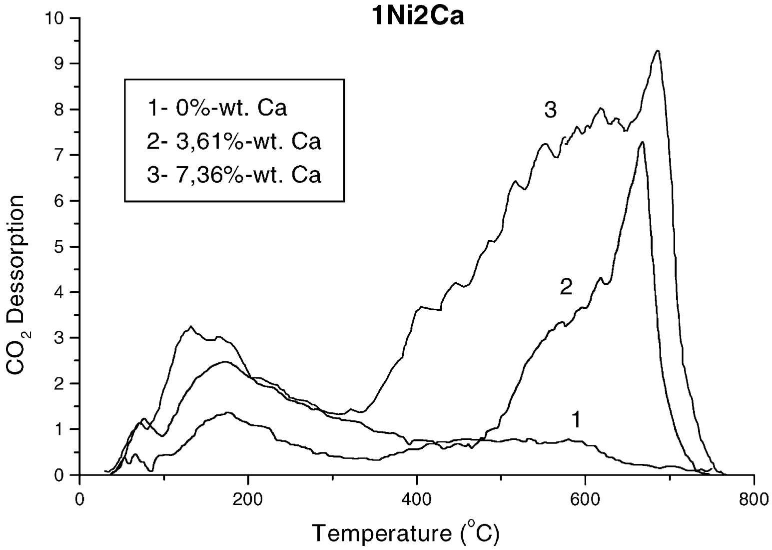

Fig. 10. TPD-CO_2 profile of 1Ni2Ca samples.

methane, with increasing calcium content in both sets of samples.

This increase in CO_2 adsorption with increasing calcium content can be verified in the results of CO_2 temperature-programmed desorption analysis (TPD-CO_2). In Figs. 10 and 11 it can be seen that the CO_2 desorption continues at temperatures up to 800 °C, and that the amount desorbed at high temperatures rises with increasing calcium content (the peak at about 700 °C increases) for any addition order of calcium and nickel ions. This indicates that a greater quantity of CO_2 is present on the support at the reaction temperature at higher Ca contents, as described on catalytic results.

Fig. 12 shows the area under the TPD-CO_2 curves, which is directly proportional to the amount of ad-

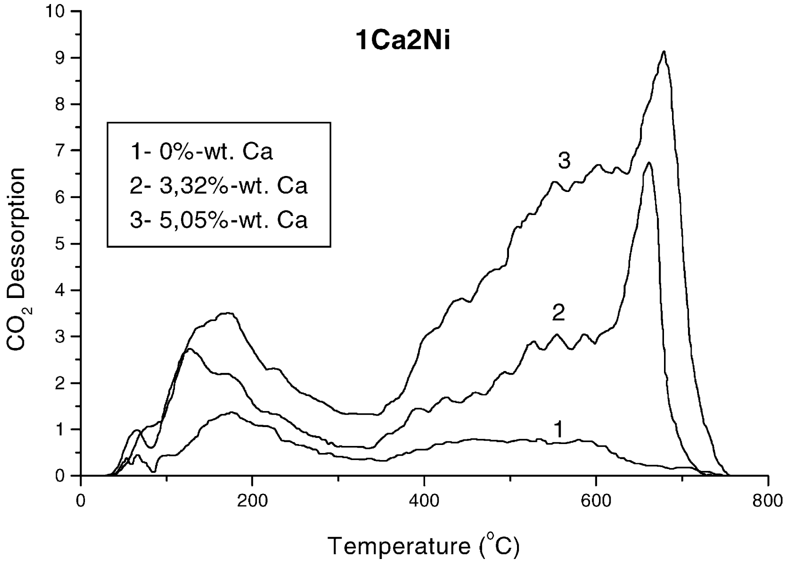

Fig. 11. TPD-CO_2 profile of 1Ca2Ni samples.

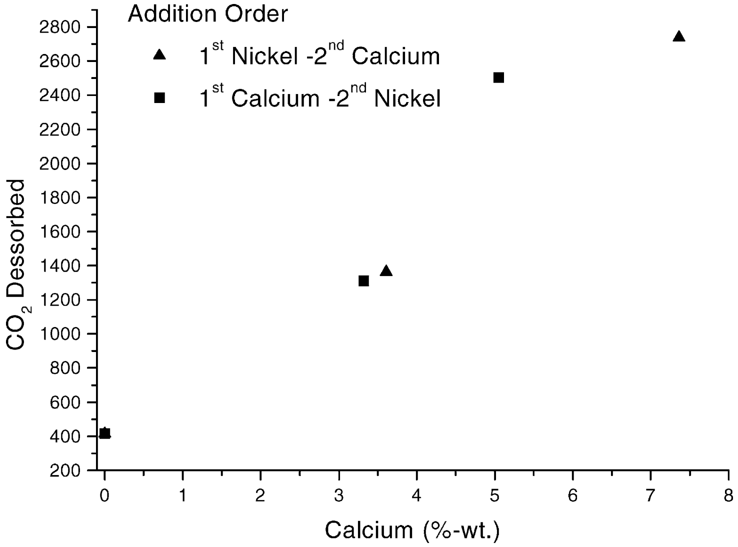

Fig. 12. Change in amount of desorbed CO_2 with amount of calcium.

sorbed CO_2 in the catalyst. It can be seen in this figure that this quantity tends to increase with the quantity of calcium, irrespective of the addition order of calcium and nickel on the alumina.

The fact that CO_2 conversions are larger than those of methane at higher calcium contents is due to the reverse of water–gas shift (RWGS) reaction which becomes important at high abundance of CO_2.

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Evidence for the increase of its importance can be seen in Fig. 13, where a decrease of the H_2/CO ratio

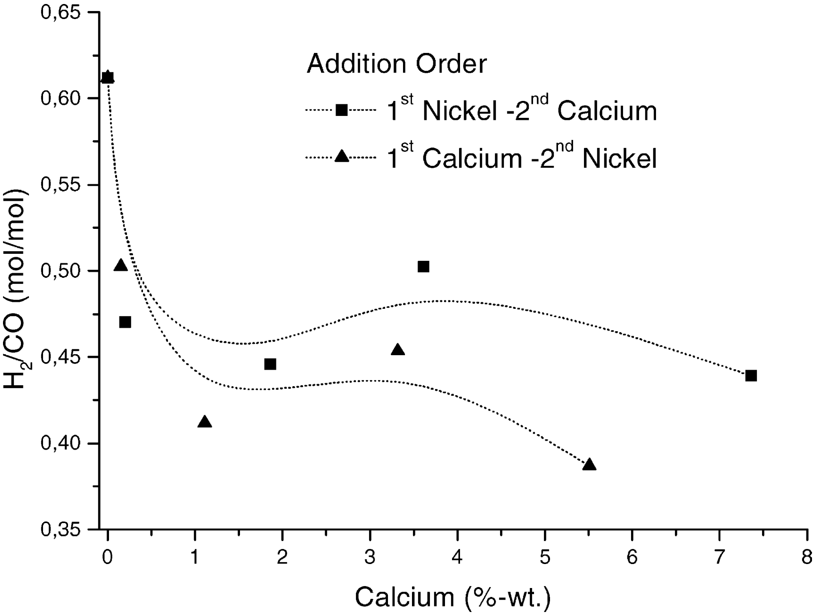

Fig. 13. Change in H_2/CO ratio after 20 h reaction with Ca.

with the calcium content increase is observed, due to this reaction consuming H_2 and releasing CO. It can also be seen that for those samples where the order of addition is 1Ca 2Ni, this decrease is even more pronounced.

The fact that the H_2/CO ratio remains smaller than 1, even when the methane conversion is higher than that of CO_2 (lower contents of calcium) is due to carbon deposition over the catalyst which occurs through the deposition of a paraffin polymeric $–CH_2–$ chain, which is slowly transformed into a less reactive polyaromatic deposit, which tends to form graphite [8], so that the carbon accumulation occurs together with hydrogen, decreasing the quantity of hydrogen in the product in relation to CO.

At higher calcium contents, this ion, being very rich in electrons, increases the catalyst electron density, resulting in a lower methane conversion, since its adsorption on the catalyst active site is caused by the nickel electronic deficiency [8]. Thus, the reduced methane conversion with increasing calcium content observed in Figs. 8 and 9 at higher Ca contents can be attributed to this increase in nickel electron density. This phenomenon also causes the decrease in CO_2 conversion.

4. Conclusions

It can be concluded that the incorporation of calcium into nickel catalysts supported on alumina results in changes in its structure and catalytic performance in the methane reforming reaction with CO_2.

At the structural level, it interacts with the support and lowers its resistance to sintering. In this interaction it competes with nickel and favors the formation of reducible species of Ni at lower temperatures, mainly when the nickel is added after the calcium. When deposited on alumina after nickel, calcium agglomerates in oxide granules over small pores, blocking them, which, in association with the sintering, decreases the catalyst specific surface area of catalyst.

During the reaction, it acts in two ways: when present in lower contents, it increases the CO_2 conversion by forming oxides strongly ionic and attracting this gas to the catalyst surface, increasing the methane conversion. At high contents, both methane and CO_2 conversions decrease, probably by an increase of nickel electron density, decreasing the adsorption of methane on it and, thus, its conversion, which in turn causes the decrease in CO_2 conversion.

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