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Carbon dioxide reforming of methane over 5 wt.% nickel calcium aluminate catalysts – effect of preparation method

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Abstract

The effect of the preparation method on the catalytic properties and performance of 5 wt.% Ni on calcium aluminate (molar $CaO/Al_2O_3=1/2$) in the reaction of CO_2 reforming of CH_4 was investigated. The techniques employed for the preparation were the incipient wetness and total blending. The catalyst sample prepared by the deposition of Ni on already formed calcium aluminate proved to be more active with lower coke deposition for the reaction of reforming than the samples prepared by the total blending technique where the nickel compound was premixed with Ca and Al compounds. The differences in activity were attributed to different amounts of active NiO on the surface of the prepared samples as it was proved from XPS spectra and H_2-TPD profiles. Specific desorption peaks, which appeared in TPD profiles of catalysts prepared by total blending technique and calcined at 700°C and 900°C, were associated with hydrogen spillover to the support. Furthermore, long term testing of the catalyst prepared by the incipient wetness technique showed no loss of activity with low coke deposition. TPO experiments conducted using $^{13}CH_4/CO_2/He$ mixture demonstrated that the adsorbed carbon species are formed via the CH_4 and CO_2 molecular routes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; CO_2 reforming; Nickel catalysts; Calcium aluminates

1. Introduction

The reforming reaction of methane with carbon dioxide to synthesis gas (CO/H_2) is a very attractive route for energy generation and chemicals production [1]. The synthesis gas produced by this reaction has a high carbon monoxide content which is effective for the synthesis of valuable oxygenated chemicals [1,2].

Considerable research efforts over the past few years have been directed towards the development of active and selective catalysts for the CO_2 reforming of CH_4. Numerous supported catalysts have been tested, especially nickel- and noble metal-based catalysts, and they have been found to exhibit promising catalytic performance [3–10]. Conversions of CH_4 and CO_2 to synthesis gas, approaching those defined by thermodynamic equilibrium, can be obtained over the most aforementioned catalysts as long as contact times are kept long enough. One of the major problems encountered towards the application of this process is the deactivation of the catalysts due to carbon deposition. The catalysts based on noble metals are reported to be less sensitive to coking compared to Ni-based catalysts [4]. However, the fact that these noble metals are expensive and of limited availability makes the

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development of Ni-based catalysts, for appropriate industrial practice, a challenge to the catalytic scientific community.

To overcome the problem of coking on Ni catalysts Rostrup-Nielsen suggested that partial sulphiding of the catalyst leads to a drastic decrease in the number of sites for carbon formation, while sufficient sites for the reforming reaction are maintained. Based on this finding the SPARG process has been developed for dry reforming of CH_4 [11]. As was recently reported by various investigators, the addition of alkali or alkaline earth oxides to Ni-based catalysts is effective in preventing coke formation [12–16]. Calcium aluminate mixed oxides proved to be very stable and active catalysts for hydrocarbon cracking [17] as well as for the partial oxidation of methane with very low coke deposition when promoted with nickel [18]. The high activity and stability of Ni/CaO–Al_2O_3 in the carbon dioxide reforming of methane was also confirmed by Gadalla and Bower [6].

Recently Goula et al. [19] claimed a 5 wt.% Ni on calcium aluminate catalyst is active for the reforming of methane and that the support composition (CaO/Al_2O_3 ratio) affects the catalyst stability, the amount and the reactivity of the carbon species formed during reaction and the relative proportion of reaction routes leading to carbon formation. It was suggested that the catalyst with support molar composition CaO/Al_2O_3=1/2 exhibits superior activity and lower coke deposition than the one supported on CaO/Al_2O_3 with 12/7 molar ratio.

The aim of the present work was to study the effect of the preparation method of 5 wt.% Ni on calcium aluminate (CaO/Al_2O_3=1/2) catalysts on the surface properties and catalytic performance in the reaction of carbon dioxide reforming of methane.

2. Experimental

2.1. Catalyst preparation and characterisation

Two techniques were used for the preparation of the catalysts containing 5 wt.% metallic Ni: the incipient wetness and the total blending technique.

The carrier employed for the preparation of the supported Ni catalyst was a mixed calcium aluminate oxide (CaO/Al_2O_3=1/2) which was prepared by mechanical mixing of $CaCO_3$ (J.T. Baker) and γ-Al_2O_3 (Catapal) followed by calcination at 1100°C for 20 h. Details on the preparation and calcination procedure of the support $CaO{\cdot}2Al_2O_3$ have been reported in the literature [17]. The resulting calcium aluminate support was ground to obtain a particle size between 250–350 μm. The carrier was impregnated with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Merck) so as to yield 5 wt.% metal loading. After impregnation, the sample was dried and calcined in air for 4 h at 600°C to decompose the nitrates, and then, at 900°C for another 10 h. This catalyst was designated as Ni/CaAlO.

The procedure applied for the preparation of the catalysts by the technique called total blending was as follows: appropriate amount of $Ni(NO_3)_2{\cdot}6H_2O$ (Merck) and stearic acid were dissolved in distilled water and blended with γ-Al_2O_3 (Catapal) and $CaCO_3$ (J.T. Baker). After thorough mixing the blend was extruded to 1/8 inch. The extrudates were dried overnight at 105°C and calcined at 600°C for 4 h. The sample was divided into three portions each of which was calcined at different temperature for 48 h; the temperatures were 700°C, 900°C and 1100°C. The final catalysts with a nominal metallic Ni content of 5 wt.% and CaO/Al_2O_3 molar ratio of 1/2 were ground to 250–350 μm. The samples were designated as NiCaAlO(T_{calc}) where T_{calc} is the calcination temperature used.

The BET surface area of the catalyst samples was measured using a Micromeritics Accusorb 2100E instrument. The crystal phases of the catalysts were identified by X-ray diffraction (XRD) analysis using a Siemens D500 diffractometer. X-ray photoelectron spectroscopy (XPS) was used for surface analysis and characterisation of fresh samples, employing a Leybold LHS10 spectrometer equipped with a single channel detector coupled with an Al K_α radiation source.

The reducibility of the catalysts was studied by temperature programmed reduction (TPR) under hydrogen (10% H_2/Ar) flow with a heating rate of 10°C min^{-1} from 50°C to 750°C. H_2-TPD profiles were obtained after initial in situ reduction at 750°C for 1 h. Following reduction, the samples were cooled to 300°C in flowing H_2 and then they were treated with H_2 at 300°C for 30 min, cooled to ambient temperature and flushed with Ar. Temperature-programmed desorption was programmed at 30°C min^{-1} from 50°C to 750°C. These experiments were carried out using a catalyst characterisation system AMI1 (Altamira Instruments) equipped with a TC detector.

2.2. *Catalyst testing*

Activity measurements were conducted at atmospheric pressure in a conventional flow apparatus using a quartz fixed bed reactor. The reactor (ID=9 mm) was electrically heated in a furnace. The axial temperature profile was measured using a chromel-alumel thermocouple placed in a thermowell centered in the catalyst bed. The products were analysed on-line by a Varian 3700 gas chromatograph equipped with a TC detector. Two columns, Porapak Q and Molecular Sieve 5A, were used in a series/bypass arrangement for the complete separation of H_2, O_2, CH_4, CO and CO_2. The atomic balances were satisfied with a maximum absolute deviation of less than 2%.

Methane and carbon dioxide at equimolar ratio (1/1) and without any diluent were used as feed with a total flow rate of 100 cc min^{-1}. The catalyst charge was diluted with quartz particles at a dilution ratio of 1/2 and was prereduced in situ at 750°C for 1 h. Runs were conducted at 700°C for 2 h at contact times corresponding to W/F=1.44 kg s mol^{-1}. In addition, the catalyst prepared via incipient wetness technique (Ni/CaAlO) was tested for an extended period of time (50 h) at 750°C, W/F=0.7 kg s mol^{-1} and CH_4/CO_2=1. The total carbon deposited on catalyst after testing was measured using a CHN-800 (Leco) elemental analyser.

Transient isotopic experiments were conducted ($^{13}CH_4$ in the feed) at 750°C in the presence of the Ni/CaAlO catalyst in a specially designed flow system for transient studies details of which have been given elsewhere [20]. The experimental procedure adopted was: after conducting the reforming reaction at 750°C for 5 min with $^{13}CH_4$ (20%)/$^{12}CO_2$ (20%) /He, the reactor was purged in He flow at 750°C for 5 min followed by cooling to 300°C under He flow. The feed was subsequently switched to a 10% O_2/He mixture, while at the same time the temperature was increased to 750°C at the rate of 30°C min^{-1} to carry out a TPO experiment.

3. Results

The surface area and crystal phases of the catalysts prepared are presented in Table 1. It can be clearly seen that the surface area of the different catalysts vary from approximately 5–100 m^2 g^{-1}. The samples NiCaAlO (700) and NiCaAlO (900) prepared via the total blending technique have relatively high surface areas, 104 and 52, respectively, while the surface area of NiCaAlO (1100) is only 5.48 m^2 g^{-1} due to the high calcination temperature applied. The sample prepared by the incipient wetness technique also has a low surface area (6.6 m^2 g^{-1}) because of the low surface area of the support used [18].

The crystal phases of the 5 wt.% Ni on calcium aluminate catalysts investigated by XRD are also presented in Table 1. Two Ni^{2+} crystal phases, NiO and $NiAl_2O_4$ were identified in all samples although in different proportions. The major crystal phase of the sample Ni/CaAlO prepared by the incipient wetness technique is that of NiO, whereas in the case of other samples, $NiAl_2O_4$ spinel phase is prevalent especially for the one calcined at the lowest temperature, 700°C. Various types of calcium aluminates were detected in the samples calcined over 900°C whereas CaO and

Table 1
Characterisation of 5 wt.% Ni on calcium aluminate (CaO/Al_2O_3=1/2 molar) catalysts

Catalyst designation	Preparation method	SSA (m^2/g)	Crystal phases[a]	
			Ni^{2+}	Support
Ni/CaAlO	Incipient wetness	6.61	NiO (+++), $NiAl_2O_4$ (++)	$CaAl_4O_7$ (+++), $CaAl_2O_4$ (+), α-Al_2O_3 (+)
NiCaAlO (1100)	Total blending	5.48	$NiAl_2O_4$ (+++), NiO (++)	$CaAl_4O_7$ (+++), $CaAl_2O_4$ (++)
NiCaAlO (900)	Total blending	52	$NiAl_2O_4$ (+++), NiO (+)	$CaAl_2O_4$ (+++), α-Al_2O_3 (++), CaO (+)
NiCaAlO (700)	Total blending	104	$NiAl_2O_4$ (+++), NiO (+)	γ-Al_2O_3 (+++), CaO (++), $CaCO_3$ (+)

[a] Determined by XRD measurements (+) weak intensity; (++) medium intensity; (+++) strong intensity.

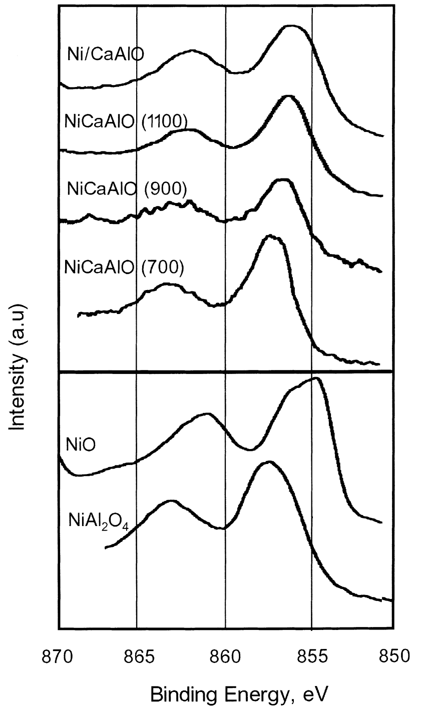

Fig. 1. XPS spectra of Ni^{2+} $2p^{3/2}$ level for catalysts and standards

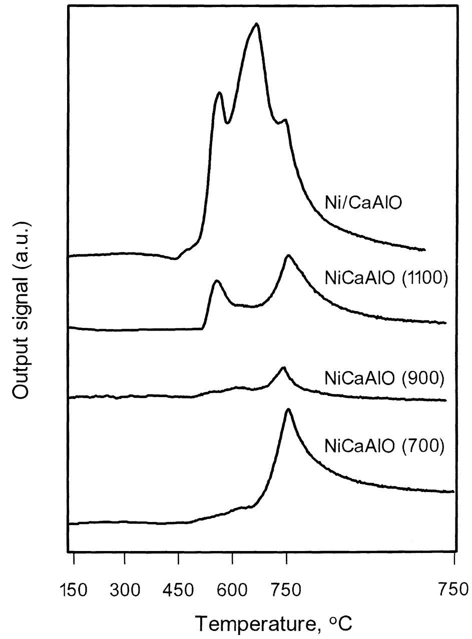

Fig. 2. Temperature-programmed reduction curves of catalysts.

γ-Al_2O_3 were the main crystal phases observed in the sample prepared by the total blending technique and calcined at 700°C.

Similar results regarding the Ni crystal phases on the catalyst surface were derived from XPS measurements (Fig. 1). The binding energies (Ni^{2+} $2p^{3/2}$) of the catalysts are between those of pure NiO (854.4 eV) and that of pure $NiAl_2O_4$ (857.3 eV) with line widths exceeding those found with the pure reference compounds. This indicates the coexistence of the oxide and aluminate-like species in the surface region. Regarding the catalyst prepared by the incipient wetness technique the Ni^{2+} binding energy (855.3 eV) is closer to that of pure NiO indicating higher proportions of Ni^{2+} in the oxidic form than in the spinel form on the catalyst surface. The samples prepared by the total blending technique exhibit Ni^{2+} binding energies that are shifted to higher values close the spinel $NiAl_2O_4$ values, especially the low temperature calcined sample NiCaAlO (700). These observations concerning the Ni phases on catalyst surface are in agreement with the bulk crystal phases identified by XRD.

The reduction characteristics of the prepared samples were studied over the range of 50–750°C. The H_2 responses as a function of temperature are given in Fig. 2. Significant differences in TPR curves were observed between the catalysts prepared using different procedures. The TPR curve for Ni/CaAlO catalyst consists of three peaks ranging from 530–750°C. The relatively higher T_{max} of reduction peaks compared to that appearing in the literature [21] for Ni/Al_2O_3 is partly due to the low rate of temperature increase (10°C min^{-1}) used in the experiments. Other important parameters that may influence the higher reduction temperature are the strong metal support interactions and the presence of Ca as was also referred to in a recent publication [22].

The catalysts prepared by the total blending technique are more difficult to be reduced. The samples calcined at 700°C and 900°C exhibit only one small peak at T_{max}=750°C while in TPR spectrum of the sample calcined at 1100°C, an additional peak at T_{max}=530°C was observed. Note that the peaks observed here correspond to the reduction of the oxidic form of Ni and not to the spinel phase of $NiAl_2O_4$. This was verified by conducting a TPR of pure $NiAl_2O_4$ under the same conditions and no

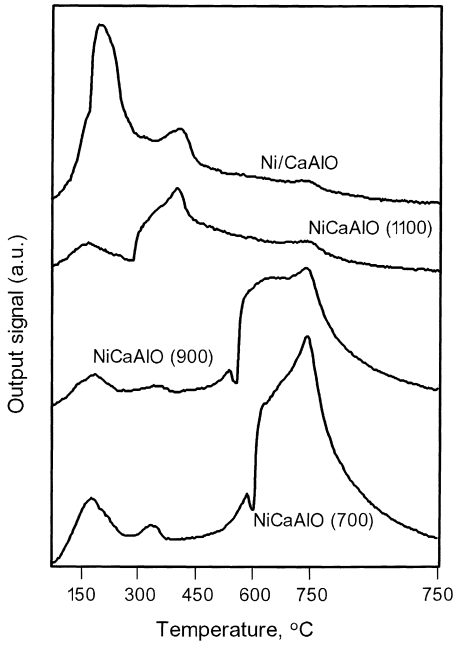

Fig. 3. Hydrogen TPD responses obtained over the 5 wt.% Ni on calcium aluminate catalysts after adsorption at 300°C.

peaks were observed in the temperature range up to 750°C.

An estimate of the number of reduced surface nickel atoms in the fresh catalyst samples was attempted by selective hydrogen chemisorption followed by TPD. The procedure of cooling the reduced Ni catalyst in continuously flowing hydrogen, prior to adsorption at 300°C was adopted in the experimental technique to ensure almost complete saturation of all possible adsorption sites. Fig. 3 shows the hydrogen responses obtained in the temperature range 50–750°C during TPD. The Ni/CaAlO catalyst exhibited broad overlapping peaks at $T_{\max}$=180°C and 400°C. In the case of the catalyst that was prepared by the total blending technique NiCaAlO (1100) the H_2 uptake was much lower at the same temperature range. As the calcination temperature decreased from 1100°C to 900°C (sample NiCaAlO (900)) the TPD profile changed. The intensity of peaks up to 500°C decreased compared to that of the NiCaAlO (1100) sample but another desorption peak over 550°C appeared. Similar pattern of desorption curve was observed in the case of the NiCaAlO (700) catalyst. The desorption peaks over 550°C appeared for the catalysts prepared by the total blending technique and calcined at 700°C and 900°C were ascribed to spillover hydrogen [23] and not to hydrogen chemisorbed on Ni sites.

The results of testing the prepared catalytic samples in the reaction of CO_2 reforming of CH_4 are presented in Table 2. The temperature used in these experiments was 700°C, the W/F_t was 1.44 kg s mol^{-1} and the feed was a mixture of CH_4 and CO_2 with a 1/1 ratio. The operating conditions for these comparative tests were selected so as to ensure that the conversion is far from equilibrium at the selected temperature.

As clearly shown in Table 2, the catalysts with the same composition (5 wt.% Ni on calcium aluminate) when prepared by different methods exhibit quite different activity in the dry reforming of methane. The Ni/CaAlO catalyst shows the highest activity. Over 50% of the CH_4 is converted to synthesis gas at the reaction temperature of 700°C while the activity of the other three samples is significantly lower. It is also shown that not only the preparation method but the calcination temperature as well greatly affects the activity of the samples. Thus, over the sample calcined at 700°C only 17% of the CH_4 is converted while on the samples calcined at 900°C and 1100°C the percentage of converted CH_4 is 39% and 37%, respectively. Though CH_4 and CO_2 were fed over the catalysts at equimolar composition, the ratio of H_2/CO produced is lower than 1 especially for the

Table 2
Activity of the 5 wt.% Ni on calcium aluminate catalysts in the CO_2 reforming of CH_4 reaction (T_R=700°C, W/F=1.4 kg s mol^{-1}, CH_4/CO_2=1/1)

Catalyst designation	CH_4 conversion (%)	CO_2 conversion (%)	H_2/CO (mol mol^{-1})	Coke on catalyst (wt.%)
Ni/CaAlO	51.32	57.11	0.85	0.2
NiCaAlO (1100)	36.96	41.64	0.77	0.4
NiCaAlO (900)	38.84	43.59	0.74	0.8
NiCaAlO (700)	17.15	21.95	0.50	2.2

samples with low activity. The deviation from the stoichiometric value is due to the significant extent of the reverse water gas shift reaction.

Another important difference observed is the amount of coke deposited after 2 h of operation. Again, coke over the catalyst Ni/CaAlO in which Ni was deposited over the already formed calcium aluminate is lower (0.2 wt.%) compared to coke deposited on catalysts where Ni was blended with the supporting oxides. More precisely the catalyst with the lowest calcination temperature has the highest coke amount, 2.2 wt.%, whereas over the NiCaAlO (1100) sample the coke is about five times lower at 0.4 wt.%.

Further studies on the activity and stability of the Ni/CaAlO catalyst were conducted since this catalyst proved to be the most active in CO_2 reforming of CH_4. Stability measurements conducted at 750°C and $W/F=0.7$ kg s mol^{-1} showed that over a testing period of 50 h there was practically no loss of activity (CH_4 conversion 62–64%), except in the first hour of reaction, where a drop in CH_4 conversion by 3–4% occurred. The coke accumulated during 50 h of continuous reaction was measured after testing and was found to be 5 wt.% on catalyst. Despite of the amount of coke deposited on the catalyst no loss of activity was observed indicating that part of this carbon was not poisonous.

The origin of carbon species formed during the reforming reaction at 750°C was investigated by conducting isotopic experiments (use of $^{13}CH_4$ in feed) to probe for the relative contribution of the CO_2 and CH_4 reaction routes to the accumulation of carbon species formed at high CH_4 and CO_2 conversions. The experiment was as follows: after conducting the reforming reaction at 750°C for 5 min with a $^{13}CH_4$ (20%)/$^{12}CO_2$ (20%)/He mixture, the reactor was purged with a flow of He at 750°C for 5 min, followed by cooling to 300°C under He flow. The feed was subsequently switched to a 10% O_2/He mixture, while at the same time the temperature was increased to 750°C at a rate of 30°C/min to carry out a TPO experiment; both $^{12}CO_2$ and $^{13}CO_2$ responses were measured.

The $^{12}CO_2$ and $^{13}CO_2$ responses illustrated in Fig. 4 are due to the oxidation of carbon species formed during the reforming reaction ($^{13}CH_4/CO_2$) via the CO_2 and the CH_4 molecular route, respectively. The amount of $^{12}CO_2$ produced was 325 μmol/g$_{cat}$ while the amount of $^{13}CO_2$ was 152 μmol/g$_{cat}$. The oxidation of carbonaceous species started at 450°C and the CO_2 responses shown in Fig. 4 indicate the presence of two types of carbonaceous species which exhibit different reactivity towards oxidation.

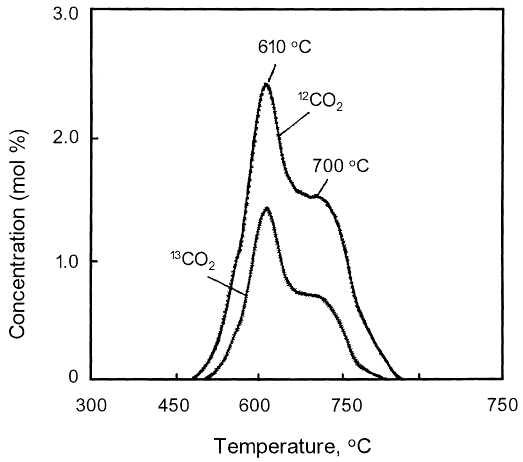

Fig. 4. Transient responses of $^{12}CO_2$ and $^{13}CO_2$ obtained during temperature programmed oxidation (TPO) of carbon species formed after reforming reaction of $^{13}CH_4$ and CO_2 at 750°C for 5 min over the Ni/CaAlO catalyst.

4. Discussion

Different methods of catalyst preparation influence the catalyst activity in the dry reforming reaction. Gil et al. [24] studied the effect of the preparation method and the nature of the support for Ni catalysts and claimed that metal support interaction is strongly dependent on the preparation method and that the reactivity of the support towards Ni plays an important role. Cheng et al. [13] suggested that the beneficial effects of adding CaO and MgO promoters to Ni/Al_2O_3 catalysts are significantly affected by the preparation method; when the promoter was impregnated prior to Ni on the alumina surface the resulting catalysts exhibited superior catalytic performance.

The present work reveals that the catalytic properties and performance of Ni supported on calcium aluminates are strongly influenced by the method applied for the preparation of the samples. The deposition of 5 wt.% Ni on stable calcium aluminate by the incipient wetness technique or the blending of Ni with the oxides of alumina and calcium leads to catalyst samples with different characteristics. The existence of two types of nickel compounds in the bulk and on the surface of the prepared samples is confirmed by XRD and XPS measurements. The Ni/CaAlO catalyst on which Ni was deposited on calcium aluminate showed a higher proportion of NiO compared to $NiAl_2O_4$. This is attributed to the very low concentration of free Al_2O_3 which implies that the reaction between NiO and Al_2O_3 for the formation of $NiAl_2O_4$ is less favorable. The opposite is valid for the catalysts prepared by the total blending technique where NiO reacts more easily with Al_2O_3.

The reducibility of the prepared samples is also different as shown in Fig. 2. The three peaks which appear in the TPR profile of the Ni/CaAlO catalyst with T_{max}=530°C, 640°C and 745°C could be ascribed to different nickel particle morphologies or to different type of Ni sites. The other catalysts prepared by the total blending technique exhibit only one reduction peak at 745°C (except for the catalyst calcined at 1100°C that shows another peak with T_{max}=530°C). The high temperature required for the reduction of these samples may be attributed to the strong interaction between the NiO crystallites and the Ca–Al phases in agreement with literature data [22]. Comparing the areas under the TPR curves it can be concluded that the preparation technique influences the degree of reduction and that a much higher degree of reduction is obtained with the sample Ni/CaAlO.

Hydrogen chemisorption capacity of the prepared samples is strongly dependent on the preparation method and on the calcination temperature as shown in Fig. 3 where H_2 TPD profiles of the catalysts are presented. In the case of the Ni/CaAlO catalyst much of the H_2 is desorbed up to a temperature of 200°C and this is attributed to hydrogen chemisorbed on the surface of metallic Ni. The small shift of the maximum of this peak to higher temperatures than those reported in the literature for Ni/Al_2O_3 catalyst [25] could be caused by the higher adsorption temperature used in the present experiments and/or by the presence of calcium in the support. Since the hydrogen adsorption on Ni/Al_2O_3 is an activated process as reported by Weatherbee and Bartholomew [25] and the increase in adsorption temperature results in higher desorption temperature, the observed shift in the Ni/CaAlO catalyst is quite reasonable.

A second broad and not well resolved peak with a maximum at 400°C present in the TPD profile is assigned to strongly bonded Ni in the subsurface of the metal catalyst. Several other authors have also found hydrogen desorbing at high temperature (>300°C) on supported Ni when the catalyst was exposed to hydrogen during the cooling from the reduction temperature to the adsorption temperature [21,25,26].

The high temperature peaks (>550°C) which appear in the TPD profiles of the catalysts NiCaAlO calcined at 700°C and 900°C are not ascribed to H bonded to Ni but rather to H spilled over the support. Proof of hydrogen spillover on alumina supported metals was first claimed by Kramer and Andre [23]. Analogous suggestions of hydrogen spillover have not appeared in the literature for the catalysts supported on CaO–Al_2O_3. However, it is evident from the TPD profiles that when NiO is blended with CaO and Al_2O_3 and the calcination temperature is lower than 900°C, a significant amount of hydrogen dissociated on Ni is spilled over to the support. The reason why the spillover phenomenon appears only with catalysts calcined at 700°C and 900°C and not with catalyst calcined at 1100°C may be the existence of free CaO in the support of the former catalysts (see Table 1); this hydrogen dissociated on metallic nickel migrates towards the basic sites of CaO.

As shown in Table 2 the Ni/CaAlO catalyst prepared by the incipient wetness technique is the most active and has the lowest affinity for carbon formation. The higher activity of this catalyst is directly related to the amount of H_2 uptake (desorption temperature up to 250°C) that corresponds to metallic Ni on the surface. The H_2 uptake of Ni/CaAlO (Fig. 3) is much higher than the other catalysts prepared using the total blending technique, and this can explain the higher activity of this sample. The conversion over the NiCaAlO (700) catalyst is very low although the H_2 uptake (T_{des}<250°C) is relatively higher than the uptakes of the other two samples calcined at 900 and 1100°C. The low activity measured after 2 h of testing may be due to rapid deactivation of the catalyst caused by the high amount of coke deposited on the surface. Furthermore, there is no evidence from the experimental data presented in this work that the spillover hydrogen facilitates the formation of syngas from the reactants.

The aforementioned discussion leads to the conclusion that the preparation techniques greatly affect the catalytic properties of the samples. Impregnation of Ni on the already formed calcium aluminate results in catalyst with increased amount of active surface Ni while blending of Ni precursor with the Ca and Al compounds has an negative effect on the dispersion of active Ni sites.

The Ni/CaAlO catalyst exhibits stable catalytic performance at 750°C for 50 h time on stream despite the amount of coke deposited on the catalyst surface. Based on the work related to the activity behaviour observed over various Ni-based catalysts [6] it can be suggested that for the Ni/CaAlO catalyst no crystal phase transformations in the support composition and/ or creation of Ni sites during reaction occurs. This is due to the fact that a high calcination temperature was used for the support (1100°C) and for the final catalyst (900°C) preventing, therefore, any further solid state reactions to take place under favourable reaction conditions. The good stability of the catalyst should be mainly related to its sites location and the extent to which this carbon participates as an active intermediate species in the reforming reaction.

The isotopic TPO experiments presented in Fig. 4 allowed the verification of the origin and quantitative determination of carbon accumulation derived from CH_4 and CO_2 molecules after a given time on stream. In similar isotopic experiments conducted by Swaan et al. [8] over 4% Ni/SiO_2 two CO_2 peaks were identified with T_m=500°C and 650°C and the proportion of carbon originating from CO_2 as opposed to CH_4 was found to be 1.5 a value very close to that obtained in present work. On the contrary, in the case of the reforming reaction over a Rh/Al_2O_3 catalyst it was shown that carbon accumulated on the catalyst surface is mainly derived from the CO_2 molecule [27]. These results demonstrate the different kinetics of carbon formation and removal steps occurring during reforming reaction of CH_4 with CO_2 over supported Rh and Ni surfaces. It could be suggested that reaction steps found in the sequence from CH_4 to CO formation are faster over the Rh than the Ni surface.

The isotopic TPO demonstrate the existence of mainly two kinds of carbon species free of chemically bound hydrogen (no H_2O was obtained during TPO). Taking into account results reported in literature, concerning the characterisation of carbon during CO_2 reforming reaction and steam reforming over Ni-based catalysts [28,29] it can be suggested that the high temperature peak of CO_2 could be assigned to amorphous or graphitic forms of carbon and the low temperature peak to filamentous carbon. The similar shape of the CO_2 responses ($^{13}CO_2$ and $^{12}CO_2$) versus temperature indicates that carbonaceous species mainly arise from CO disproportionation, since CO is produced from both CH_4 and CO_2.

5. Conclusions

The following conclusions can be drawn from the results of the present study on carbon dioxide reforming of methane to synthesis gas over 5 wt.% Ni on calcium aluminate catalysts.

The preparation method greatly affects the catalyst properties. The catalyst prepared by the incipient wetness technique reveals a higher proportion of NiO than $NiAl_2O_4$ on the surface whereas the opposite was found with catalysts prepared by the total blending technique. The samples prepared by total blending are more difficult to be reduced because of the stronger metal-support interactions.

The TPD studies demonstrated the surface heterogeneities of the catalyst with at least three different adsorption states. Different H_2 uptakes were obtained with all catalysts up to 450°C. High temperature (T>550°C) desorption peaks appeared in TPD profiles of the samples prepared by the total blending technique and calcined to 700°C and 900°C were attributed to hydrogen spillover from active sites to the support.

Significant differences were observed in the activity of catalysts and the coking tendency. The most active catalyst with the least coke deposits was the catalyst prepared by dry impregnation of Ni on the already formed calcium aluminate. The carbonaceous species accumulated during reaction were found to originate from both reactants, CH_4 and CO_2.

The catalysts prepared by premixing of Ni with Ca and Al compounds were less active with higher coke deposits, especially the sample calcined at 700°C, due to the low dispersion of active Ni on the catalyst surface. The lower dispersion of active Ni was ascribed to the intimate contact of Ni with Ca and

Al oxides leading to the formation of inactive spinel-type compounds.

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