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Characterization and activity in dry reforming of methane on NiMg/Al and Ni/MgO catalysts

A. Djaidja [a,b,*], S. Libs [b], A. Kiennemann [b], A. Barama [a]

[a] *Laboratoire de Chimie du Gaz Nnaturel, Faculté de Chimie, USTHB BP.32.El-Alia, 16111 Bab-Ezzouar, Alger, Algeria*
[b] *ECPM-LMSPC UMR CNRS 7515 25, Rue Becquerel, 67087 Strasbourg, France*

Abstract

Dry reforming of methane has been investigated on two series of catalysts either prepared by co-precipitation: $n(\mathrm{Ni}_x\mathrm{Mg}_y)/\mathrm{Al}$, $\mathrm{Ni}_x\mathrm{Mg}_y$ and $\mathrm{Ni}_x\mathrm{Al}_y$ or prepared by impregnation: Ni/MgO (mol% Ni = 5, 10). The catalysts, calcined at 600–900 °C, were characterized by different techniques: BET, H_2-TPR, TPO, XRD, IR, and TEM-EDX analysis. The surface BET (30–182 $m^2 g^{-1}$) decreased with increasing the temperature of calcination, after reduction and in the presence of Mg element. The XRD analysis showed, for $n(\mathrm{Ni}_x\mathrm{Mg}_y)/\mathrm{Al}$ catalysts, the presence of $NiAl_2O_4$ and NiO–MgO solid solutions. The catalyst reducibility decreased with increasing the temperature of pretreatment. The $n(\mathrm{Ni}_x\mathrm{Mg}_y)/\mathrm{Al}$ catalysts were active for dry reforming of methane with a good resistance to coke formation. The bimetallic catalyst $\mathrm{Ni}_{0.05}\mathrm{Mg}_{0.95}$ (calcined at 750 °C and tested at 800 °C) presents a poor activity. In contrast, the 5% Ni/MgO catalyst, having the same composition but prepared by impregnation, presents a high activity for the same calcination and reaction conditions. For all the catalysts the activity decreased with increasing the temperature of calcination and a previous H_2-reduction of the catalyst improves the performances. The TPO profiles and TEM-EDX analysis showed mainly four types of coke: CH_x species, surface carbon, nickel carbide and carbon nanotubes.

Keywords: Syngas; Methane; Dry reforming; Nickel catalysts; Ni–Mg–Al mixed oxides; Coke deposition

1. Introduction

Dry reforming of methane is a process which is, currently, widely studied for the purpose of promoting its use in the industry for the production of synthesis gas. The process produces, from raw materials, CO + H_2 mixture in a suitable ratio for e.g. the synthesis of oxygenate derivatives, Fischer–Tropsch and hydroformylation reactions. Besides, this process is of a great interest for environmental protection since the reaction consume two important greenhouse gases (CH_4 and CO_2) to convert them into valuable feedstock and also to increase valorization of gas-field with high CO_2 content. Many kinds of catalysts using Ni or noble metals (Ru, Rh, Pd, Ir, Pt) have been reported to be active in this reaction [1–6]. Ni catalysts have been extensively investigated because of the metal availability and economic considerations. However, with Ni catalysts, the reaction is frequently accompanied by coke formation and sintering of Ni metal particles, leading to the catalyst deactivation [7]. According to the literature data, high Ni metal dispersion over catalysts, use of basic support, addition of metal oxides as alkali or alkaline earth metal oxides in the catalysts but also, during reactivity, a strong interaction between the reduced metal, the support and the non-reduced metal may reduce coke formation [1,8]. So nickel-support interaction has been found to have an important effect on precursor reducibility [9,10] and catalytic properties [11]. Recent studies indicated that NiO/MgO or NiO/Al_2O_3 catalyst, in which NiO forms a solid solution (NiO–MgO or $NiAl_2O_4$) with the support, inhibits carbon deposition [11–14]. It was also reported that the basicity of MgO–CaO mixed oxides, used as support, prevents carbon deposition during the methane transformation reactions and improves the catalyst stability [15]. In this order, $n(\mathrm{Ni}_x\mathrm{Mg}_y)/\mathrm{Al}$ catalysts prepared by co-precipitation method and Ni/MgO prepared by impregnation were characterized by physicochemical techniques, such as BET, XRD, IR, TPR, TPO, TEM-EDX, and tested in CO_2-reforming of methane. The effects of catalyst composition, pretreatment and reaction

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* Corresponding author. Tel.: +213 21 24 80 08.
E-mail address: a_djaidja@yahoo.fr (A. Djaidja).

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conditions over the catalyst activity and stability have been studied.

2. Experimental

The catalysts, noted $n(Ni_xMg_y)/Al$, Ni_xMg_y, Ni_xAl_y, nMg/Al with ($n = 0.5$, 1, 2 and $x/y = 0.05/0.95$ or 0.1/0.9), were prepared, at room temperature, by co-precipitation method (pH = 9–10) from a mixture of Ni, Mg and Al nitrates in aqueous solution and NH_3 aqueous solution (2 M) as precipitating agent. The obtained solids were dried at 80 °C for 24 h and calcined at different temperatures (600–900 °C).

The catalysts, noted Ni/MgO (mol% Ni = 5, 10), were prepared by impregnation method. The obtained solids were dried and calcined in the same conditions than the catalysts prepared by co-precipitation.

All the catalysts were characterized by their specific surface areas, X-ray diffraction (XRD), IR-spectra, temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and transmission electron microscopy (TEM-EDX). The XRD diffractograms were recorded on a SIEMENS D-5000 diffractometer using the Cu Kα ($\lambda = 0.154$ nm) radiation. TPR experiments were performed in the temperatures range 25–900 °C (15 °C/min) using mixture of 3% H_2/Ar (52 ml/min) and 0.05 g of sample. The hydrogen consumption was analyzed by an on-line gas chromatograph. IR analysis was carried out on a NICOLET 210 apparatus. The carbon deposition was determined by temperature programmed oxidation (TPO) in the temperature range 25–900 °C (15 °C/min). The amount of carbon deposited was calculated from the CO_2 desorbed.

Catalytic testing was performed for CO_2-reforming of methane in the tubular fixed-bed quartz reactor, at the atmospheric pressure, in the temperature range $T_r = 700–800$ °C, using 0.2 g of catalyst and a molar ratio of $CH_4/CO_2 = 1:1$ at a total flow rate of 50 ml/min ($CH_4:CO_2:Ar:N_2 = 5:5:35:5$). The catalyst was reduced in situ at 800 °C for 2 h in a flow of 5% H_2/Ar (53 ml/min). The products and reactants were analyzed by gas chromatography. In all experiments, the performances were evaluated by conversion and yields. The conversion and yields are calculated as follows [16]:

$$\mathrm{CH_4\ conversion\ (\%)} = \frac{\mathrm{moles\ of\ CH_4\ converted} \times 100}{\mathrm{moles\ of\ CH_4\ in\ feed}}$$

$$\mathrm{CO_2\ conversion\ (\%)} = \frac{\mathrm{moles\ of\ CO_2\ converted} \times 100}{\mathrm{moles\ of\ CO_2\ in\ feed}}$$

$$\mathrm{Yield\ of H_2\ (\%)} = \frac{\mathrm{moles\ of H_2\ produced} \times 100}{\mathrm{2\,moles\ of\ CH_4\ in\ feed}}$$

$$\mathrm{Yield\ of\ CO\ (\%)} = \frac{\mathrm{moles\ of\ CO\ produced} \times 100}{\mathrm{moles\ of\ CH_4\ in\ feed} + \mathrm{moles\ of\ CO_2\ in\ feed}}$$

$$\frac{\mathrm{H_2}}{\mathrm{CO}}\ \mathrm{ratio} = \frac{\mathrm{moles\ of H_2\ produced}}{\mathrm{moles\ of\ CO\ produced}}$$

3. Results and discussions

3.1. Characteristics of the catalysts before reaction

3.1.1. BET

The specific surface areas of the fresh $n(Ni_xMg_y)/Al$, Ni_xMg_y, Ni_xAl_y, nMg/Al ($x/y = 0.1/0.9$ or 0.05/0.95 and $n = 2$) and Ni/MgO (Ni = 5 or 10 mol%) catalysts, included between 30–182 $m^2\,g^{-1}$, depend on the pretreatment conditions and on the catalyst composition. For $2(Ni_{0.1}Mg_{0.9})/Al$ catalyst, it decreased (from 89 to 30 $m^2\,g^{-1}$) when the temperature of calcination increased from 600 to 900 °C and after reduction (from 54 to 50 $m^2\,g^{-1}$). A strong decrease was observed in the presence of Mg (from 165 $m^2\,g^{-1}$ for $Ni_{0.05}Al_{0.95}$ catalyst to 4 $m^2\,g^{-1}$ for $Ni_{0.05}Mg_{0.95}$ catalyst). For the supported Ni/MgO catalysts, the surface areas slightly increased with Ni loading. Generally, the BET surface area decreased after reaction.

3.1.2. XRD and TPR

XRD results (Fig. 1) showed, for the $n(Ni_xMg_y)/Al$ catalysts prepared by co-precipitation and calcined at 750 °C, the presence of NiO–MgO and $MgAl_2O_4$ or $NiAl_2O_4$ solid solutions. While, for the $Ni_{0.05}Al_{0.95}$ catalyst, only the diffraction lines of γ-Al_2O_3 were observed; the NiO phase was not detected due probably to an effect of its high dispersion on the catalyst surface. A good dispersion could be the result of high interaction between Ni and Mg and/or Al.

For the MgO supported catalysts, XRD spectra (not given) showed for 5% Ni/MgO calcined at high temperature (900 °C), a complete solid solution of NiO in MgO. The formation of NiO–MgO solid solution is confirmed by the calculation of matrix-volume ($V = 73.87$ Å^3 compared to the value of the theoretical matrix-volume $V = 73.69$ Å^3 JCPDS 24-0712). The TPR, obtained from 25 to 900 °C, for this catalyst (Fig. 2), is quite similar to that observed for typical NiO–MgO complete solid solution [17,18]. All these observations and the low degree of reduction (3%) observed for this catalyst during the TPR, show clearly the formation of a complete solid solution

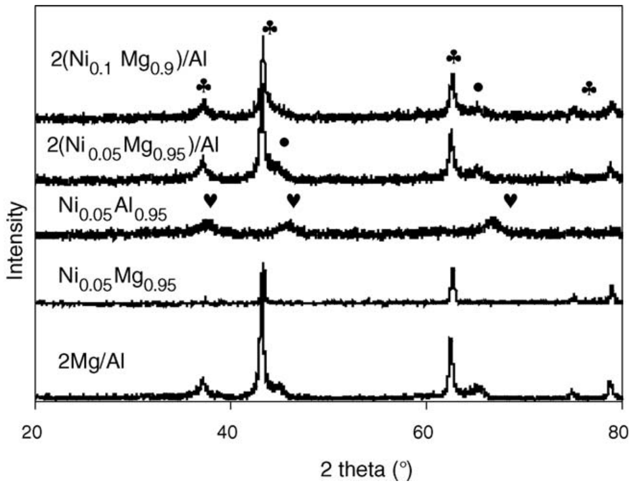


Fig. 1. XRD of $n(Ni_xMg_y)Al$ catalysts calcined at 750 °C. (●) $MgAl_2O_4$ or $NiAl_2O_4$, (♣) NiO–MgO or MgO and (♥) γ-Al_2O_3.

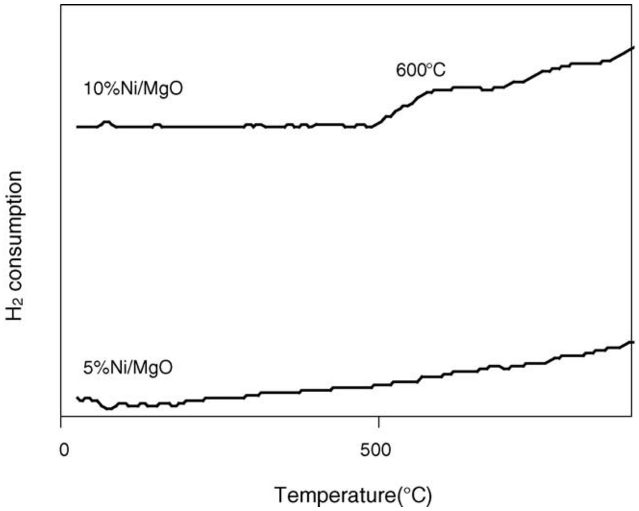


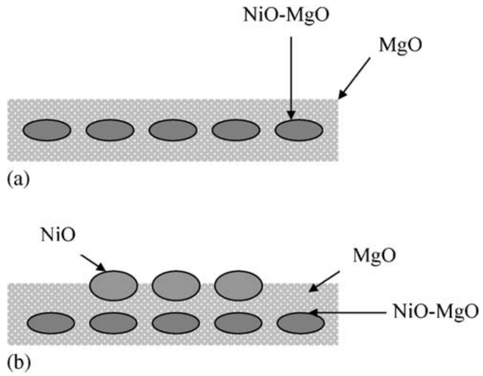
Fig. 2. TPR curves of Ni/MgO catalysts calcined at 900 °C.

NiO–MgO. On the other hand, for 10% Ni/MgO catalyst pretreated in the same conditions, besides the presence of solid solution, a signal of free NiO is observed at 600 °C (Fig. 2). These observations can be illustrated by Scheme 1.

For the $n(Ni_xMg_y)/Al$ catalysts, with different ratios $n = 0.5$, 1, 2, the increase of the amount of Al favored the formation of $MgAl_2O_4$ or $NiAl_2O_4$ (Fig. 3).

For the H_2-reduced catalysts (Fig. 4), the XRD analysis showed the presence of Ni metallic phase with a weak signal. This low reducibility could be due to the interaction Ni–Mg and/or Ni–Al, which stabilizes the valence 2 of Ni committed in the structure [19] or the formation of small Ni particles.

The TPR profiles (Figs. 5 and 6) showed, for the $2(Ni_xMg_y)/Al$ formulations ($x/y = 0.05/0.95$, 0.1/0.9) calcined at 750 °C, only one reduction peak at 840–873 °C ascribed to the reduction of stable Ni^{2+} compounds (NiO–MgO or $NiAl_2O_4$ formed during calcination) where Ni^{2+} is in strong interaction with MgO and/or Al_2O_3. The bimetallic $Ni_{0.05}Mg_{0.95}$ presents a reduction peak at 640–665 °C which was associated to the reduction of Ni species in low interaction with MgO or to small Ni particles. For all catalysts studied, the reduction peaks are



Scheme 1. Structural image of solid solution catalysts with low and high nickel content. (a) 5% Ni/MgO catalyst: formation of a complete solid solution NiO–MgO and (b) 10% Ni/MgO catalyst: formation of a partial solid solution, NiO–MgO + free NiO.

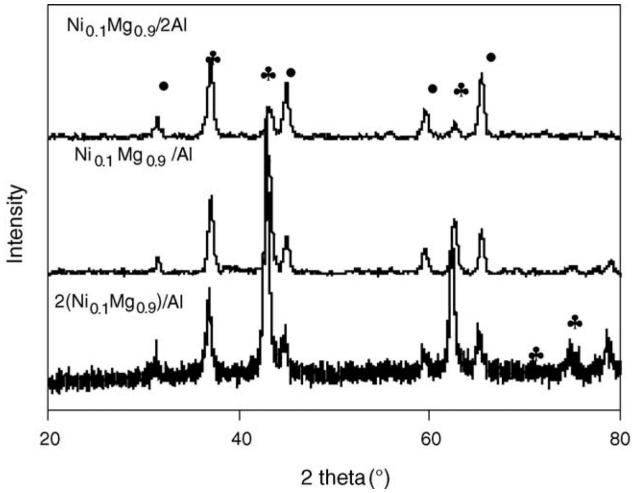


Fig. 3. XRD of $n(Ni_xMg_y)Al$ catalysts ($x/y = 0.1/0.9$; $n = 0.5$, 1, 2), calcined at 900 °C. (●) $MgAl_2O_4$ or $NiAl_2O_4$, (♣) NiO–MgO or MgO and (♥) γ-Al_2O_3.

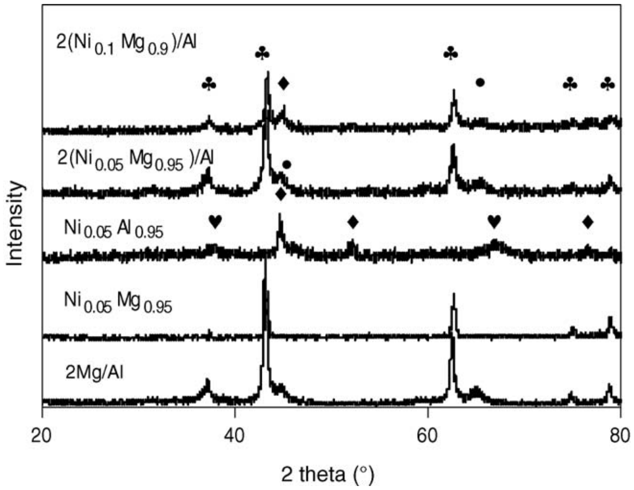


Fig. 4. XRD after reduction of $n(Ni_xMg_y)Al$ catalysts calcined at 750 °C, $T_{red} = 800$ °C. (●) $MgAl_2O_4$ or $NiAl_2O_4$, (♣) NiO–MgO or MgO, (♥) γ-Al_2O_3 and (◆) Ni.

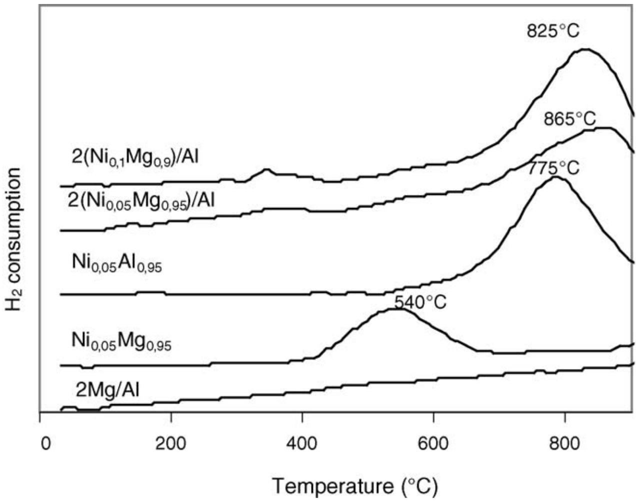


Fig. 5. TPR profiles of $n(Ni_xMg_y)Al$ catalysts calcined at 600 °C.

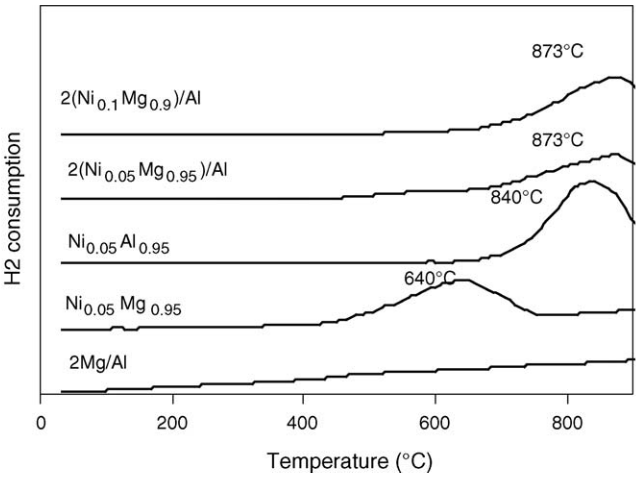


Fig. 6. TPR profiles of $n(Ni_xMg_y)Al$ catalysts calcined at 750 °C.

moved toward high temperatures when the temperature of calcination increases from 600 to 750 °C (Figs. 5 and 6); it is probably an effect of the progressive incorporation of Ni in the structure of NiO–MgO and/or $NiAl_2O_4$ solid solutions.

3.1.3. TEM-EDX

TEM-EDX analysis of $2(Ni_{0.05}Mg_{0.95})/Al$ catalyst, conducted after calcination at 750 °C, is illustrated on Fig. 7a and b. It can be seen (Fig. 7a) that the sample exhibits uniform particle distributions. We noticed, according to the diagram of Fig. 7b, the high homogeneity of this system, which supports the realization of NiO–MgO and $NiAl_2O_4$ or $MgAl_2O_4$ solid solutions. It is, also, showed (Fig. 7a), that free NiO is not observed on this catalyst, which confirmed the formation of solid solutions.

3.1.4. IR analysis

IR results showed, for all catalysts, calcined at 600 °C, the presence of characteristic bands of MO or M^IOM^{II} oxides, of CO_3^{2-} and OH species. For the catalysts prepared by co-precipitation (Fig. 8a and b), the OH band intensity increased with the amount of Al and decreased when the calcination temperature passed at 750 °C.

3.2. Catalytic activity

The catalysts $n(Ni_xMg_y)/Al$, Ni_xMg_y, Ni_xAl_y, nMg/Al ($x/y = 0.1/0.9$ or $0.05/0.95$ and $n = 2$) (prepared by co-precipitation) and 5% Ni/MgO (prepared by impregnation) are tested in CO_2-reforming of methane at 700–800 °C with the molar ratio $CH_4/CO_2 = 1$. The catalytic testing were carried out over catalysts previously reduced (r) and non-reduced (nr). The obtained results are summarized in Tables 1 and 2. These results show that the $CH_4 + CO_2$ reaction leads exclusively to synthesis gas ($CO + H_2$) with high CH_4 conversion (about 97%, which is close to the thermodynamic equilibrium), high yields of H_2 and CO (reaching 95% and 94%, respectively) and low rate of coke

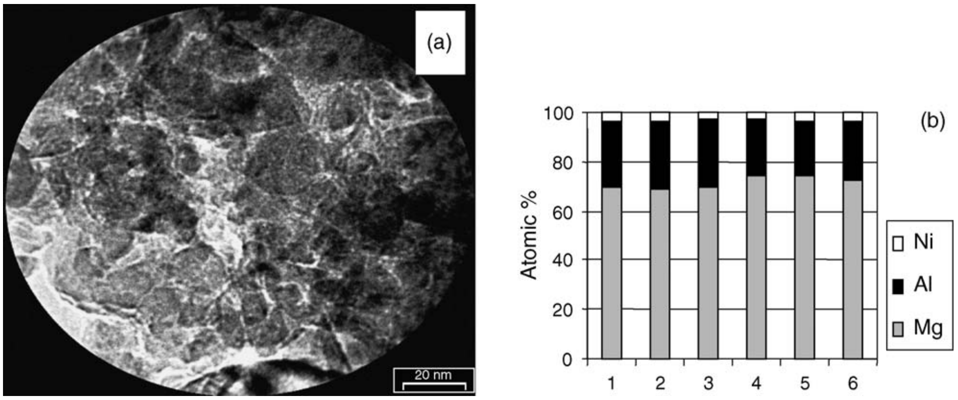


Fig. 7. TEM-EDX analysis of the fresh $2(Ni_{0.05}Mg_{0.95})Al$ catalyst calcined at 750 °C. (a) STEM image and (b) EDX elementary distribution, $d_{analyzed} = 20$ nm.

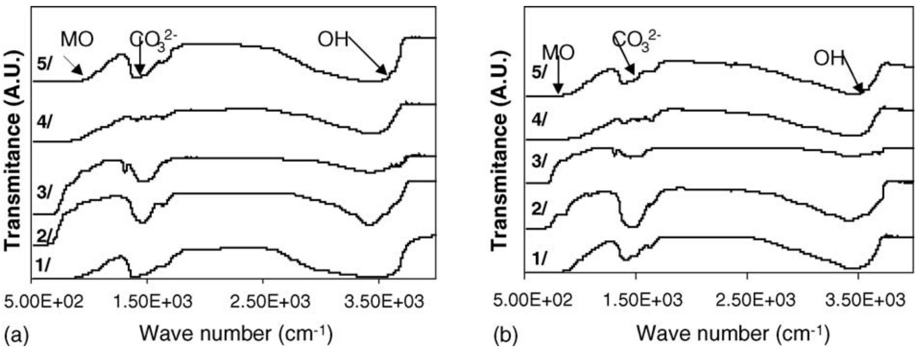


Fig. 8. IR analysis of $n(Ni_xMg_y)Al$ and 5% Ni/MgO catalysts: (a) calcined at 600 °C and (b) calcined at 750 °C. (1) 2Mg/Al, (2) 5% Ni/MgO, (3) $Ni_{0.05}Mg_{0.95}$, (4) $Ni_{0.05}Al_{0.95}$ and (5) $2(Ni_{0.05}Mg_{0.95})/Al$.

Table 1
Effect of calcination temperature (T_c) and reaction temperature (T_r) on the catalytic properties of $2(Ni_{0.1}Mg_{0.9})/Al$ solid in $CH_4 + CO_2$ reaction; $CH_4/CO_2 = 1$

T_c (°C)	T_r (°C)	% Conv. (CH_4)	% Conv. (CO_2)	% Yield (H_2)	% Yield (CO)	Coke	H_2/CO
600	700 (nr)	71.3	74.6	75.6	70.7	–	1.1
	750 (nr)	96.5	97.4	95.5	91.3	–	1.1
	800 (nr)	97.1	98.1	95.6	94.2	5.5×10^{-5}	1.0
750	700 (nr)	6.3	0.7	0.1	0.7	–	0.1
	700 (r)	93.7	85.4	85.3	74.2	–	1.2
	750 (nr)	10.8	9.5	1.3	6.7	–	0.2
	750 (r)	97.2	88.2	89.4	77.3	–	1.2
	800 (nr)	97.5	96.3	96.0	81.4	5.5×10^{-5}	1.2
	800 (r)	97.5	88.7	90.3	78.2	1.1×10^{-4}	1.2
900	700 (nr)	13.0	2.6	0.0	0.5	–	0.1
	750 (nr)	33.9	37.9	19.0	28.8	–	0.7
	800 (nr)	97.6	98.1	95.6	88.1	6.0×10^{-5}	1.1

Coke: mol of carbon mol^{-1} of ($CH_4 + CO_2$) converted h^{-1}.

Table 2
Effect of the composition and the preparation method (co-precipitation (C.P), impregnation (Imp.)) of the catalysts on the catalytic performances: $T_c = 750$ °C, $T_{red} = 800$ °C (2 h, 5% H_2/Ar), $T_r = 800$ °C, $CH_4/CO_2 = 1$

Catalyst	Prep. method	% Conv. (CH_4)	% Conv. (CO_2)	% Yield (H_2)	% Yield (CO)	Coke	H_2/CO
2Mg/Al	C.P	0.1	0.8	0.1	1.1	4.2×10^{-5}	0.1
$Ni_{0.05}Mg_{0.95}$	C.P	1.1	1.4	0.5	1.1	3.3×10^{-5}	0.1
5% Ni/MgO	Imp.	97.1	98.1	95.7	90.6	6.4×10^{-5}	1.1
$Ni_{0.05}Al_{0.95}$	C.P	96.2	98.8	96.3	79.2	1.3×10^{-4}	1.2
$2(Ni_{0.05}Mg_{0.95})/Al$	C.P	97.2	92.2	92.9	79.0	1.1×10^{-4}	1.2
$2(Ni_{0.1}Mg_{0.9})/Al$	C.P	97.5	88.7	90.3	78.2	1.1×10^{-4}	1.2

Coke: mol of carbon mol^{-1} of ($CH_4 + CO_2$) converted h^{-1}.

deposition. The most important coke deposition is observed on the catalyst without Mg loading. Over the $2(Ni_{0.1}Mg_{0.9})/Al$ catalyst, the catalytic activity increases with increasing the temperature of reaction; the highest activity and selectivity in syngas were obtained at $T_r = 800$ °C (Table 1). A previous H_2-reduction of the catalyst improves generally the catalytic performances. The best yield of synthesis gas ($CO + H_2$) was obtained after a calcination of the solid at 600 °C. The 2Mg/Al catalyst without nickel, calcined at 750 °C, reduced at 800 °C and tested at 800 °C, presented a poor activity (about 1% for CH_4 conversion). This catalyst, corresponding to a very low consumption of H_2 during the TPR, does not seem to undergo reduction. So, we assigned this low reforming activity to the absence of metallic phase, which is necessary to adsorption and activation of the reactants. Otherwise, $Ni_{0.05}Mg_{0.95}$ catalyst (without Al) tested in previous conditions, although reducible, presented also a poor activity towards the CO_2-reforming of CH_4 (with about 1% of CH_4 conversion); the low activity of this catalyst could be related to its low surface area (4 $m^2 g^{-1}$ against 54–165 $m^2 g^{-1}$ for the Al content catalysts). Whereas, 5% Ni/MgO catalyst, having the same composition of $Ni_{0.05}Mg_{0.95}$ solid but prepared by the impregnation method, is very active (97% of CH_4 conversion) and very selective (95% and 91%, respectively of H_2 and CO selectivity) and presents a low amount of coke deposit (6.4×10^{-5} mol of carbon/mol of ($CH_4 + CO_2$) converted h). This difference between the two catalysts could be attributed to the low BET surface area of $Ni_{0.05}Mg_{0.95}$ catalyst (4 $m^2 g^{-1}$ against 46 $m^2 g^{-1}$ for 5% Ni/MgO) and to the accessibility of the reactants to the Ni active sites, which seems difficult on Ni–Mg solid.

3.3. Characterization of the catalysts after reaction

The BET surface areas decreased generally after reaction (for example from 54 to 25 $m^2 g^{-1}$ for $2(Ni_{0.1}Mg_{0.9})/Al$ catalyst). XRD analysis of $n(Ni_xMg_y)/Al$ catalysts, depicted in Fig. 9, show the presence of metallic phase Ni^0 with a weak

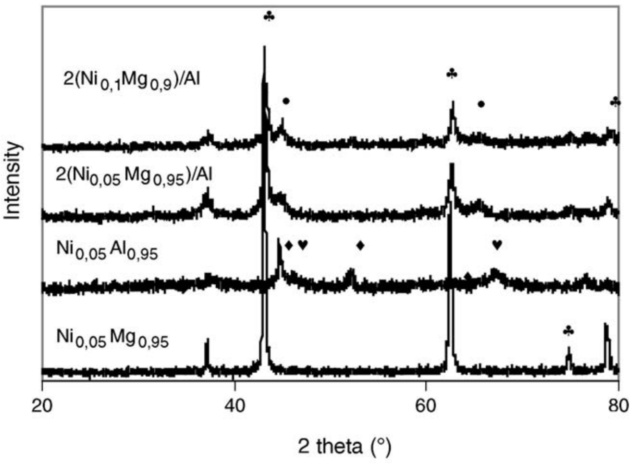


Fig. 9. XRD of $n(Ni_xMg_y)/Al$ catalysts after reaction T_c: 750 °C, T_r: 800 °C; CH_4/CO_2 ratio: 1. (●) $MgAl_2O_4$ or $NiAl_2O_4$, (♣) NiO–MgO or MgO, (♥) γ-Al_2O_3 and (◆) Ni.

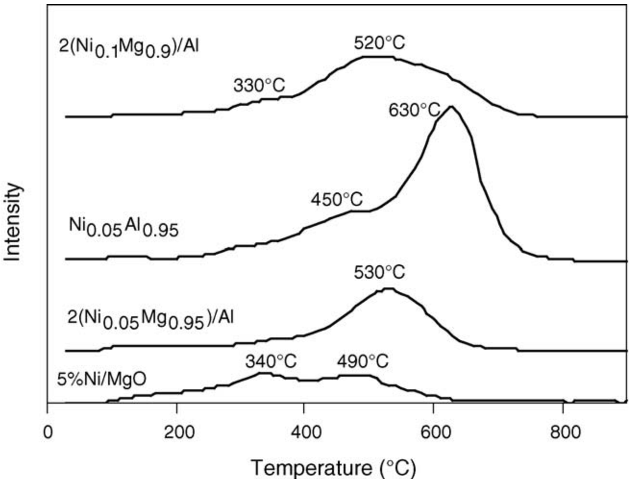


Fig. 10. TPO curves of $n(Ni_xMg_y)/Al$ and Ni/MgO catalysts after reaction. T_c: 750 °C, T_r : 800 °C and CH_4/CO_2 ratio: 1.

signal which is more obvious on the catalyst without Mg. The NiO, present in the catalysts, undergoes a low reduction because Ni^{2+} is incorporated into the structure NiO–MgO or $NiAl_2O_4$.

After reaction, the aged samples were subjected to TPO treatment to investigate carbon deposition. The amount of coke formed on the $n(Ni_xMg_y)/Al$ and Ni/MgO catalysts, during dry reforming, was estimated from the amount of CO_2 desorbed during the TPO experiments. The TPO profiles (Fig. 10) show generally four peaks of desorption at 330–340, 450–490, 520–530 and 630 °C ascribed to different types of coke. The two first peaks could be assigned to coke containing hydrogen (CH_x species) and/or surface carbon, the third one to the nickel carbide and the last peak to carbon nanotubes. All catalysts show low amounts of coke formation ($<1.3 \times 10^{-4}$ mol of carbon/mol of $(CH_4 + CO_2)$ converted h^{-1}). The amount of coke is relatively low on the Mg-containing catalysts (Table 2 and Fig. 10). The decrease of coking rate, when Mg concentration in the catalyst increases, is probably a consequence of the basic properties of MgO [20–22].

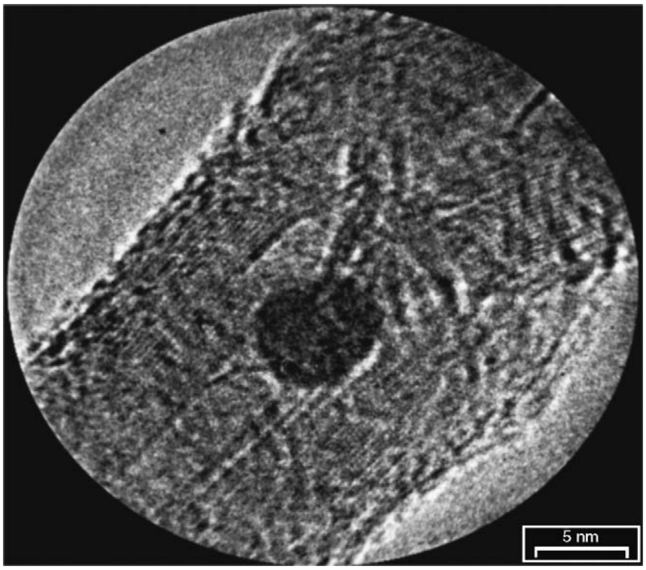


Fig. 11. Carbon nanotubes formation after reaction of $Ni_{0.05}Al_{0.95}$ catalyst: T_c: 750 °C, T_r: 800 °C and CH_4/CO_2 ratio: 1.

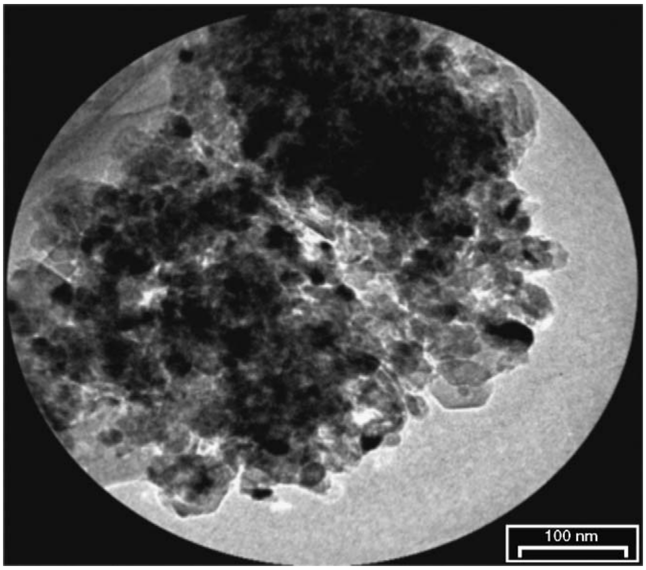


Fig. 12. TEM analysis of $2(Ni_{0.1}Mg_{0.9})/Al$ catalyst after reaction: T_c = 750 °C, T_r: 800 °C and CH_4/CO_2 ratio: 1.

TEM analysis of used $n(Ni_xMg_y)/Al$ and Ni_xAl_y catalysts (after 2 h of reaction at 800 °C), represented on Figs. 11 and 12, evidence the presence of coke deposit detected by TPO. Regarding the coke structure, the coke formed on $Ni_{0.05}Al_{0.95}$ catalyst (Fig. 11) shows a well structured forms (nanotubes) while a non-structured coke seems to have been formed on the $n(Ni_xMg_y)/Al$ catalysts (Fig. 12).

4. Conclusion

We may conclude that NiMg/Al catalysts, prepared by coprecipitation method and Ni/MgO, prepared by impregnation, are suitable catalysts for selective dry reforming of methane producing good yields of hydrogen and carbon monoxide with high CH_4 conversion. The catalysts are remarkably active even at the lowest reaction temperature studied (700 °C); they show a low carbon deposition even at the highest reaction temperature. A previous reduction of the solids improves their catalytic activity. The activity results indicate that CH_4 conversion and CO and H_2 selectivity approach that predicted by thermodynamics. The catalytic behaviour of these catalysts could be explained in terms of the reducibility and also of the good dispersion of Ni species due to the interactions between Ni and Mg–Al.

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