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Research article

Hydrogen Production by Catalytic Steam Reforming of Methane on Ni catalysts Prepared by Impregnation Under Microwave Irradiation Heating

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Abstract

Two nickel based catalysts 10%wtNiO/γ-Al_2O_3 were prepared by impregnation method with or without microwave irradiations heating, characterized and tested for methane steam reforming reaction (SRM).

The principal objectives are the effect of using microwave irradiations heating on the catalytic performances and coke formation. Various techniques including TGA-DTA, XRF, SEM, XRD, particles size and BET were used to characterize catalysts. Temperature programmed oxidation (TPO) experiments of formed carbon species deposited on the catalysts were conducted on a thermogravimetric analyzer in air. 10%wtNiO/γ-Al_2O_3 catalyst obtained with microwave irradiations heating showed excellent catalytic activity with high CH_4 conversion and high H_2 and CO yields. These performances are related to a surface enrichment with a homogeneous nickel nitrates precursor deposition during heating step under microwave irradiations, leading therefore after reduction, to high dispersion of nickel particles, better activity and slight coking tendency.

Keywords: Hydrogen, Syngas, Microwave, Nickel, steam-reforming,

Introduction

Catalytic reforming technology of methane has been widely studied for use in the large- scale production of hydrogen or carbon monoxide based on various processes i.e., CO_2 reforming of methane [1], partial oxidation of methane [2] and steam reforming of methane [3]. The methane-reforming process is therefore widely studied because of its importance in the petrochemical industry [4]. In addition, due to the increase in H_2 demand and the importance of synthesis gas as a major feedstock for C_1 chemistry and fuel cells, methane reforming reactions become more important. Otherwise, hydrogen production has received considerable attention [5-7]. Although steam reforming of methane (SRM) is a very energy-intensive process due to highly endothermic property of the reaction. The obtained H_2/CO ratio (about 3) is well suited for processes requiring a H_2 rich feed (such as ammonia synthesis and petroleum refining process).

The reaction can be represented by Eq.(1).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^\circ_{298°C} = +206\ kJ.mol^{-1} \qquad (1)$$

This overall reaction occuring at high temperature (800°C), is always followed by the water gas shift reaction (WGS) producing CO_2; co-product of the synthesis gas Eq.(2).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^\circ_{298°C} = -41\ kJ.mol^{-1} \qquad (2)$$

However, the high temperature of steam reforming reaction favours several routes of carbon formation [3], via Boudouard Eq.(3) reaction and methane decomposition Eq.(4).

$$2CO \rightarrow C + CO_2 \qquad \text{(Boudouard reaction)} \qquad (3)$$

$$CH_4 \rightarrow C + 2H_2 \qquad (4)$$

The total conversion of methane into syngas (H_2+ CO) by steam requires minimizing CO_2 and Carbon formation.

To develop Ni-based catalysts with improved performances and lower coking tendency, a new preparation method based on impregnation with heating under microwave irradiations was considered.

It's well known that microwave heating process presents reduced time required for synthesis, clean, cost effective and energy effective [8,9].

Materials and Method

-Catalysts synthesis

Microwave irradiations heating (NA1 catalyst)

The domestic microwave equipment used in this work operates at 2.45 GHz, which is the most common operating frequency for microwave devices. γ-Al_2O_3 support was impregnated through interaction (wet soaking) with nitrates nickel $Ni(NO_3)_2,6H_2O$ solution containing the required amount of nickel precursor to obtain 10wt% of nickel content. The aqueous suspension was placed in microwave oven with an output power of 100W and stirred until total water evaporation. The obtained wet powder was further dried overnight in an oven at 50°C then calcined under flow air at 700°C/2h in a muffle furnace (heating rate of 5°C.min^{-1}).

Conventional thermal (NA2 catalyst)

γ-Al_2O_3 was impregnated with $Ni(NO_3)_2,6H_2O$ aqueous solution at the proportion of 10wt%NiO. The resulted solution was vigorously stirred on a heating plate at 80°C until total water evaporation. The resulting wet powder was dried overnight in an oven at 50°C and finally calcined under flow air at 700°C/2h (heating rate of 5°C.min^{-1}).

The size of the used pellets is between 0.200 and 0.315mm for both catalysts (NA1 and NA2).

-Characterizations

TGA-DTA analyses were performed under air between 20°C and 500°C at a heating rate of 10°C.min^{-1}. At 500°C, the run was continued for 30min. XRD analyses were performed on a D5000 Siemens diffractometer using the CuKα radiation (λ= 0.15406 nm). The crystallite size was calculated using Eva XRD data by the Scherer equation. The morphology of the catalysts surface was characterized by SEM (JEOL- JSM-840). BET areas were calculated from the N_2 adsorption isotherms at 77K using a SA310 Coulter sorptiometer. Temperature programmed oxidation (TPO) experiments of carbon species formed on the catalysts were conducted on a thermogravimetric analyzer (Shimadzu TGA-50) in air from 25°C to 900°C with a flow rate of 80 mL.min^{-1} and a heating rate of 10°C.min^{-1}.

-Catalytic test

The catalytic performances were tested in the steam reforming of methane reaction, converting, under water steam, methane to synthesis gas reaction. The CH_4/H_2O reaction was carried out between 500-700°C, in a continuous flow fixed-bed tubular quartz reactor working at atmospheric pressure. The reactor is disposed in a tubular oven, connected to a temperature regulator. The catalyst (0.2g) is first pretreated at 500°C for 1h under hydrogen atmosphere 5%H_2/Ar at a flow rate of 1.2 L.h^{-1} (heating rate of 5°C.min^{-1}). The working temperature is readdening using a millivoltmeter connected to a chromel–alumel thermocouple. The mixture of the reactants CH_4/H_2O was obtained by bubbling 10%CH_4/Ar with a flow of 1.2 L.h^{-1} in the saturator at 65°C followed by a condenser cooled to 0°C. At 65°C, H_2O/CH_4 molar ratio reaches a value of 3. The reactants and products were analysed online using Delsi 121ML TCD Gas Chromatograph equipped with Carbosieve column. The activity of catalysts was evaluated at steady state. Uncertainty on methane conversion was evaluated at 10%.

The CH_4 conversion and H_2 and CO yields are calculated as follows:

$$CH4\ Conversion(\%) = \frac{\text{moles of CH4 converted x 100}}{moles\ of\ CH4\ in\ feed}$$

$$Yield\ of\ CO(\%) = \frac{\text{moles of CO produced x 100}}{\text{moles of CH4 in feed}}$$

$$Yield\ of\ H2\ (\%) = \frac{\text{moles of H2 produced x 100}}{\text{3 moles of CH4 in feed}}$$

Results and Discussion

-TGA-DTA of non calcined catalyst

Before calcination step, TGA-DTA measurement was performed under flow air between 20 and 500°C (slope 10°C.min^{-1}) for NA1 wet powder. A sample analysis is shown in Figure 1.

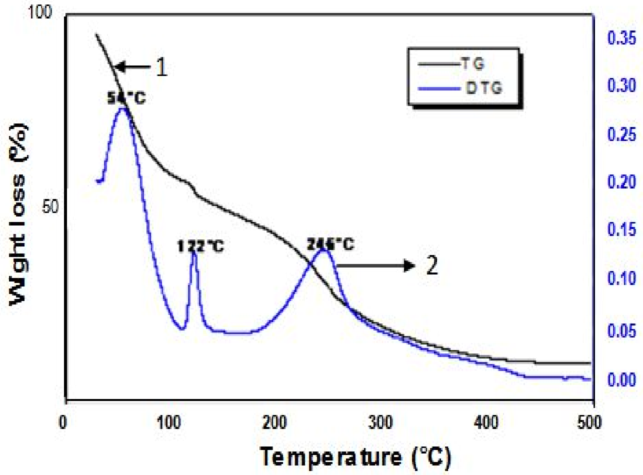

Figure 1: TGA (1) and DTA (2) of non calcined NA1 catalyst.

The first weight loss is attributed to the removal of physisorbed water, the second one is related to the endothermic dehydration of nickel nitrates between 80 and 230°C.

The third weight loss occurring between 230 and 420°C corresponds to the nickel nitrates decomposition. No mass loss is observed beyond this temperature. As a conclusion, all nitrates are completely decomposed at the chosen calcination temperature (700°C).

-SEM

SEM morphology of NA1 and NA2 catalysts are depicted in Figure 2. The microwave heating catalyst showed NiO particles regularly deposited over all alumina support, then better dispersion of actives sites (Figure 2b) compared to the conventional heating catalyst, giving NiO particles with some non homogenous agglomerates on the surface (Figure 2a).

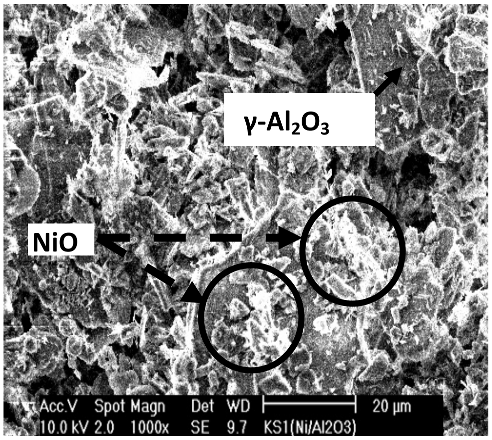

Figure 2a: SEM micrograph of NA2 catalyst.

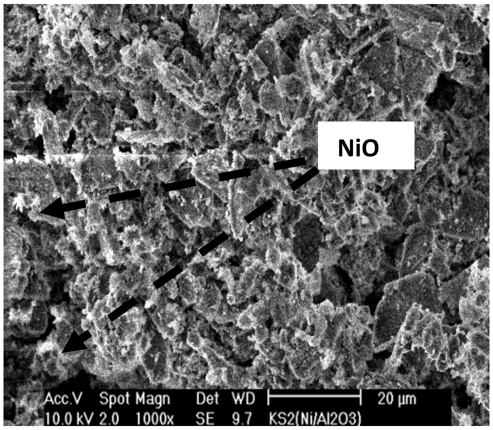

Figure 2b: SEM micrograph of NA1 catalyst.

During the convective heating process, moisture evaporates from the outside resulted from the thermal gradient [10,11]. The gradient causes the outward flow from the inside to the outside of the bulk material leading to an accumulation of nitrate precursor in the outer region of the support. This convective heating leads then to low dispersion and increase of the average nickel particle sizes during calcination operation. Under microwave heating, by minimizing the drying time at lower temperature, particles agglomeration phenomenon decreases sensitively. The formed active NiO particles obtained during calcination are smaller and uniform [12]. Others studies have reported their research respectively about successfully obtained homogenous dispersion of V_2O_5 on the surface of SiO_2 and higher Co particles distribution on SiO_2 support under microwave irradiations heating [8]. According to their research results, V_2O_5 and Co particles agglomerate on the silica support under conventional heating.

-XRD

The XRD patterns of NA1 and NA2 catalysts are shown in Figure 3 and Figure 4. The diffraction peaks at 2θ=37.3, 43.3 and 62.9° characterise the NiO phase (JCPDS file no.47-1049) and those at (2θ= 33.6, 37.5, 39.4, 45, 67.4°) are attributed to γ-Al_2O_3 phase (JCPDS file no 46-1131). These results are in agreement with previously reported 2θ values respectively of NiO [13] and γ-Al_2O_3 [14]. No more additional diffraction peak could be clearly observed. $NiAl_2O_4$ phase was not detected by XRD under the present calcination temperature conditions.

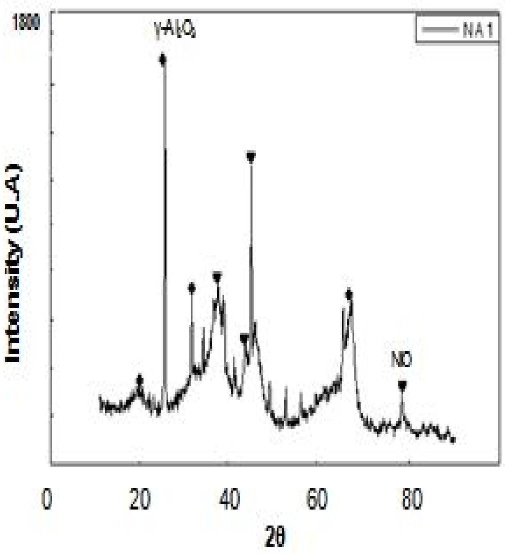

Figure 3: XRD pattern of NA1 catalyst.
♥NiO, ◆γ-Al_2O_3

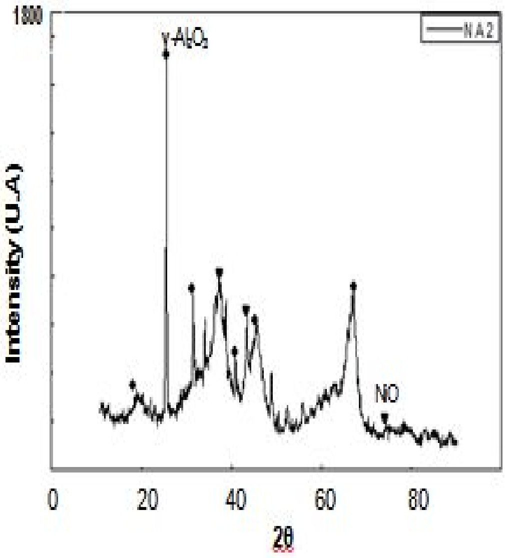

Figure 4: XRD pattern of NA2 catalyst.
♥NiO, ◆γ-Al_2O_3

Otherwise, NA1 and NA2 catalysts show the same NiO pattern peaks with different intensity. The intensity of the NiO peaks increases in the case of microwave heating catalyst. Such results were observed by Zabova et al. [11]. The obtained material through microwave drying presenting smaller nitrates aggregates on alumina conduces to better crystallinity.

Average NiO crystallite diameter using Scherer equation from XRD is given in table 1.

Table 1: Crystallite size of NiO

Catalyst	Ni% (XRF)	Crystallite size (nm)
NA1	10.50	25.40
NA2	10.37	27.39

Smaller NiO particles sizes were achieved from microwave heating (25.40 nm) compared with those provided by conventional heating one (27.39 nm).

- BET

Table 2 depicts the nitrogen BET surface areas of NA1 and NA2 catalysts. From nitrogen physisorption, type I isotherm is obtained corresponding to microporous materials.

Table 2: BET surface areas of microwave and conventional heating catalysts.

Catalyst	S_{BET} (m^2/g)
NA1	93
NA2	78

Both NA1 and NA2 catalysts have similar values of surface areas 93 and 78 m^2/g respectively.

- Reactivity device

Table 3 lists obtained catalytic results (CH_4 conversion, CO and H_2 yields) over NA1 and NA2 samples in the temperature range of 500-700°C once the reaction steady-state is reached (3.5h).

Table 3: Catalytic performances on NA1 and NA2 catalysts at some temperatures

Catalyst	**Temperature (°C)**														
	500			**550**			**600**			**650**			**700**		
	CH_4	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**
NA1	53	33	49	71	45	72	92	70	79	96	74	82	99	80	92
	CH_4	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**	**CH_4**	**CO**	**H_2**
NA2	37	26	32	51	35	46	65	48	55	68	51	61	80	63	68

Hydrogen and carbon monoxide are obtained beginning at 500°C over both NA1 and NA2 catalysts previously reduced under hydrogen atmosphere at 500°C for 1h. The methane consumption increases with temperature for both NA1 and NA2 catalysts. Microwave heating process seems to affect sensitively the global conversion of methane, CO and H_2 yields. CO and H_2 yields obtained with microwave heating catalyst are much higher than those obtained with conventional heating one, reaching at 700°C, 92% against 68% for H_2 and 80% against 63% for CO. These results could be related to the availability of homogenously dispersed and size-controlled Ni active sites on the alumina surface for NA1 catalyst; consequence of a better dissociative adsorption of methane CHx species. CO is mainly transformed into carbon by Boudouard reaction Eq.(3) on agglomerated nickel particles sites for NA2 catalyst.

In both cases, NA1 and NA2 catalysts lead to Ni° and γ-Al_2O_3 phases after steam reforming reaction.

-Coke formation and TPO of used catalysts

Eventual carbon deposits formed during methane steam reforming reaction were investigated by temperature programmed oxidation (TPO) experiments on a TGA.
The XRD pattern of NA2 used catalyst after 9 hours reaction time indexes only Ni and γ-Al_2O_3. This result indicates (i) that the deposited carbon is too much little to be detected by XRD and/or (ii) the deposited carbon is present in amorphous phase.

The deposited carbon was calculated and given in table 4. It can be seen that over NA1 catalyst, carbon is more easily oxidized with a CO_2 peak occurring around 550°C giving the lowest coking activity (0.4mol of carbon /g_{Ni}/h). In NA2 catalyst, carbon burning-off at 660°C gives highest coking activity (2.2mol of carbon /g_{Ni}/h). Such results suggest that nickel is present as small particles regularly dispersed on the surface and thus avoids or limits an excessive coke formation. With microwave heating process, the heat is supplied homogeneously through the whole of the material and evaporation takes place not only at the surface of catalyst, but also in the core of the grain. This lead to a much more homogeneous deposition of Ni particles (as evidenced by SEM analysis) and the catalytic activity should benefit from this surface enrichment conducting to less coke deposition [8].

In conclusion, the Ni particles in the conventional heating catalyst partly agglomerate on the surface showing lower and non uniform distribution with increase of the average particle size leading to more coke deposition.

Table 4: Amount of carbon deposition on catalysts determined by TGA after CH_4/H_2O reaction.

Catalyst	T of carbon oxidation (°C)	deposited coke [a]	Time on stream (h)
NA1	530	0.4	9
NA2	660	2.2	9

(a) Moles of carbon /g_{Ni}/h.

The lower carbon oxidative temperature peak is ascribed to the elimination of amorphous carbon species deposited on the surface of support. The higher one is due to the removal of filamentous carbon species.

Conclusion

On the basis of the results presented in the present work on the preparation, characterization and catalytic activity measurements of 10%wt NiO/γ-Al_2O_3 catalysts, it can be concluded that:

(i) The microwave drying method provides high catalytic activity with high H_2 and CO yield.

(ii)The microwave drying method leads to small Ni particles regularly dispersed on the surface and the catalytic activity should benefit from this surface enrichment conducting to less coke deposition.

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