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DESIGN OF ADVANCED CATALYSTS FOR HIGH TEMPERATURE CONVERSION PROCESSES

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Abstract. *Ni-based catalysts most widely used in carbon dioxide reforming of methane - i.e., the dry reforming reaction – because they have very important advantages. Advantages: High and cheap activity and selectivity, Low cost and good activity than precious metals; but involve high carbon (coke) deposition. Coke deposition on these catalysts has a significant influence on their cracking activity and selectivity and is the main reason for catalyst deactivation. Deactivation of the catalysts. This work reports the state of the art of hydrotalcite-based catalysts for the MRD reaction and provides a comprehensive overview of catalyst characterizations. Complete characterization of the catalysts in relation with their key properties (selectivity, activity...).*

Keywords: MDR reaction, Ni-Mg, reactivity, climate change, hydrogen

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1. Introduction

In recent decades, the planet Earth has suffered from climate change due to rising temperatures and greenhouse gases, especially carbon dioxide and methane. To solve this issue, academia and industry are trying to find a suitable solution to protect the environment for future generations. In addition, the need for clean, renewable energy is very important for the economy, industry and the development of society and living standards. Hydrogen is one of the best clean energy carriers.

Many sources are used to produce hydrogen: water electrolysis to produce green hydrogen [1] and methane reforming for grey, bleu hydrogen production [2].

Natural gas remains the safest and cleanest fossil fuel. Methane is the main component of natural gas. Methane reforming is therefore the natural gas upgrading process studied by steam reforming, oxidation and dry reforming [3].

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In this work, we focus on the study of methane dry reforming (MDR) as an application not yet used in industry. This process is very interesting for its dual impact: consumption of greenhouse gases (CH_4 and CO_2). In addition, the production of synthesis gas (H_2, CO) with an equimolar ratio ($H_2/CO = 1$), a unit required in industry notably for the Fischer Tropsch process [4].

The MDR reaction is studied at a high temperature of 1000°C. This temperature is not recommended in the industrial and energy-economic sector, so catalysts are used to apply the MDR process at lower temperatures, i.e. 650°C [5]. Unfortunately, the catalysts are rapidly deactivated by the sintering of the active phase and the deposition of carbon on the catalytic surface, preventing the application of the MDR reaction in industry to date.

Different types of catalysts are used for the MDR reaction [6-8], such as metal oxides, zeolites, MCM-41, nickel ferrites, noble metal catalysts. Nickel-based materials are mainly used for this process due to their availability, low cost and ease of synthesis in the laboratory.

The Ni-active phase remains the best catalyst for the MDR process. For this purpose, we chose materials with a defined double lamellar hydroxide (HDLs) structure, where the Ni phase is placed in a specific position in the HDL structure.

HDLs materials are anionic clays whose structure is based on a stack of positively charged sheets starting from the $Mg(OH)_2$ brucite, where Mg is replaced by divalent and/or trivalent metals with an anionic radius value close to Mg^{2+} [9]. Their general chemical formula is $\boldsymbol{[M_{1-x}^{2+}\, M_x^{3+}\, (OH)_2]^{x+}[A^{n-}_{x/n}].m\ H_2O}$ with M^{2+}, M^{3+}, A^{n-} and n^- represent divalent, trivalent metallic cations occupying octahedral positions in sheets. A^{n-}: interlayer anions (CO_3^{2-}, NO_3^-, Cl^-, OH^-) or organic anions and a charge in interlayer ion, x is molar fraction and m present the number of water molecules located in inter lamellar space [10].

This type of material has several important chemical properties [11], such as:

- High base characteristics,
- Exchange anions,
- High specific surface area, particularly after heat treatment,
- Memory effect: the structure can be regenerated after heat treatment at a calcination temperature not exceeding 450°C by placing the mixed oxides in a solution containing the appropriate anion.
- Good dispersion of the divalent and trivalent phases during preparation. Calcining materials at over 450°C leads to good dispersion of the metal phase which improves the synergetic effect, properties required in catalysis,
- Easy preparation method, particularly in the laboratory, as they are less abundant in nature.

According to their properties, HDLs calcined or non-calcined are used in different applications like catalysts or supported catalysts [12-13]. In addition, they are employed in catalysis domain, cosmetic, CO_2 capture, pharmaceutical and biotechnology through intercalation the bioactive molecule in HDL structure, photocatalyst, water treatment and electrochemical applications.

Mixed oxides catalysts from Ni (Mg) /Al generic hydrotalcite are prepared by crystallization solid phase (CSP) by using our specific conditions. The mixed oxides are obtained by calcination at 450°C for 6 h. Then, they are reduced at 650°C to form Ni^0 active phase. The purpose of this work is a comparative study to examine the position of the active phase into defined structure materials. In addition, the examination of the synergy effect Ni^0-Mg in the NiMgAl for DMR reaction. Catalytic reactivity, stability, and carbon deposit have been investigated.

2. Experimental

2.1. Catalysts preparation method

Catalysts used in this study were prepared by synthesis of the corresponding hydrotalcite-like material $((M^{2+})/(M^{3+}) = 2)(M^{2+} = Ni^{2+}$ or $Ni^{2+} + Mg^{2+}$, $M^{3+} = Al)$, by the crystallisation solid phase (CSP) method at basic constant pH (pH=11.0) at room temperature. During the synthesis, the solution **A** (M^{3+} ,M^{2+}) was added at constant rate, to the solution **B** (CO_3^{2-}, NaOH). The obtained gel was washed and dried over night at 80°C. The hydrotalcite-like compound was converted into derived oxide catalyst by calcinating for 6h at 450°C.

3. Analysis methods

The aim of this work is to determine the structural, textural and chemical-physical properties of the solids. In addition, to find a correlation between the properties, reactivity and behavior of the catalysts, various physico-chemical analyses were used and are described in this section.

3.1. Atomic Absorption spectroscopy (AAS)

The elemental composition of the samples was determined by Atomic Absorption Spectroscopy (AAS). Using a Spectro-Analytical Instruments, Horiba Jobin–Yvon, Ultima spectrometer. An amount of the solid sample was dissolved in a mixture of HNO_3 and HF acids. The measurements were obtained by the method of addition of standard solution using a Perkin-Elmer analyst equipment.

3.2. Brunauer–Emmett–Teller (BET) analysis

The specific surface of the samples (BET surface) was measured with NOVA 2000e apparatus by adsorption of nitrogen, at − 196°C by running some sorption/desorption cycles to investigate the nature of the pores from the adsorption isotherms. Before analysis, the samples underwent degassing under vacuum at 150°C for 2 h.

3.3. X-Ray diffraction (XRD) analysis

Powder X-ray diffraction (XRD) patterns were recorded with Siemens D-501 equipment, using CuK_α *radiation* in the 2θ range between 10 and 80°.

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where λ is the wavelength of $CuK\alpha$ (λ =1.5418 Å), β_{hkl} is the half width of the peak, and θ is the Bragg's diffraction angle.
Crystallite size was evaluated using the Scherrer's formula (Eq.1) [(14)].

$$d_{hkl} = d_{hkl} = \frac{0.9\lambda}{B_{hkl}\cos\theta} \qquad \text{(Eq.1)}$$

where: λ is the wavelength of $CuK\alpha$ (λ = 1.5418 A), βhkl is the half-width of the peak, and θ is the Bragg's diffraction angle.
The dispersion (D%) of the particles Ni^0 after reduction was estimated using the following equation (Eq. (2)) [15]

$$D(\%) = \frac{971}{d_{Ni\,(Å)}} \qquad \text{(Eq.2)}$$

3.4. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) profiles were performed using a TriStar 3000 V6.01A apparatus equipped with a TCD detector. The reduction of samples was subsequently treated under 5% H_2/ Ar with a flow rate of 50 mL/min from room temperature to 950°C with a heating rate of 10°C/min.

3.5. D Catalytic testing

The catalytic activity measurements were carried out under atmospheric pressure in a fixed-bed tubular reactor ("U" shaped), using approx. 100 mg of catalysts between two pompoms of quartz wool. Before reacting, the sample was reduced in-situ under hydrogen flow at 700°C for 1h. Then, the reactor was cooled down to the desired temperature and the reactant mixture ($CH_4/CO_2/Ar$) was passed through the reactor. The $H_4/CO_2/Ar$ molar ratio was 20/20/60 with a total flow rate of 30 mL/min. During the reaction testing, a cold-water trap containing acetone and CO_2 was used to condense the water formed during the catalytic test. The effluent gases from the reactor were analyzed by gas chromatography with a TCD detector and using porapak/molecular sieve.

4. Results and discussions

4.1. Characterization

4.1.1. Atomic Absorption spectroscopy (AAS) and BET analysis

Table 1. Catalysts Chemical properties.

Catalyst	$x = \frac{nM^{3+}}{n(M^{2+} + M^{3+})}$	$\frac{nM^{2+}}{nM^{3+}}$	Chemical composition	Ni/Mg ratio	Specific surface m²/g
					Calcined
NiAl	0.30	2.30	$Ni_{0.69}Al_{0.31}$	--	119
NiMgAl	0.31	2.19	$Ni_{0.14}Mg_{0.55}Al_{0.31}$	0.25	170

The chemical composition of the synthesized samples is shown in Table 1. The elemental analyses of the two solids corresponded well to the nominal value. The results confirmed that the value of the ratio between divalent and trivalent metals was close to the value set before preparation. In agreement with several studies, the ratio $M^{2+}/ M^{3+} = 2$ was considered as the best to obtain high crystallinity [16]. Similarly, the molar ratio (x) between M^{3+} and $(M^{3+} + M^{2+})$ (see Table I) indicates that the structure is pure hydrotalcite ($0.2 \leq x \leq 0.33$) [16].

The specific surface area of the two samples is 119 m²/g and 170 m²/g for the NiAl-c and NiMgAl-c samples, respectively. According to the literature, the presence of Mg in the hydrotalcite matrix increases the specific surface area due to its dispersive effect.

4.1.2. XRD characterization

The XRD patterns of the calcined and uncalcined samples are grouped together in Figure 1. The results indicate that these materials show clear symmetrical reflections in the (003), (006), (110) and (113) planes. Broad asymmetric reflections in (102), (105) and (108) planes were also obtained (Figure 1a). No diffraction peaks of other phases were detected, suggesting that the Mg cations have been isomorphically replaced by Ni and Al in the brucite-like layers.

The HDL interlayer space calculated from the peak (003) using the Bragg equation depends on the geometry and the anion size. These values were approximately 7.30 and 7.62 Å for NiMgAl and NiAl, respectively. It was a typical value compared to the work of Iglesias et al. [17]. However, Figure 1b of the calcined samples shows the formation of mixture phases; NiO and MgO. In addition, Al_2O_3 was well dispersed in the MgO matrix (NiMgAl), without the formation of a spinel phase.

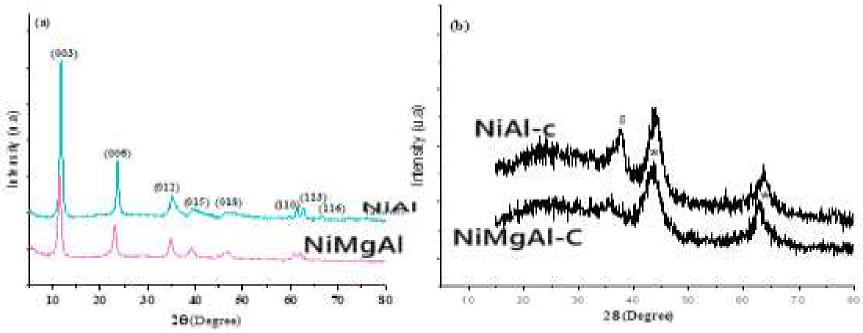

Figure 1: XRD Diffractograms for non-calcined and calcined samples

4.1.3. Temperature programmed reduction (TPR) characterization

The TPR profiles of the calcined samples are shown in Figure 2. NiAl-c and NiMgAl-c showed broad peaks located at 650°C and 800°C, respectively, which were attributed to the presence of segregated NiO or assigned to the reduction NiO into Ni^0. This reduction temperature was higher than for pure NiO.

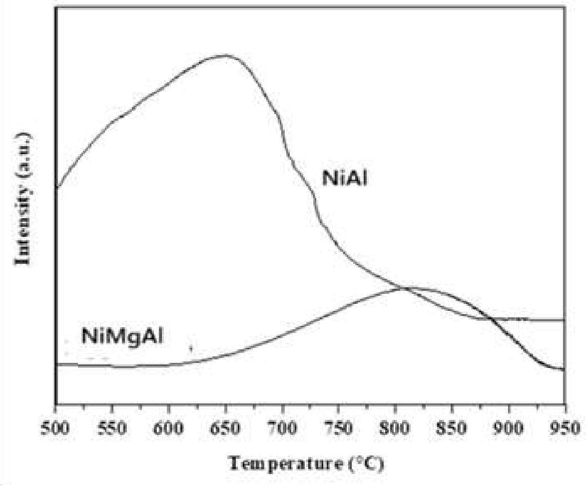

Figure 2: RTP profiles of samples

For RTP: we simply indicate the range 500-950°C

5. Catalytic testing

The literature review showed that all metals in Group VIII are suitable catalyst bases for the dry reforming of methane ($CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO_2$). This reaction is thermodynamically favored in the temperature range above 650°C [18].

Dry reforming of methane is a reaction with a double impact. From an environmental point of view, it reduces two greenhouse gases, CH_4 and CO_2, and from an energy point of view, it leads to the production of synthesis gas ($CO + H_2$)

[19]. Synthesis gas contains hydrogen, which is the energy carrier of the future. This process is even more interesting industrially, and therefore economically, as the H_2/CO ratio remains close to unity, which is the ideal value required for the manufacture of heavy hydrocarbons and oxygenated derivatives (alcohols, acids, etc.) [20]. From a thermodynamic point of view, the CO_2 molecule is stable and would require reducing agents such as hydrogen or methane. Hence the need to involve the dry reforming of methane more in various industrial processes.

The dry reforming reaction of methane is catalyzed by several types of catalytic systems, namely: supported catalysts, zeolites, mesoporous materials (MCM-41), HMS-type mesoporous silicate materials, and, of course, noble metal-based systems (Pt, Pd, Rh, Ru, etc.). The latter are highly active, selective, and resistant to carbon deposition, but their cost limits their large-scale use. Nickel- and cobalt-based catalysts, while effective, have the advantage of being much less expensive. However, their tendency to deactivate through sintering and/or carbon deposition remains a major problem.

Thus, at low temperatures, the CO dismutation reaction ($CO \leftrightarrow CO_2 + C$)) is strongly favored, leading to rapid poisoning of the catalyst [20]. The equilibrium of this reaction shifts toward the reactants as the temperature increases. Unfortunately, at high temperatures, catalyst sintering and deactivation by methane cracking ($CH_4 \leftrightarrow C + 2 H_2$) become significant.

The main challenge is to develop more efficient materials to overcome these technical difficulties. Numerous solutions can be found in literature. One of these consists of depositing the active phase in a well-defined structure such as hydrotalcites. These various reasons led us, in the context of this thesis, to use these mesoporous solids as catalytic systems.

These catalytic materials derived from hydrotalcites seemed suitable and appropriate for this application due to their many intrinsic properties, such as:

- the ability to disperse the active phase evenly and extensively,
- relatively large specific surface areas,
- their mesoporous nature, a property sought after in the field of catalysis,
- their acid-base and redox nature, which can be modulated according to the metal cations introduced into the matrix of the base solid.

This section will be devoted to the study of the dry reforming reaction of methane in the presence of two catalysts: NiMgAl, NiAl. In general, we propose to examine the following parameters:

- effect of the nature of the metals introduced into the hydrotalcite matrix,
- effect of the presence of Mg^{2+},
- synergistic effect of the coexistence of Ni^{2+} and Mg^{2+} (NiMgAl system),

For operating conditions for dry methane reforming tests, a mass of 0.02 g of catalyst is placed in a U-shaped quartz reactor.

- Before each catalytic test, the samples are activated by in-situ reduction under a hydrogen flow (D_{H2} = 20 mL/min) from room temperature to 700°C for 1 hour.
- Pressure: P = 1 atm.
- The reaction mixture is composed of CH_4: CO_2: He = 10:10:80 (D_{Total} = 50 mL/min).
- The results of the catalytic reactivity will be discussed in terms of the evolution of CH_4 and CO_2 conversions as well as the H_2/CO ratio as a function of reaction time.

- **Study of catalyst stability over time**

We examined the stability and evolution of the reactivity of our samples at 700°C over time. The choice of reaction temperature was based on data from the literature and previous laboratory work, which showed that interesting catalytic performances could be obtained in the temperature range 650 - 700°C [20]. To do this, the reduced catalytic load is placed in the reactor and subjected to the reaction mixture (CH_4, CO_2). The reaction temperature is increased at a heating rate of 4°C/min from ambient to 700°C, which is maintained for this study for more than 15 hours of operation.

At 700°C, the main products of this reaction are H_2 and CO. The conversion rates of CH_4 and CO_2, as well as the selectivity (H_2/CO ratio), in the presence of NiMgAl and NiAl catalysts, are shown in Figures 3.

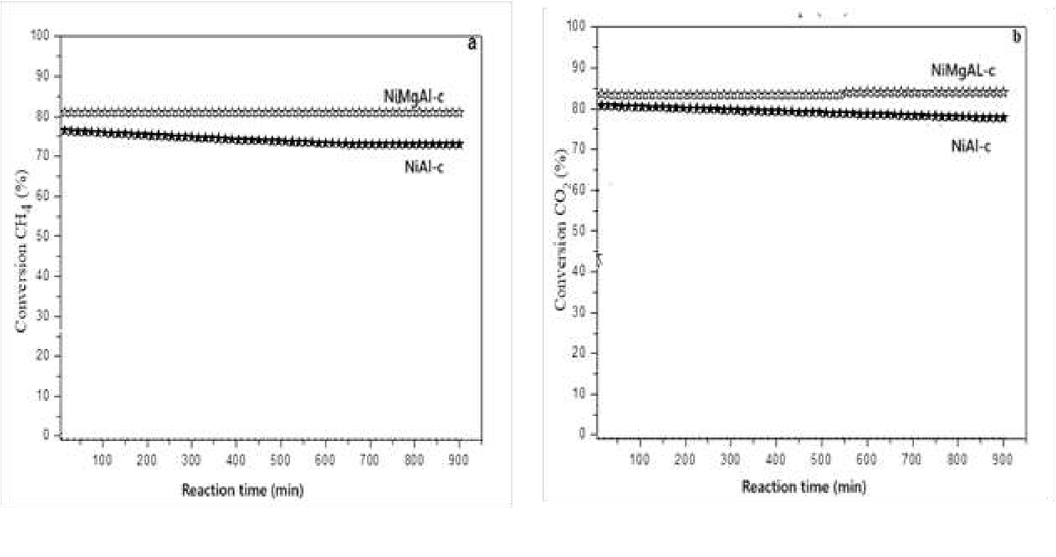

Figure 3: Evolution of CH_4 (a) and CO_2 (b) over time during the reaction at 700°C in the presence of NiMgAl-c and NiAl-c catalysts.

Considering the results obtained, we observed that the catalytic behavior of the catalysts is completely different. Consequently, the nature of the cation or active species directly influences the reactivity of our catalytic systems.

The results grouped in Figure 3 show that all catalysts: NiMgAl-c, NiAl-c, are active from the moment they come into contact with the reaction mixture. The CH_4 conversions are 81% and 73%, respectively in the presence of the NiMgAl-c and NiAl-c catalysts, while the CO_2 conversions are 84% and 78%, respectively. We have thus calculated the synthesis gas selectivity's, illustrated here by the H_2/CO ratio, which under our conditions reach values of around 0.97 and 0.94 respectively (Figure 4).

The difference in catalytic behavior between the two nickel-based catalysts, NiMgAl-c and NiAl-c, is mainly because Ni^0 is the species recognized as the main active phase in the reaction examined and under these catalytic testing and synthesis operating conditions. This Ni^0 species has been mentioned in the literature [21].

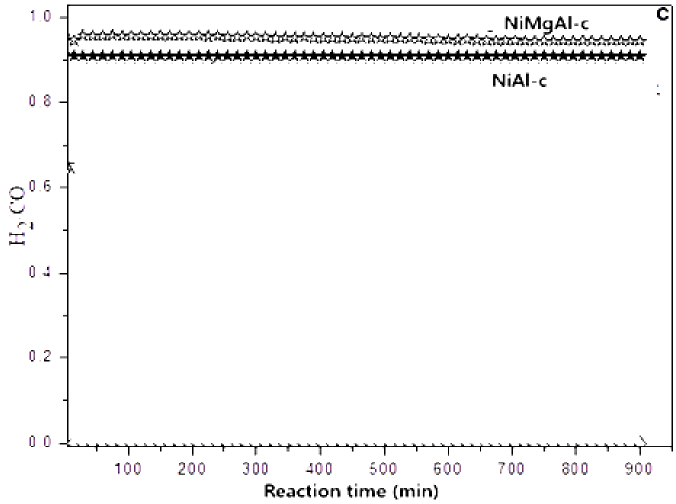

Figure 4: Evolution of H_2/CO selectivity over time during the reaction at 700°C in the presence of NiMgAl-c, NiAl-c catalysts.

Furthermore, for all catalysts, CO_2 conversions are slightly higher than those of CH_4, suggesting the occurrence of secondary reactions, in particular the reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$) which tends to increase the CO_2 conversion and also CO production, which becomes higher than that of H_2 [22].

To facilitate the comparison and interpretation of the results obtained, Table 2 summarizes the evolution of CH_4 and CO_2 conversions recorded at 700°C, the

H_2/CO ratio, particle size and dispersion (D%), and the specific surface areas of the reduced catalysts.

Table 2: CH_4 and CO_2 conversions, H_2/CO ratio after 15 hours of reaction at 700°C, particle size of (Ni^0) (nm), and particle dispersion D (%) of reduced catalysts.

Catalysts	Conversion		Selectivity H_2/CO	Size of the particles (nm)	D (%)	Xc (%)
	CH_4 (%)	CO_2 (%)		$(Ni^0)^a$		
NiMgAl-c	81,0	84,0	0,97	5,0	19	97,9
NiAl-c	73,0	78,0	0,94	9	11	95,0

Considering these results, we note that the NiMgAl-c solid exhibits the best catalytic performance. Several factors may explain this catalytic behavior: textural properties (specific surface area), reducibility, and acid-base properties. Indeed, the NiMgAl-c solid has a higher specific surface area than the NiAl-c solid, 171 vs. 100 m^2/g, respectively. Furthermore, the presence of Mg cations enhances the basicity of the catalyst, which reduces its tendency to deactivate due to carbon deposition [15]. Thus, the basicity ranking of the two samples is as follows: NiMgAl-c > NiAl-c [23].

The size of the nickel particles is a determining factor in the catalytic profile of our solids. The results obtained show that the Ni^0 particle size in the case of NiMgAl-c and NiAl-c solids is in the order of 5 and 9 nm, respectively (Table 2). Indeed, the catalytic performance of solids is even more significant when the particle size is smaller. The formation of the NiO-MgO solid solution in the case of the NiMgAl-c solid leads to good dispersion of the active phase, which promotes the formation of fine metal particles. Our results are consistent with the literature, which has widely demonstrated the doping effect of Mg in both dry reforming and methane steam reforming reactions [24].

Conclusions

Ni(Mg)Al hydrotalcite based catalysts were prepared by the coprecipitation method at a fixed pH=11.Above 450°C. The samples were tested in dry reforming of methane, the catalytic activity of catalysts can be classified as follows: NiMgAl-c> NiAl-c. It is explained by the doping Mg effect in NiMgAl-c

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Notations and/or **Abbreviations**

DMR: Dry methane reforming

CSP: Crystallization Solid Phase

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