

# Hydrogen production via methane dry reforming process over CoAl and CoMgAl-Hydrotalcite derived catalysts

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**Abstract.** Co<sub>0.67</sub>Al<sub>0.31</sub> and Co<sub>0.14</sub>Mg<sub>0.54</sub>Al<sub>0.31</sub> hydrotalcite based catalysts were prepared by a co-precipitation method at a fixed pH=11, exhibiting a suitable hydrotalcite structure to be used as a catalyst in the reaction of the dry reforming of methane (DRM). Calcination at 450 °C provides the best conditions to prepare the most adapted structure and morphology to be later used in the DRM reaction. The samples were characterised by XRD, FTIR, SEM and it was shown that they exhibit a specific surface in the 30-70 g/cm<sup>2</sup> and a crystallite size of approximately 20 nm. The results of the TPR analysis showed clearly that CoAl-HT has better catalytic performances than CoMgAl-HT. This result can be explained by the presence of the Co<sup>0</sup> for the catalyst CoAl-HTc-R and the total absence in the sample CoMgAl-HTc-R. The solid CoMgAl-HTc-R requires high reduction temperature compared to CoAl-HTc-R due to the strong CoO-MgO interactions.

**Keywords:** dry reforming of methane, hydrotalcite, Co<sup>0</sup>-catalyst, hydrogen, syngas

**Track Name:** Advanced Technology and Renewable Energy (Climate Change)

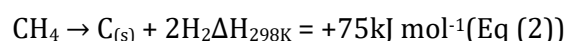
## 1. Introduction

Environmental issues and global warming resulting from the use and emission of greenhouse gases are two of the most important challenges of the 21<sup>st</sup> century. Therefore, reducing the emission of these greenhouse gases or at least converting thermo-industrial products is intensively investigated. The dry



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reforming of methane (DRM) reaction to produce syngas ( $\text{CO} + \text{H}_2$ ), a process extensively investigated in the last few decades [1]. Compared to the steam reforming reaction [2], DRM reaction produces syngas with lower  $\text{H}_2/\text{CO}$  ratio [1], which is more appropriate for the Fischer-Tropsch and methanol syntheses [1, 2]. Hence, the DRM reaction can contribute to the reduction of two greenhouse gases, what may render its utilization as an environmentally friendly process [1, 3]. Unfortunately, severe deactivation of catalysts, mostly caused by sintering of the nickel particle (active phase) and the filamentous carbon deposition which leads to the reactor blockage, [1, 3] hamper an industrialisation. The carbon formation on the catalytic active surface are owing to the inverse Boudouard's reaction (**Eq. 1**) and methane decomposition (**Eq. 2**)



The dry reforming of methane (DRM) by  $\text{CO}_2$ : ( $\text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{CO} + 2 \text{H}_2$ ,  $\Delta H_{298\text{K}} = +247 \text{ kJ/mole}$ ) is an attractive reaction to produce  $\text{H}_2$  as clean energy source and e-mobility [3]. This reaction can be carried out at high temperatures (1000-1200 °C) without catalysts [1, 3] but at the cost of the facility lifetime due to corrosion and materials issues. This can be partially alleviated by using supported noble metals (Ru, Rh and Pt) but not affordable industrially. Ni-based catalysts are among the best catalysts which exhibit comparable behaviour to noble metals. However, they undergo rapid poisoning and deactivation by carbon deposition and sintering. Confining of nanoparticles in core-shell and the core-sheath based structures can exert a spatial restriction, hinder their sintering and of carbon deposit [4]. "Solid phase crystallization (SPC)" materials ( $\text{ANiAl}_{11}\text{O}_{19-x}$  (A= Ca, Sr, Ba, La) [5], pychlore  $\text{A}_2\text{B}_2\text{O}_7$  [6], perovskite  $\text{ABO}_3$  [7], solid solution type AO-BO [8], spinel  $\text{AB}_2\text{O}_4$  [5], ferrite spinel [9] and hydrotalcite [10-12] allow to obtain homogenous distributed metallic phases in a well-defined crystal structure. HT compounds are lamellar anion clays of general formula  $[\text{M}_{1-x}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are the divalent and trivalent cations,  $\text{A}^{n-}$  is the interlamellar anion of valence  $n$ ,  $x = [\text{M}^{3+}]/([\text{M}^{3+}] + [\text{M}^{2+}]$  and  $0.20 < x < 0.33$  [10, 11] are prepared by solid-phase crystallization method to obtain a pure lamellar and well crystallized structure. Calcined hydrotalcite materials form mixed-metal oxides having a high thermal stability and a great dispersion of fine metal active phase (after reduction) are well suited for DRM [10, 13-15]. Bhattacharyya et al. [16] compared supported HT catalysts as  $\text{Ni}/\text{Al}_2\text{O}_3$  or  $\text{Ni}/\text{MgAl}_2\text{O}_4$ . The substitution of Ni for Mg leads to the higher Ni metallic particle dispersion. For  $\text{Ni}/\text{CeO}_2$  catalysts, Ni particles are stabilized on the  $\text{CeO}_2$  surface (reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  and the mobility of oxygen species) [17]. For semi-conductor perovskite  $\text{LaNiO}_3$ , amorphous phase NiO (not detected by classical XRD) was evidenced [18]. For  $\text{Ni}/\text{ZrO}_2$  catalysts, XAS results have shown a lower coordination number of Ni in the sample treated with CO than that with  $\text{H}_2$  [19]. For  $\text{NiAlMg}$  reduced by  $\text{H}_2$  at 850 °C, the  $\text{Ni}_{1-x}\text{Mg}_x\text{O}$  remained partially unreduced depending on Ni content [20]. Recently, we have shown that the thermal pre-treatment strongly influences the activity and selectivity of the catalysts during DRM reaction [12]. The exchange of Ni for Co was investigated with the synthesis of CoAl and CoAlMg based hydrotalcite catalysts.

## 2. Materials and Experimental Techniques

### 2.1 Materials

CoAl-HT and CoMgAl-HT samples with  $\text{M}^{2+}/\text{M}^{3+}$  ratio equal to 2 were prepared by a co-precipitation method at a fixed pH (i.e., 11) from a solution containing the appropriate amounts of nitrate salts of  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ . Sodium carbonate solution (1M) was added dropwise to the nitrate solution while the pH was maintained constant by adding NaOH solution (1M) under vigorous stirring at room temperature. The obtained slurry was hydrothermally treated at 70 °C for 15 h, washed several times

using bi-distilled water until a neutral pH of the filtrate was reached. The recovered solid was dried overnight in an oven at 80 °C and crushed to get a homogeneous fine powder. Finally, the powder was calcined in the air in an oven at 450 °C for 6 h with a heating increment of 4 °C/min. The corresponding products are named M<sup>2+</sup> M<sup>3+</sup>-HTc. Temperature programmed reduction (TPR) profiles were determined using a TriStar 3000 V6.01A apparatus equipped with a TCD detector. Prior to reduction, specimens (approx. 20 mg) were flushed with argon in a quartz reactor tube, heated at 120 °C for 2 h under an argon flow with a heating rate of 5 °C/min and cooled afterwards to room temperature. Samples were submitted to a 5% H<sub>2</sub>/Ar flow up to 950 °C with a 10 °C/min rate. The obtained solids are labelled M<sup>2+</sup> M<sup>3+</sup>-HTc-R.

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 pompons 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<sub>4</sub>/CO<sub>2</sub>/Ar) was passed through the reactor. The CH<sub>4</sub>/CO<sub>2</sub>/Ar molar ratio was 20/20/60 with a total flow rate of 30 mL.min<sup>-1</sup>. During the reaction testing, a cold-water trap containing acetone and CO<sub>2</sub> 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. The catalytic properties were evaluated in terms of CH<sub>4</sub> and CO<sub>2</sub> conversions (Eq. 3), H<sub>2</sub>/CO selectivity (Eq. 4) and carbon deposition (Eq. 5), as follows:

$$a_i = \frac{D^{\text{in}} X_i^{\text{in}} - D^{\text{out}} D_i^{\text{out}}}{D^{\text{in}} X_i^{\text{in}}} \quad (\text{Eq. 3})$$

$$S_{H_2/CO} = \frac{n_i' H_2}{n_i' CO} \quad (\text{Eq. 4})$$

$$X_c (\%) = \frac{D^{\text{out}} (X_{CH_4}^{\text{out}} + X_{CO_2}^{\text{out}} + X_{CO}^{\text{out}})}{D^{\text{in}} (X_{CH_4}^{\text{in}} + X_{CO_2}^{\text{in}})} \times 100 \quad (\text{Eq. 5})$$

where,

$a_i$ : catalytic activity (conversion) while  $i$  represents CH<sub>4</sub> or CO<sub>2</sub>.

$D^{\text{in}}/D^{\text{out}}$ : flow rate of the effluent in/out.

$X_i^{\text{in}}/X_i^{\text{out}}$ : CH<sub>4</sub> or CO<sub>2</sub> composition in/out.

$m_{\text{cat}}$ : catalyst amount.

$n_i'$ : rate of CO or H<sub>2</sub>.

$X_c$ : carbon balance.

## 2.2 Techniques

The chemical composition was determined by Atomic Absorption Spectroscopy (AAS) using Spectro-Analytical Instruments Horiba Jobin-Yvon, Ultima spectrometer. Before the analysis, the dissolution of 100 mg of the solids was affected in the presence of 20 ml of aqua regia, then further diluted to 100 ml with distilled water. Powder X-ray diffraction (XRD) patterns were recorded with Siemens D-501 equipment, using CuK $\alpha$  radiation in the 2 $\theta$  range between 10 and 80°. The average crystallite sizes of Co<sup>0</sup> following reduction were estimated from Scherrer's formula. Specific surface measurements were carried out using a NOVA 2000e volumetric adsorption analyzer at -196 °C (liquid nitrogen). Before the analysis, the powder was degassed under vacuum at 150 °C for 2 h. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer model number spectrometer. Over 32 scans were taken to improve the signal-to-noise ratio in the wavelength range (400 - 4000 cm<sup>-1</sup>). The analysis was

performed on ca. 4 mg of powder mixed with 100 mg of dried spectroscopic KBr pressed into pellets. Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were performed using a Netzsch STA 409 PC/PG instrument under air as purge gas from room temperature up to 850 °C with a heating rate of 10 °C/min using alumina crucibles. Scanning electron microscopy images (SEM) of the products were recorded on a Hitachi S-4800 instrument equipped with a field emission filament using an acceleration voltage of 5 kV and a working distance of 10 mm.

### 3. Results and Discussion

#### 3.1 Structural and textural properties of CoAl-HTc and CoMgAl-HTc compounds

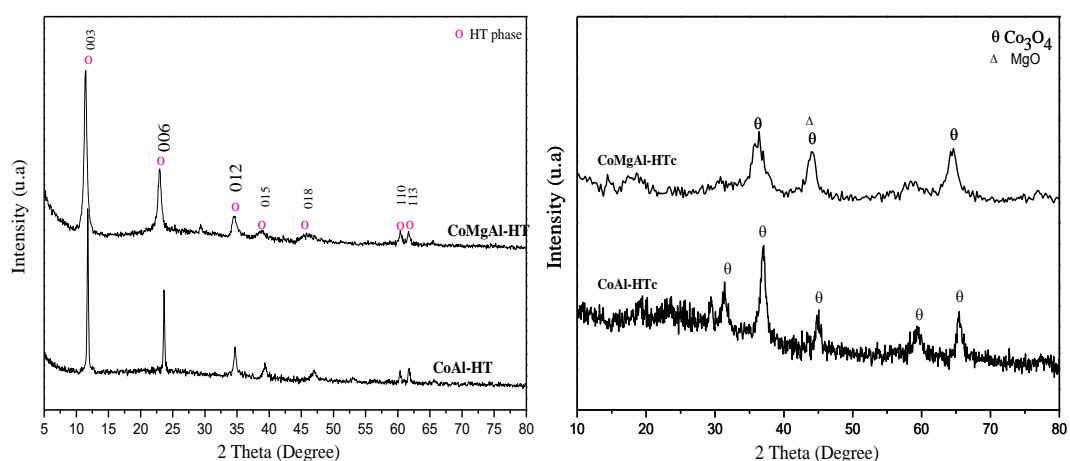
The chemical compositions of the synthesized samples are summarized in Table 1. The values of the ratio between the divalent and trivalent metals were found to be close to 2 indicating that hydrotalcite formed. XRD analysis confirmed the presence of the crystallised hydrotalcite based phases (Table 2) in comparison to natural hydrotalcite compounds. By combining DTA/TGA, two thermal events were observed in the 100-350 °C temperature range. The dehydration of CoAl-HT and CoMgAl-HT occurs between 100 and 210 °C whereas the decarbonation/dehydroxylation at 250 and 350 °C, respectively. With the CoMgAl sample, the temperature area is much broader and included some solid phase transformation as it was shown by the presence of mixed oxides by XRD. In both cases, the sample underwent a mass loss of approximately 30 % and about 400 °C no thermal event was recorded. Once calcinated, the structure become partially amorphous with the presence of oxide MgO, Co<sub>3</sub>O<sub>4</sub> or even mixed oxide such as CoAl<sub>2</sub>O<sub>4</sub>. FTIR spectra of the synthesized materials exhibit the general features often reported for the hydrotalcite like materials[10]. The presence of mixed oxide is important as it involved the presence of oxides with different oxidation states that affect the catalytic properties. The apparent bands recorded at ~ 3400 cm<sup>-1</sup> were attributed to OH stretching vibrations in the brucite-like layers or to the adsorbed and interlayer water molecules. The band around 1625 cm<sup>-1</sup> was assigned to H-O-H deformation mode confirming the presence of water molecules in the interlayer region. The BET specific surfaces were measured by nitrogen absorption and found close to ~ 77 and 30 m<sup>2</sup> g<sup>-1</sup> for CoMgAl-HT and CoAl-HT, respectively. The values of pore diameters for both solids non calcined and calcined lie between 4 and 7 nm. These values are typical of mesoporous materials. No significant pore size increase was observed with the addition of magnesium in the sample CoMgAl-HT. It turns out that the specific surface area and pore diameter are enhanced by the presence of Mg in hydrotalcite structure. From the SEM pictures, well dispersed agglomerates (crystallite size: approx. 20 nm from XRD measurements) are produced. After calcination, it is evident that there is a microstructural changes and reduction of the size of the agglomerates.

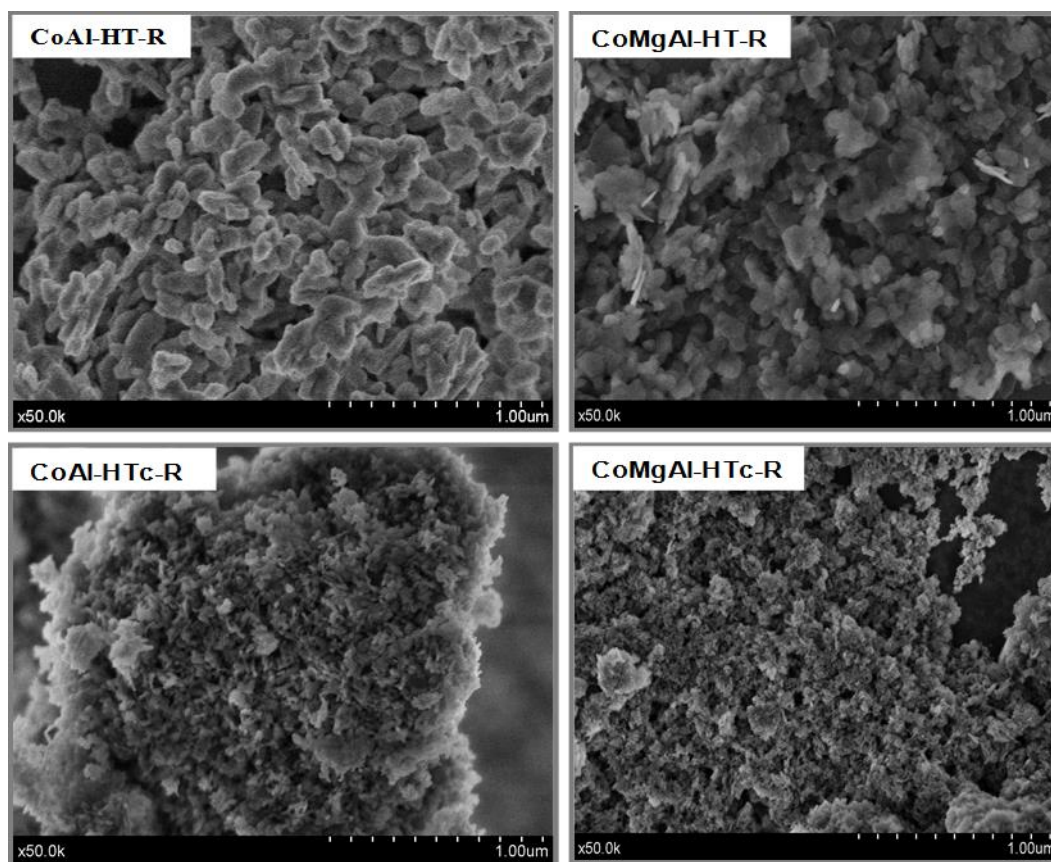
**Table 1.** Chemical composition and formula of calcined samples.

	Molar ratio $x = \frac{nM^{3+}}{n(M^{2+} + M^{3+})}$	$R = \frac{nM^{2+}}{nM^{3+}}$	Chemical formula
CoMgAl-HTc	2.20	0.31	$Co_{0.14}Mg_{0.54}Al_{0.31}$
CoAl-HTc	2.03	0.33	$Co_{0.67}Al_{0.31}$

**Table 2.** Crystallographic data of calcined samples \* R: Hydrotalcite natural reference, MgAl-HTc[10]

	$d_{003}(c=3d_{003})$ (Å)	$a = 2 d_{110}$ (Å)	$c / a$
MgAl-R*	7.58 (22.74)	3.04	7.48
CoMgAl-HTc	7.74 (23,23)	3.06	7.59
CoAl-HTc	7.47 (22.41)	3.02	7.42

**Figure 1.** XRD patterns of non-calcined (left) and calcined (right) samples. Top pattern: CoMgAl-HTc and bottom pattern: CoAl-HTc.



**Figure 2.** SEM pictures of CoAl and CoMgAl samples (c: calcinated; c-R: calcinated and reduced).

### 3.2 Reactivity

The stability and evolution of the reactivity of the samples over time at 700 °C was investigated. The choice of the reaction temperature was based on available data from the literature and previous laboratory investigations, which showed that interesting catalytic performance could be obtained in the temperature range 650-700 °C [1, 21]. The reduced catalytic charge was placed in the reactor and subjected to the reaction mixture (CH<sub>4</sub>, CO<sub>2</sub>). The reaction temperature was increased with a heating rate of 4 °C/min from ambient to 700 °C, which was maintained for this study for more than 15 hours in the frame of this work. At 700 °C, the main reaction products were H<sub>2</sub> and CO. The conversion rates of CH<sub>4</sub> and CO<sub>2</sub> as well as the selectivity (H<sub>2</sub> / CO ratio), in the presence of the catalysts CoMgAl-HTc-R and CoAl-HTc-R. The difference in catalytic behaviour between the nickel-based and the cobalt-based catalysts is mainly due to the high activity of Ni<sup>0</sup> for this reaction under our operating conditions [12, 21, 22].

In the case of cobalt-based catalysts, significant catalytic inertia was observed in the case of the CoMgAl-HTc-R sample, unlike CoAl-HTc-R, which exhibits an appreciable activity and selectivity maintained beyond 11h of work (Table 3). The recorded CH<sub>4</sub> and CO<sub>2</sub> conversions reach 38% and 57 % respectively with an H<sub>2</sub> / CO selectivity of around 0.70. The comparison of the reduction profiles of the cobalt-based samples showed that the solid CoAl-HTc-R clearly exhibits the formation of the Co<sup>0</sup> species at 700 °C unlike the solid CoMgAl-HTc-R whose profile of reduction only shows the formation of cobalt oxides. This is confirmed by XRD analysis after reduction at 700 °C, which confirms the absence of Co<sup>0</sup> with CoMgAl-HTc-R sample (Figure 4). Figure 3 illustrates the presence of Co<sup>0</sup> species and cobalt oxides in the case of two samples CoAl-HTc-R and CoMgAl-HTc-R respectively. It was confirmed that Co<sup>0</sup> species constitute, like the Ni<sup>0</sup> species, the active phase for the dry reforming reaction of methane. The comparison of the catalytic performances of the solids CoMgAl-HTc-R and

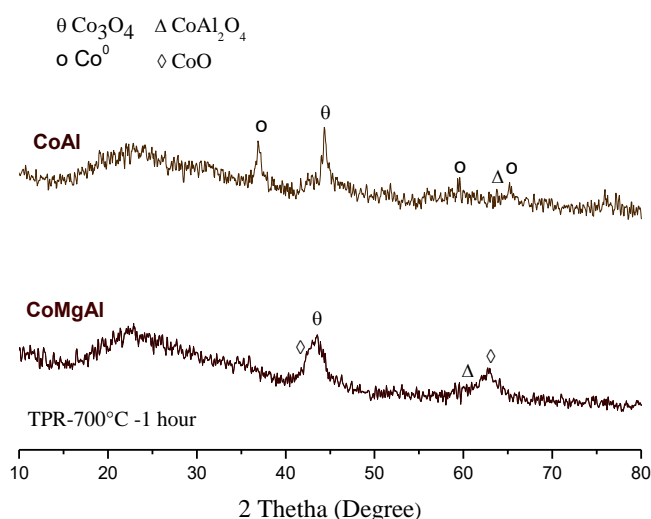
CoAl-HTc-R (Figure 4, Figure 5) leads us to conclude that the  $\text{Co}^0$  (as active phase) is formed at high reduction temperatures which can exceed 700 °C. This can be enhanced by the presence of Mg cations, which retard the reduction of cobalt and/or nickel in the catalyst.

In addition, the conversion of  $\text{CO}_2$  is slightly higher than those of  $\text{CH}_4$ , suggesting the course of side reactions, in particular the reverse reaction of gas with water (RWGS) ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2$ ) which tends to increase the conversion of  $\text{CO}_2$ . Several factors can explain the catalytic behaviour such as: textural properties (specific surface), reducibility and acid-base properties. Indeed, regarding these results, it was noticed that CoAl-HTc-R has the best catalytic performances than that of the solid CoMgAl-HTc-R. It is generally accepted that bimetallic catalysts exhibit higher performance than those of monometallic systems. In this same context, it has been reported in the literature [1, 3] that the addition of a low content of a given metal, such as Co, Fe, Ce, Cu, Mn, to nickel deposited on a support such as  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ , could improve the catalytic performance of Ni/ $\text{Al}_2\text{O}_3$  and Ni/Si reference solids while minimizing carbon deposition. Halliche et al. examined the doping effect of the Ni /  $\alpha\text{-Al}_2\text{O}_3$  and Ni/ $\text{SiO}_2$  system with metallic additions, such as Ce, Co and Fe[23]. It was found that the effect of the dopant depended on its nature. It demonstrated the beneficial effect of the synergy caused by the addition of Co and Ce, unlike Fe, which would help deactivate the catalyst whether supported on alumina or silica.

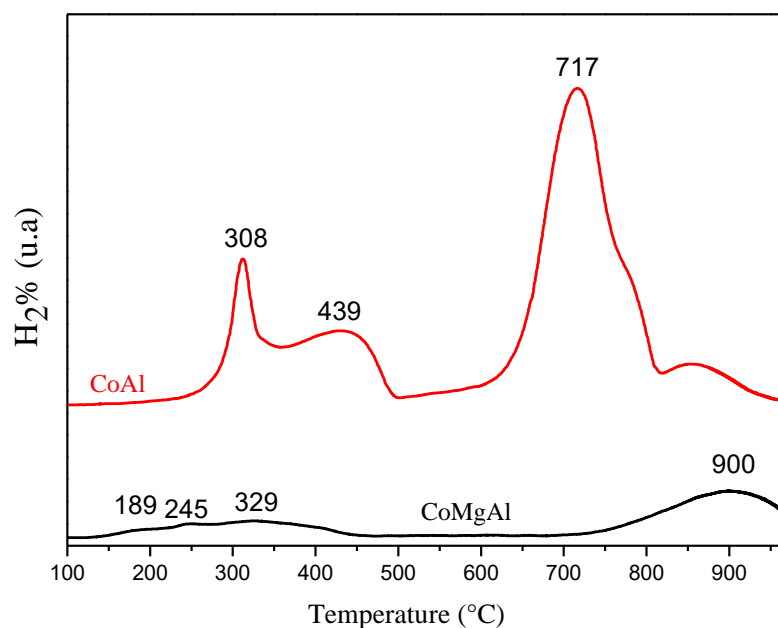
In summary, and considering both the nature of the cations introduced as well as the presence of Mg and Co and their synergistic effect, we can classify the catalytic performances of the samples examined according to their decreasing order, as follows: CoAl-HTc-R >>> CoMgAl-HTc-R.

**Table 3.** Conversion and selectivity rates CoAl and CoMgAl catalysts.

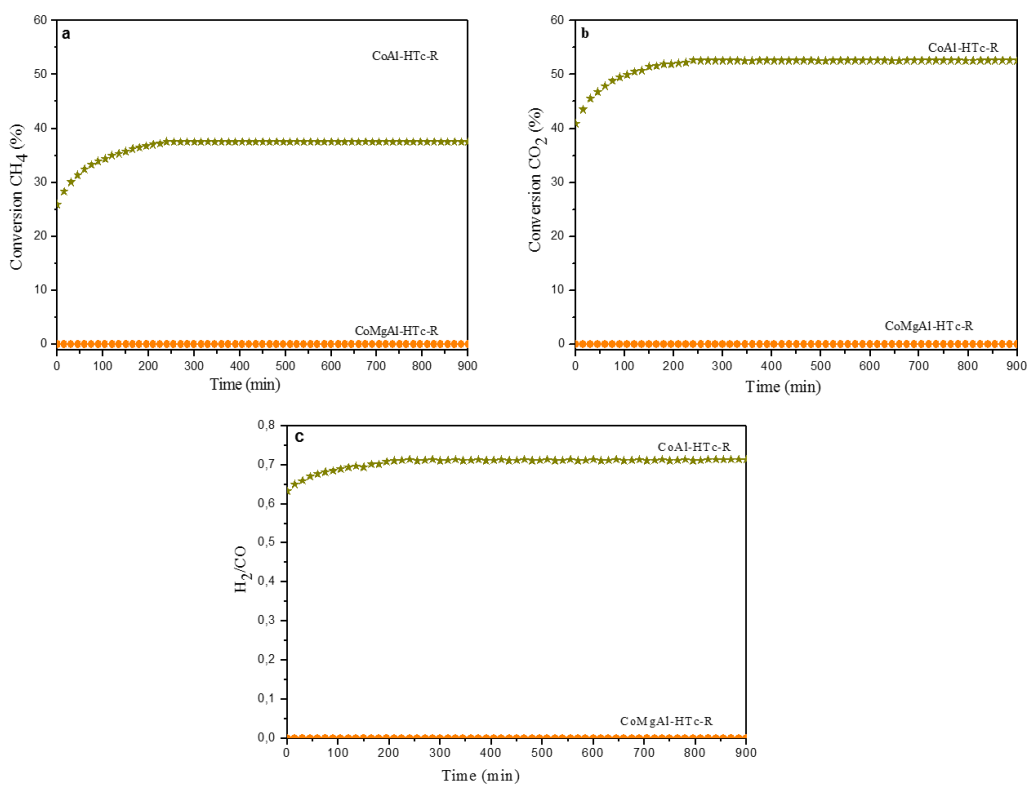
	$\text{CH}_4$ (%) conversion rate	$\text{CO}_2$ (%) conversion rate	Selectivity $\text{H}_2/\text{CO}$
CoMgAl-HTc	0	0	0
CoAl-HTc	38	57	0.7



**Figure 3.** XRD patterns of non-calcined and calcined samples after RTP 700 °C for 1 hour



**Figure 4.** Reduction temperature profiles (RTP) of CoAl and CoMgAl catalysts.



**Figure 5.** Evolution of the conversions rate of CH<sub>4</sub> (a), CO<sub>2</sub> (b) and H<sub>2</sub> / CO selectivity vs. time reaction at 700 °C for CoMgAl-HTc-R and CoAl-HTc-R.



#### 4. Conclusions

CoAl and CoMgAl hydrotalcite based catalysts were prepared by a co-precipitation method at a fixed pH=11. Above 450 °C, no reaction occurs during the calcination step.

The two samples were tested in dry reforming of methane, the catalytic activity of catalysts can be classified as follows: CoAl-HT >>> CoMgAl-T. This result can be explained by the presence of the Co<sup>0</sup> for the catalyst CoAl-HTc-R and the total absence in the sample CoMgAl-HTc-R.

The solid CoMgAl-HTc-R requires high reduction temperature compared to CoAl-HTc-R due to the strong CoO-MgO interactions.

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