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Novel Ni-La-Hydrotalcite derived catalysts for CO₂ methanation

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Abstract

A series of hydrotalcite-derived mixed oxides containing Ni/Mg/La/Al obtained by thermal decomposition were characterized by XRD, CO₂-TPD and H₂-TPR. The results confirm the formation of periclase-like materials, and the addition of lanthanum resulted in the formation of a separate phase. The incorporation of 2 wt.% of lanthanum leads to an increase of the catalytic performance at temperatures from 250 to 300°C with CO₂ conversion of 46.5-75% and CH₄ selectivity of 99-98%. The activity is directly connected with basicity that increases with the incorporation of La into the HT-derived catalysts.

Keywords: CO₂ methanation, hydrotalcite, nickel, Lanthanum

1. Introduction

The CO₂ concentration increase in atmosphere, which is considered to be one of the anthropogenic causes of global warming, has led to renewed interest in CO₂ hydrogenation (Sabatier reaction). This process offers the possibility of storing off-peak renewable energy, i.e. in the form of water-electrolysis hydrogen, and, at the same time, treating CO₂ as raw material, to produce storable and transportable fuels (methane), or other commodities [1]. This way of producing of gaseous and/or liquid fuels may become an effective method of stabilizing CO₂ emissions, in a global zero-emission closed cycle.

Catalytic CO₂ methanation has been deeply studied using catalysts containing group VIII B metals (Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt) on different supports (Al₂O₃, SiO₂, ZrO₂, CeO₂, mixed oxides of Ce-Zr and TiO₂) [2]. The catalytic systems containing Ni, Ru and Rh were the most effective [3-6]. Though much cheaper than Ru and Rh, Ni-based catalysts suffer from deactivation at low temperatures due to the strong interaction of Ni with CO and the formation of mobile carbonyls, which leads to the sintering of the active phase [7, 8]. The choice of the support is furthermore important since it may determine the adsorptive properties of the catalytic system and the interaction support-active phase [2]. Acid-basic properties of oxides derived from hydrotalcites (HT) can be tailored for specific catalytic applications such as for CO₂ valorization through dry reforming [9]. However, to date few publications deal with CO₂ methanation over HT-derived catalysts [10, 11]. Gabrovska et al. [10] studied co-precipitated NiAl-HT-based materials with different content of nickel (21, 32 and 42 wt.%) in which the catalytic activity strongly depended on Ni content, reduction and reaction temperatures. He et al. [11] reported that well-dispersed and stable nickel particles could be obtained through the decomposition of Ni-containing HTs, and claimed that this fact together with the existence of strong basic sites resulted in enhanced methanation activity.

It is nowadays well known that lanthanum can modify the redox properties of a catalytic material. In fact, the incorporation of lanthanum into Ni-containing HT-derived catalysts led to a beneficial effect on the nickel dispersion, catalytic activity and suppressed the formation of carbon in dry methane reforming [9]. However, there is no information in the existing literature dealing with the influence of the presence of La in HT-derived catalysts for CO₂ methanation. The aim of this work is thus to study the properties and activity of modified hydrotalcite-like materials containing Ni, La, Al and Mg as prospective catalysts for CO₂ methanation, with low Ni loadings.

2. Experimental

2.1. Synthesis of the materials

Hydrotalcites containing M(III) trivalent and M(II) divalent metals (Al, La, Mg, Ni,) with M(III)/(M(III)+M(II)) molar ratio of 0.25, (Table 1), were prepared through a co-precipitation method at constant pH (from 9.5 to 10). Two aqueous solutions, of respectively the mixed nitrates of the divalent and trivalent metals and of sodium hydroxide (1M), were added dropwise into a flask containing an aqueous solution of sodium carbonate, under vigorous stirring at 65°C and constant pH. The mixture was aged for 24 h at 50°C, then filtered, washed with deionized water and dried at 80°C overnight. The obtained materials were finally calcined at 550°C for 5 h. The nominal (assumed) concentration of the components is listed in Table 1.

2.2. Physico-chemical characterization

The HT-derived catalysts were characterized by XRD, TPR and TPD-CO₂. XRD measurements were carried out using PANalytical-Empyrean diffractometer, equipped with CuK_α ($\lambda=1.5406\text{\AA}$) radiation source, within 2 θ range from 3 to 90°, (step-size=0.02°/min). Ni

crystallite sizes were calculated for the catalysts after reduction and reaction using the Scherrer equation. Temperature programmed reduction (H₂-TPR) profiles were obtained using BELCAT-M (BEL Japan) apparatus equipped with a thermal conductivity detector (TCD). The calcined materials were first outgassed at 100°C for 2h and then reduced using 5% H₂/Ar at the heating rate of 7.5°C/min from 100 °C to 900 °C. For each measurement a sample of 60 mg was taken. CO₂ Temperature programmed desorption (CO₂-TPD) was performed on the same device. The materials were degassed for 2 h at 500°C and then cooled to 80°C. Subsequently a mixture of 10% CO₂/He was fed for 1h in order to adsorb CO₂, followed by desorption of weakly adsorbed CO₂ using a flow of He for 15 minutes. In order to measure the evolution of CO₂, the material was heated up under He flow at 10°C/min from 80°C to 900°C. The concentration of evolved CO₂ was measured with a TCD detector.

2.3. CO₂ hydrogenation experiments

CO₂ methanation was studied in a tubular quartz reactor heated by an electric furnace. Temperature was measured and controlled inside the catalytic bed with the aid of a K-type thermocouple. A reactant flow of 100 ml/min (GHSV=12,000 h⁻¹) containing H₂/CO₂/Ar = 12/3/5 was sent to the reactor. The products were analyzed using an on-line Varian GC4900 micro-chromatograph equipped with a TCD detector. Prior to the reaction the catalysts were reduced in situ at 900°C for 1h under 10% H₂/Ar. The catalytic activity was then determined from 250 to 450°C. At each temperature the sample was kept for 30 minutes in steady-state operation.

3. Results and discussion

3.1. From the hydrotalcite precursors to the mixed oxides derived materials

Figure 1 shows the diffractograms acquired for the fresh hydrotalcite (a), the hydrotalcite-derived catalyst (NiLa4-HT) obtained upon calcination (b), the reduced (c) and the spent (d)

HT-derived catalyst. The patterns obtained for fresh HT show the typical reflections of layered-structured hydrotalcites [13]. In the case of the HT containing higher amounts of lanthanum, i.e. NiLa4-HT and NiLa2-HT (not shown), separate phases arising from $\text{La}_2(\text{CO}_3)_2(\text{OH})_2$ and $\text{La}_2\text{O}_2\text{CO}_3$ were as well observed. Upon calcination, XRD patterns evidence the typical reflections of a periclase-like structure at $2\theta = 35.3, 43.5$ and 63° . Lanthanum carbonates are as well observed as a separate phase, as well as La_2O_3 . The reflections corresponding to this isolated lanthanum carbonate phase disappear for the catalysts submitted to reduction in 10% H_2/Ar . These patterns reveal the existence of a metallic Ni phase. The crystal sizes for such Ni particles are in the range 8-9 nm, see Table 2, similar to those reported in the existing literature for Ni-containing HT-derived catalyst [14]. Crystal sizes remained practically unchanged in the catalysts employed in the methanation reaction, i.e. 8-10 nm crystal size calculated for the spent catalysts.

3.2. Basicity and active sites

Fig. 2 contains the CO_2 -TPD profiles acquired for the different HT-derived catalysts after reduction under 10% H_2/Ar . TPD profiles were deconvoluted into three Gaussian peaks, corresponding to weak ($138\text{-}150^\circ\text{C}$), medium strength ($232\text{-}251^\circ\text{C}$) and strong ($349\text{-}374^\circ\text{C}$) basic sites, as shown in Table 2. Low strength basic sites correspond to surface OH^- , medium to Lewis acid-base pairings and strong arise from low-coordination surface O^{2-} [15].

Though the incorporation of only 1 wt.% of lanthanum leads to a slight decrease in total basicity, the amount of basic sites, i.e. sites able to chemisorb CO_2 , generally increases upon La-loading. Moreover, from peak deconvolution it seems that medium strength basic sites are more present in the La-doped HT-derived catalysts, i.e. its concentration increases from 60 $\mu\text{mol/g}$ for Ni-HT to 113 $\mu\text{mol/g}$ and to 87 $\mu\text{mol/g}$, for the catalysts respectively containing 2 and 4 wt.% of La. Let us remark here that the differences between basicity for Ni-HT's containing 1 wt.% and 2,4 wt.% of La might be as well caused by a partial blocking of the

basic sites in the mixed oxide hydrotalcite-derived material, upon the introduction of low amounts of lanthanum and its compensation through the formation of new basic sites after incorporation of 2 and 4 wt.% of La.

Fig. 3 shows the H₂-TPR profiles for the calcined HT-derived catalysts. They all exhibit one wide asymmetric peak arising from the reduction of nickel oxide species to metallic Ni⁰ (814-846°C). This higher reduction temperatures vis-à-vis the much lower temperatures expected for the oxidation of either bulk NiO or dispersed NiO crystallites points to the existence of a thermally stable phase of Mg(Ni,Al)O in the form of a solid solution of mixed oxides, and thus to a very strong interaction between the nickel species and the Al-Mg hydrotalcite matrix [9,16]. The addition of La visibly shifts the reduction of Ni-species to lower temperatures, i.e. from 846°C for Ni-HT to 814-821°C for NiLa1-HT and NiLa4-HT, respectively. Additionally, a shoulder appears at ca. 690°C for NiLa2-HT and NiLa4-HT (2 and 4 wt.% of La, respectively), which can be assigned to isolated and more weakly bonded NiO species. Moreover, for NiLa2-HT an additional weak peak can be as well observed at temperatures ca. 400 and 490°C that may correspond to bigger bulk NiO crystallites. Lucredio et al. [17] showed that low amounts of lanthanum resulted in further stabilization of the Ni-phase and thus increased reduction temperatures, at higher La-loadings, however, TPR reduction temperature decreased, pointing to weakened interaction between Ni-species and the hydrotalcite matrix [18]. Nickel-containing materials obtained upon calcination of hydrotalcites form homogenous mixed oxides (periclase structure), where NiO and MgO interactions are very strong, resulting in the need of harsh reduction conditions, in contrast to Ni impregnated supports, where the nickel is more likely to be deposited on the surface, and then the reducibility may be expected to be much higher than for hydrotalcite systems. The obtained H₂-TPR results are in good agreement with literature reports [11].

3.3. Catalytic activity towards CO₂ hydrogenation

The CO₂ conversion measured during the methanation experiments is plotted in Fig. 4, for the different HT-derived catalysts and as a function of reaction temperature. The thicker continuous line represents the CO₂ conversion forecasted by the thermodynamic equilibrium for this reaction. Thermodynamics predicts complete CO₂ conversion at low reaction temperatures, decreasing with increasing temperature, since the other routes start to be favored, such as all the set of reforming reactions, resulting in the formation of undesirable side-products such as CO. At 250°C, the CO₂ conversions measured in the presence of the different HT-derived catalysts are still far away from the maximal thermodynamic conversion limit. The highest conversions are obtained for the catalysts containing 2 and 4 wt.% of lanthanum, i.e. 46.5% and 46% for NiLa2-HT and NiLa4-HT, respectively. Activity towards CO₂ methanation is thus promoted in the presence of La, as a consequence of increased basicity, concretely in terms of medium strength basic sites, and looser interaction of Ni-species and the Al-Mg hydrotalcite matrix, resulting in enhanced reducibility. Indeed, the difference in catalytic activity is in good agreement with much higher basicity shown for catalysts containing 2 and 4 wt.% of La. As observed by XRD, La forms separate phases and is not introduced into the hydrotalcite structure. Therefore, the changes in basicity are a consequence of two opposing effects: partial blockage of hydrotalcites basic sites by lanthanum oxide and the introduction of new basic sites by the latter. For the catalyst with 1% La, the decrease of hydrotalcite basic sites could not be compensated (due to low amount of new added basic sites), in contrast to HTLa2 and HTLa4, where the overall effect was positive. As reported by Pan et al. [19] the reaction of CO₂ methanation on nickel containing catalysts involves (i) H₂ dissociative adsorption on metallic nickel and (ii) CO₂ adsorption on basic sites, thus making it necessary to find an optimum composition of the catalysts. Pan et al. also suggested that the presence of medium strength basic sites resulted in improved

catalytic activity due to the promoted formation of monodentate formate species, which is an active intermediate in methane formation. However, as reaction temperature increases CO₂ conversion converges to similar values independently of the HT-derived catalysts used. At temperatures higher than 400°C, methanation and its side-reactions become temperature-promoted and the intrinsic features of each catalyst leading to improved performance at lower temperatures are no longer that important. Moreover, at temperatures higher than 400°C, a loss in reaction selectivity can be expected. The selectivity towards methane production measured for the different catalysts during the activity tests is plotted in Fig. 5 as a function of temperature. In the low temperature range almost complete selectivity to methane was measured for all the catalysts tested, i.e. 98 to ca. 99% at 250°C. As expected, selectivity slightly decreases with increasing temperature. As expected, selectivity slightly decreases with increasing temperature for samples Ni15, Ni15La2 and Ni15La4, while for the Ni15La1 sample the selectivity towards methane increased from 400°C to 450°C, which is in the range of experimental error. No other product except CO and CH₄ were registered. The selectivities to CO were between ca. 1 and 3% (3% for the most active Ni15La2 at 450°C). The amounts of registered CO are relatively low, it is rather difficult to discuss a relationship between the selectivity and basicity, or any other property of the studied catalysts. We can only roughly say that, a priori, the samples with the highest amount of basic sites (Ni15La2 and Ni15La4) show the highest and the lowest selectivity towards methane. Let us note here that the catalytic activity was found to remain completely stable after 5h time on stream, without further evolution of basicity and no modification of Ni-crystal size on the spent catalysts (Table 2).

Conclusions

La-promoted Ni-Mg-Al hydrotalcite-derived catalysts were prepared through co-precipitation, characterized and tested in the CO₂ hydrogenation reaction. The introduction of La affected the CO₂ adsorption capacity of the catalysts through the introduction of medium strength basic sites. The presence of La also influenced the interaction of Ni-species with the Mg-Al matrix. In HT-derived catalysts, Ni-species are found commonly in the form of mixed oxides solid solutions together with Mg and Al oxides. Lanthanum increases the reducibility of Ni-species by means of softening the interaction between them and the HT matrix. Both increased basicity, in terms of medium strength basic sites, and increased Ni-reducibility results in much higher activity at low temperatures for such La-promoted HT-derived catalysts.

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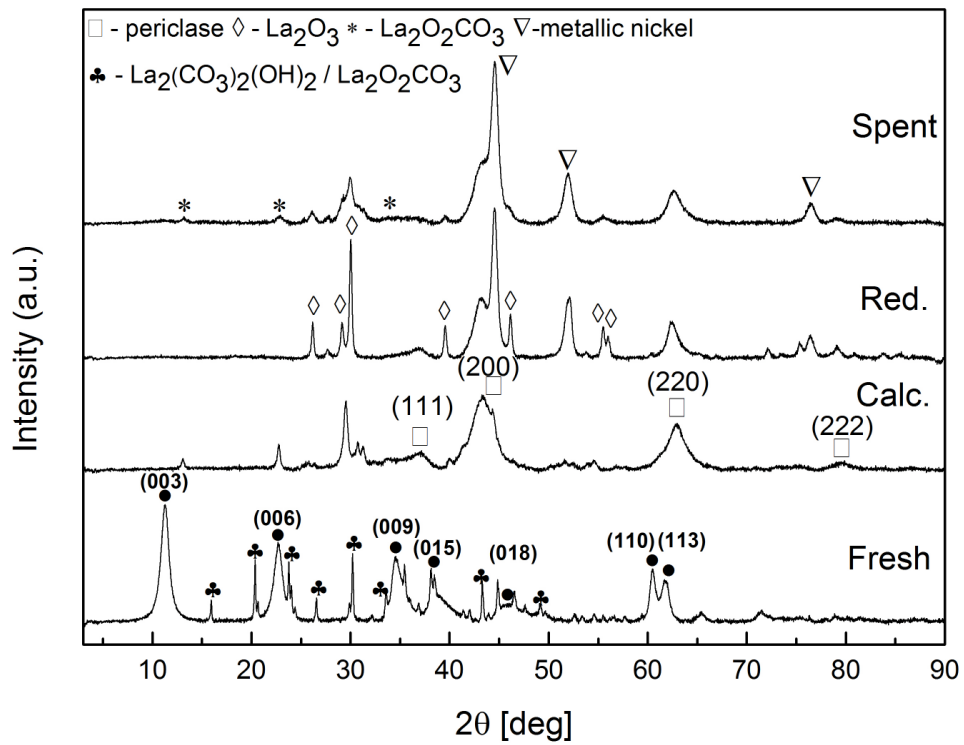


Figure 1. XRD patterns for NiLa4-HT (fresh, calcined, reduced and spent)

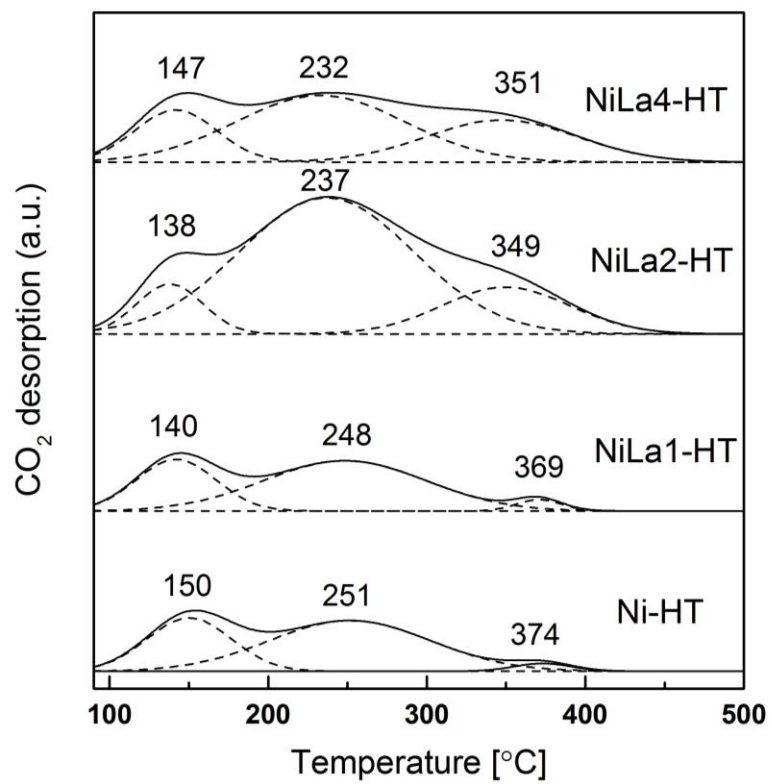


Figure 2. CO₂-TPD profiles for the reduced HT-derived catalysts.

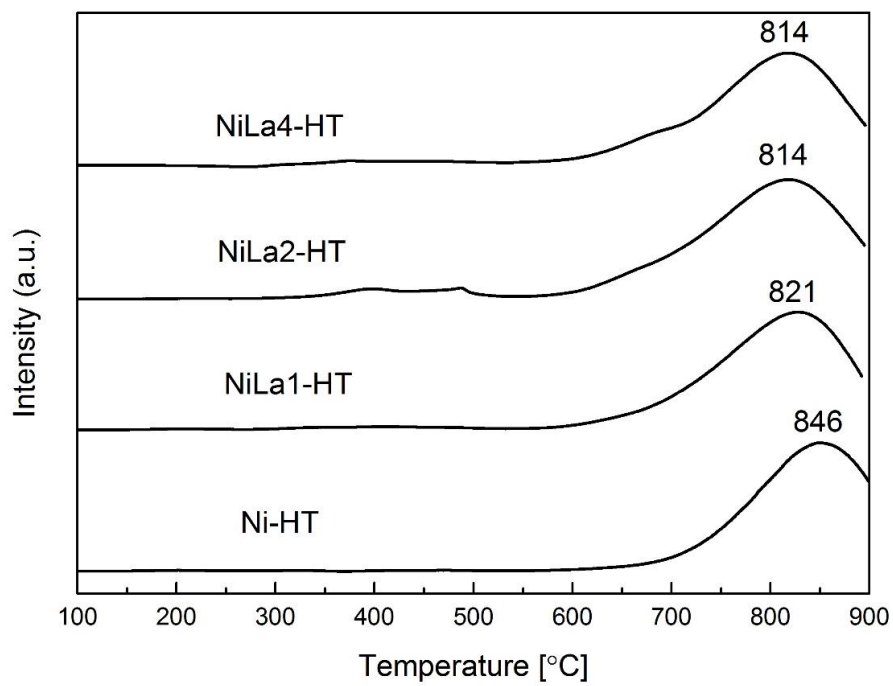


Figure 3. H₂-TPR of mixed oxides

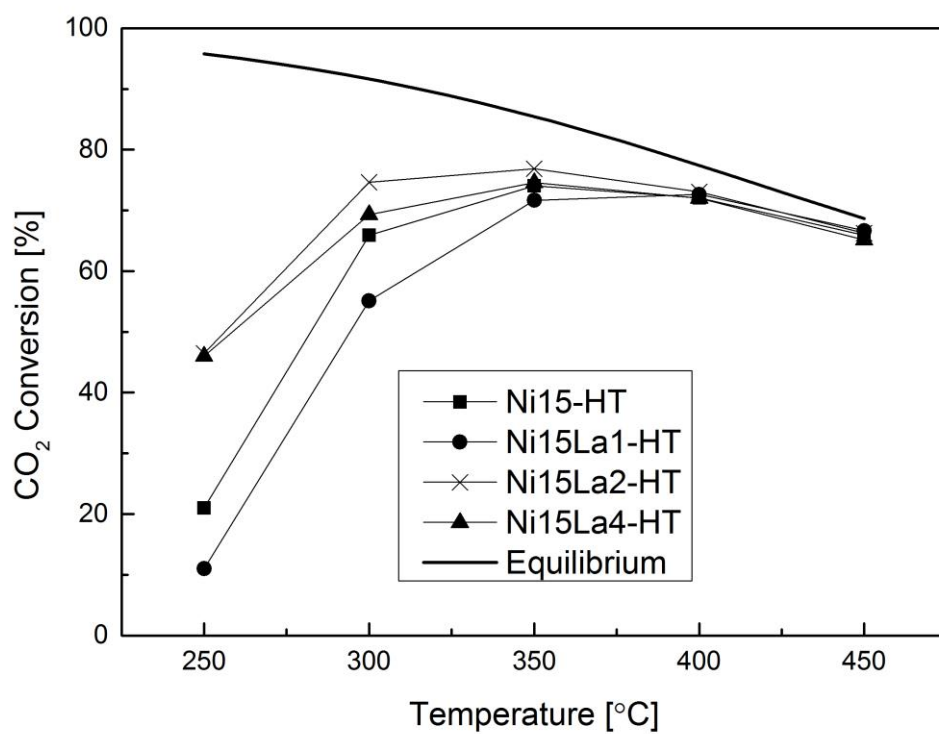


Figure 4. CO₂ Conversion versus temperature for obtained mixed oxides

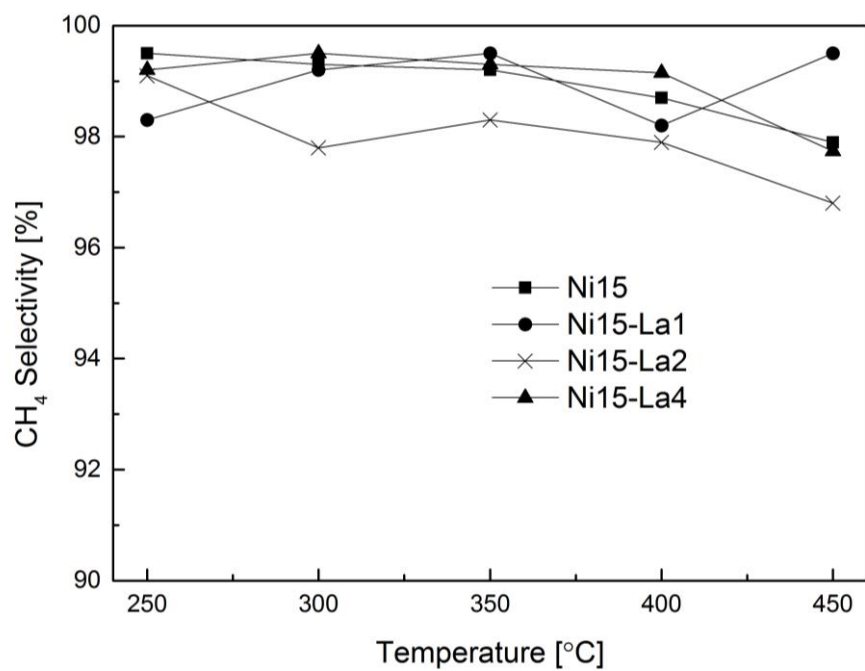


Figure 5. CH₄ Selectivity versus temperature for obtained mixed oxides

Table 1. Nominal concentration of trivalent and divalent cations in the prepared catalysts

$[\text{Me}_y\text{Mg}_x\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3^{2-})_{0.125}\cdot 0.5\text{H}_2\text{O}$						
Catalysts	Metal content [wt.%]				La/Al ratio	$\frac{M(III)}{M(II) + M(III)}$
	Ni	La	Mg	Al		
Ni-HT	15	-	15.8	8.1	-	0.25
NiLa1-HT	15	1	15.6	7.9	0.03	0.25
NiLa2-HT	15	2	15.4	7.6	0.07	0.25
NiLa4-HT	15	4	15.0	7.1	0.11	0.25

Table 2. Crystallite size of Ni^o particles (measured by XRD) and basicity of different NiLa-HT samples (from CO₂-TPD)

Catalyst	Crystallite size [nm]		Total basicity [$\mu\text{mol/g}$]	Weak sites 138-150°C	Medium sites 232-251°C	Strong sites 349-374°C
	Reduced	Spent		[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]
Ni-HT	8	8	82	7	60	15
NiLa1-HT	9	8	55	21	30	4
NiLa2-HT	9	9	139	12	113	14
NiLa4-HT	9	10	122	21	87	14