



Short communication

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.

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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 [10,11,12]. 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 (1 M), 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

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

Catalysts	[Me _y Mg _x Al _{0.25} (OH) ₂](CO ₃ ²⁻) _{0.125} · 0.5H ₂ O					M(III) M(II)+M(III)
	Metal content [wt.%]				La/Al ratio	
	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

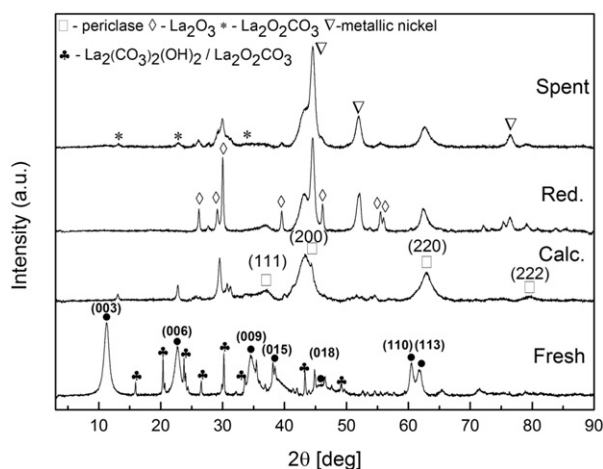


Fig. 1. XRD patterns for NiLa4-HT (fresh, calcined, reduced and spent).

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-Empréan diffractometer, equipped with CuK_α (λ = 1.5406 Å) radiation source, within 2θ 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 2 h 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 1 h in order to adsorb CO₂, followed by desorption of weakly adsorbed CO₂ using a flow of He for 15 min. 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 1 h under 10% H₂/Ar. The catalytic activity was then determined from 250 to 450 °C. At each temperature the sample was kept for 30 min in steady-state operation.

3. Results and discussion

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

Fig. 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 La₂(CO₃)₂(OH)₂ and La₂O₂CO₃ were as well observed. Upon calcination, XRD patterns evidence the typical reflections of a periclase-like structure at 2θ = 35.3, 43.5 and 63°. Lanthanum carbonates are as well observed as a separate phase, as well as La₂O₃. The reflections corresponding to this isolated lanthanum carbonate phase disappear for the catalysts submitted to reduction in 10% H₂/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 CO₂-TPD profiles acquired for the different HT-derived catalysts after reduction under 10% H₂/Ar. TPD profiles were deconvoluted into three Gaussian peaks, corresponding to weak (138–150 °C), medium strength (232–251 °C) and strong (349–374 °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 O²⁻ [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 CO₂, 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 μmol/g for Ni-HT to 113 μmol/g and to 87 μmol/g, for the catalysts respectively containing 2 and 4 wt.% of La. Let us remark here that the differences between basicity for Ni-HTs

Table 2
Crystallite size of Ni⁰ particles (measured by XRD) and basicity of different NiLa-HT samples (from CO₂-TPD).

Catalyst	Crystallite size [nm]		Total basicity [μmol/g]	Weak sites 138–150 °C [μmol/g]	Medium sites 232–251 °C [μmol/g]	Strong sites 349–374 °C [μmol/g]
	Reduced	Spent				
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

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