The influence of lanthanum incorporation method on the performance of nickel-containing hydrotalcite-derived catalysts in CO$_2$ methanation reaction

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ABSTRACT

A series of hydrotalcite-derived mixed oxides containing Ni/Mg/La/Al and obtained by thermal decomposition, were characterized by XRD, H$_2$-TPR, CO$_2$-TPD, elemental analysis and low temperature nitrogen sorption techniques. The results confirm the formation of periclase-like structured materials. The catalysts containing lanthanum, incorporated by different methods, i.e. co-precipitation, impregnation and ion-exchange, showed outstanding catalytic activity at 300 °C, with CO$_2$ conversions around 36–87% and CH$_4$ selectivity of 98–99%.

1. Introduction

The increasing concentration of carbon dioxide in the atmosphere – considered as one of the anthropogenic sources of global warming – is forcing our nowadays society to seek for new strategies and processes for CO$_2$ valorization and recycling. The process of carbon dioxide hydrogenation offers the possibility of storing excess energy in the form of chemical compounds, such as methane or higher hydrocarbons [1]. The hydrogen needed for the reaction can be obtained via water electrolysis, using off-peak renewable energy (solar, wind, etc). The hydrogenation of CO$_2$ yielding methane as the main product, also known as methanation, together with other chemical CO$_2$ valorisation routes, such as dry reforming, reverse water gas shift, and Fischer-Tropsch or methanol/ethanol synthesis, may contribute in a near future to reducing CO$_2$ emissions, via the production and utilization of liquid and/or gaseous synthetic fuels in global zero emission cycles.

Of the mentioned processes, CO$_2$ methanation is the best developed currently with several projects on the scale bigger than laboratory one, or small industrial installation being tested. Some Power-To-Methane plants in European Union are listed Table 1, among others in Falkenhagen, Brandenburg – Store & Go EU project (consortium of 27 partners from six European countries) with an innovative honeycomb or structured wall reactor for methanation at 1000 kW scale for utilization of carbon dioxide from biomass related processes. There is also a Swiss demonstration Power-to-Gas plant (700 kW), under the same project (Store & Go). Additionally, one of the larger installations

at Wertle – Audi AG with 6300 kW should be mentioned.

The CO$_2$ methanation reaction is an exothermic reaction that is thermodynamically feasible at ambient temperatures. However, it is strongly limited by its reaction kinetics and thus needing the presence of an active and selective catalyst. Several catalytic systems have been investigated, including metals of the VIIIB group (Fe, Ru, Co, Rh, Ir, Ni, Pt). The catalytic systems containing Ru, Rh and Ni were found to be the most active in CO$_2$ methanation reaction [2–5]. However, the most studied catalysts are those containing Ni, because in comparison to other active materials it is (i) cheaper and (ii) shows acceptable activity in the reaction of CO$_2$ hydrogenation.

Various supports of Ni catalysts were under investigation, such as Al$_2$O$_3$, TiO$_2$, La$_2$O$_3$, zeolites etc. [6–11]. Rahmani et al. investigated Ni impregnated Al$_2$O$_3$ catalysts, where the Ni content ranged from 10 to 25 wt.% [8]. They found that the activity of the catalysts increased with increasing content of nickel from 10 to 20 wt.%. However for the catalyst containing 25 wt.% of Ni the activity decreased which was explained by increased crystallite size and lower surface area. Song et al. prepared Ni impregnated (10 wt.%) La$_2$O$_3$ catalysts and found that the formation of La$_2$O$_2$CO$_3$ played a key role in the activation of carbon dioxide [9]. Almost similar observations were made by Gao et al. who tested NiLaO$_3$ perovskite catalysts [10]. Graca et al. tested Ni impregnated USY zeolite promoted with Ce [7]. The obtained results indicated that the increase of the amount of impregnated Ni increased the activity of the catalysts in CO$_2$ methanation reaction, due to higher amount of Ni^0 species after reduction. Moreover, the addition of Ce led

Table 1
Power-To-Methane plants in European Union (source: europeanpowertogas.com).

Project	Installed Power [kW]	Methanation principle	Electrolysis technique	Country	Status
Schwandorf – Eucolino: Schmack & Viessmann (MicrobEnergy GmbH)	250	Biological	Alkaline & PEM	Germany	Finished
Niederaussem	300	Chemical	PEM	Germany	Finished
Foulum – Electrochaea	250	Biological	PEM	Denmark	Finished
Rozenburg	10	Chemical	PEM	Netherlands	Operational
Wertle – Audi AG (Etogas)	6300	Chemical	Alkaline	Germany	Operational
Rostock – Exytron Demonstrationsanlage	21	Unknown	Unkown	Germany	Operational
Falkenhagen – DVGW	1000	Uknown	Unkown	Germany	Operational
Solothurn (Store & Go)	700	Biological	PEM	Swiss	Planned
Alzey – Exytron Null-Emission-Wohnanlage (Exytron GmbH)	63	Unknown	Alkaline	Germany	Planned
Stralsund (Fachhochschule Stralsund)	20	Unknown	Alkaline	Germany	Planned

to a further improvement of the catalytic activity, which was attributed to the presence of CeO_2 which promotes the conversion of CO_2 to CO. Tada et al. tested Ni containing catalysts (10 wt.%) loaded on different supports and found that the activity formed a sequence: Ni/CeO_2 > Ni/α-Al_2O_3 > Ni/TiO_2 > Ni/MgO [11]. The higher activity was explained as a result of much higher CO_2 adsorption ability of Ni/CeO_2 catalyst in comparison to Ni/α-Al_2O_3, while Ni/TiO_2 and Ni/MgO showed very poor activity at low temperature (250 °C).

On the other hand, only a few publications deal with CO_2 methanation over hydrotalcite-derived catalysts. Such materials, also called double layered hydroxides, may, after appropriate treatment form nano-oxides. The key advantage is that they may contain alumina and nickel in close (and strong) contact, with the additional possibility of introducing magnesia, as well as several other additives, both into and onto the structure, and were shown to have excellent properties e.g. in dry reforming of methane [12–15]. In case of CO_2 methanation, several aspects such as the amount of Ni, the size of Ni crystallites, Ni reducibility and basicity of hydrotalcite-derived materials were investigated. Gabrovska et al. studied co-precipitated nickel-containing Al-HT-derived materials with varying content of nickel (21, 32 and 42 wt.%), and found that the catalytic activity was strongly dependent on Ni content, reduction conditions and reaction temperatures [16]. He et al. reported Ni-Al hydrotalcites from which well dispersed stable nickel particles could be obtained through thermal decomposition and claimed that this fact, together with the existence of basic sites of strong and medium strength, resulted in enhanced activity [17]. Basicity was also influenced by different amounts of Ni introduced into the hydrotalcite-derived catalysts, as observed by Wierzbicki et al. [18]. Fan et al. studied CO_2 methanation with differently decomposed Ni-Mg-Al hydrotalcites containing nickel, and concluded that smaller Ni particles enhanced the hydrogenation of CO_2 to methane [19]. Abate et al. tested hydrotalcite-derived catalysts containing Ni and Al (75–80 Ni wt.%) obtained by coprecipitation at different pH (8.7 and 12) [20]. The results showed that the Ni-HT catalyst obtained at higher pH showed better catalytic performance (also in comparison to a reference commercial catalyst). The authors explained that the higher CO_2 conversion could be related to higher NiO reducibility and higher nickel dispersion. It should be additionally mentioned that HT-derived catalysts are characterized by long-term stability as demonstrated by Bette et al. who used Ni-Mg-Al hydrotalcite-derived catalyst containing ~59 Ni wt.% during 50 h catalytic tests [21].

In our previous work [22], we reported that the addition of lanthanum into nickel-containing hydrotalcite-derived materials led to the formation of new medium- strength basic sites, which resulted in an increased catalytic activity of these materials in CO_2 methanation reaction. However, the applied co-precipitation method resulted in a separate phase of La species, located on the external surface of hydrotalcite structure. Thus the goal of this work was to study different (alternative) methods of lanthanum introduction i.e. impregnation with lanthanum nitrate solution and ion-exchange using La-EDTA complex, in order to investigate the influence of La-incorporation method on the

physico-chemical properties of these hydrotalcite-derived catalysts, as well as to determine the preparation route most beneficial to increase activity and selectivity of the La-modified materials in the reaction of CO_2 methanation.

2. Experimental

2.1. Synthesis of catalysts

Hydrotalcite materials containing divalent M(II) and trivalent (III) metals (Ni, Mg, Al) with M(III)/M(II) molar ratio of 0.33 were obtained using co-precipitation method at constant pH = 9.5–10. Two aqueous solutions of mixed nitrates of divalent and trivalent metals and sodium hydroxide (1 M), were added dropwise into a flask containing an aqueous solution of sodium carbonate at 65 °C under vigorous stirring and controlled pH. The mixture was aged for 24 h at 65 °C, filtered, washed with heated (50 °C) deionized water and dried at 80 °C overnight. The obtained materials were calcined at 500 °C for 5 h. Table 2 lists the prepared catalysts, together with their composition, as obtained by XRF. The incorporation of lanthanum via La-EDTA complex was performed, as described in our previous publication [10], for the fresh materials at pH = 10 for 24 h, followed by filtration, washing with deionized water, drying at 80 °C and calcination at 500 °C.

After the calcination the catalyst Ni21 was impregnated using a 50 ml solution containing lanthanum in the amount of 2 wt.% of the catalyst. The solution was mixed for 5 h, followed by evaporating and calcination at 500 °C. The obtained catalyst was named Ni21La1.1$_{(IMP.)}$.

Lanthanum was also introduced by co-precipitation method as described in detail in our previous work [9]. The obtained catalysts are designated Ni21La$x_{(y)}$, where 21 denotes the content of Ni (in wt.%), x is the introduced amount of La (in wt.%), while index (y) is the method of La introduction (CP = co-precipitation; IMP = impregnation; IE = ion exchange).

2.2. Physico-chemical characterization

All obtained hydrotalcite-derived catalysts were characterized by

Table 2
Specific surface area, total pore volume, elemental analysis (for calcined samples) and unit cell parameters values for reduced hydrotalcite catalysts.

Catalyst	S_{BET} [m²/g][*]	Total pore volume [cm³/g][*]	Elemental analysis[*]	
			Ni wt.%	La wt.%
Ni21	167	0.73	21.4	–
Ni21La1.8$_{(CP)}$	165	0.37	21.2	1.8
Ni21La0.4$_{(IE)}$	167	0.35	21.3	0.4
Ni21La0.9$_{(IE)}$	161	0.37	21.0	0.9
Ni21La1.4$_{(IE)}$	163	0.36	21.1	1.4
Ni21La1.1$_{(IMP.)}$	157	0.33	21.2	1.1

[*] For calcined catalysts.