



## Yttrium promoted Ni-based double-layered hydroxides for dry methane reforming

Katarzyna Świrk<sup>a,b</sup>, Maria Elena Gálvez<sup>a</sup>, Monika Motak<sup>b</sup>, Teresa Grzybek<sup>a</sup>, Magnus Rønning<sup>c,\*</sup>, Patrick Da Costa<sup>a,\*</sup>

<sup>a</sup> Sorbonne Université, Institut Jean Le Rond d'Alembert, CNRS, 2 Place de la Gare de Ceinture, F-78210, Saint-Cyr-l'École, France

<sup>b</sup> AGH University of Science and Technology, Faculty of Energy and Fuels, Adama Mickiewicza Avenue 30, 30-059, Cracow, Poland

<sup>c</sup> Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Sælandsvei 4, N-7491, Trondheim, Norway



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### ABSTRACT

Yttrium modified Ni-based double-layered hydroxides were tested as novel catalysts in dry methane reforming. The catalysts were characterized by XRF, BET analysis, XRD, TPR-H<sub>2</sub>, TPD-CO<sub>2</sub>, TGA/DSC-MS, H<sub>2</sub> chemisorption and TEM. Co-precipitation with yttrium (III) nitrate hexahydrate resulted in increased specific surface area, smaller Ni crystallite size, enhanced reducibility, and higher distribution of weak and medium basic sites as compared to Y-free material. The DRM catalytic tests, carried out in the temperature range of 850–600 °C, led to a significant improvement of activity, with the 1.5 wt % Y-promoted catalyst being the most efficient in converting both CH<sub>4</sub> and CO<sub>2</sub>. Moreover, the 10 h test at 700 °C further confirmed enhanced stability for this HTNi-Y1.5 catalyst. Higher CO<sub>2</sub> conversion than CH<sub>4</sub> conversion and less CO compared to H<sub>2</sub> proves that side reactions are occurring simultaneously.

### 1. Introduction

Dry methane reforming (DRM), also called CO<sub>2</sub> reforming, is considered one of the promising processes for chemical CO<sub>2</sub> utilization [1–6]. DRM leads to synthesis gas, a mixture of hydrogen and carbon monoxide, that is currently used as feedstock in liquid fuel production processes, such as Fischer-Tropsch or methanol synthesis [7]. Nowadays, syngas is traditionally produced through steam methane reforming (SMR) [5]. Still, SMR yields a syngas with a far too high H<sub>2</sub>/CO ratio and needs to be consequently pre-treated when used in liquid fuel synthesis. For instance, the production of dimethyl ether requires H<sub>2</sub>/CO ratio close to unity [2]. This value can be easily obtained through dry methane reforming. In spite of this, DRM has not yet been fully launched on industrial scale because of its large demand for energy and the lack of active, selective and stable catalysts [3].

Ni-based catalysts seem to be good candidates for DRM due to their availability, low cost and good catalytic performance [8,9]. However, the main drawback for their application is susceptibility to carbon formation leading to fast deactivation [3,4,6,10]. The methods proposed to improve stability of Ni-based catalysts, include, among others, the addition of a second metal and/or a promoter, or the choice of an appropriate support. The proposed second metal may be either a noble

metal (Pt, Ru, Rh, or Ir) or a transition metal (e.g. Co or Zn) [3,11–14].

Ni/Al<sub>2</sub>O<sub>3</sub> catalysts have been widely studied in DRM, yielding satisfactory catalytic activity due to the textural properties of alumina [15]. However, severe deactivation attributed to carbon formation and/or sintering of the active phase was observed [4,9]. On the other hand, the presence of a NiO-MgO solid solution is known to enhance resistance of nickel particles towards sintering and to inhibit carbon formation [16]. Additionally, with the increase of MgO loading, higher coking resistance was reported for Ni-MgO-Al<sub>2</sub>O<sub>3</sub> catalysts [17].

Double-layered hydroxides (DLHs) can be the source of prospective DRM catalyst supports, due to their layered structure and possible di- and/or tri-valent cations introduction into the layers, such as Mg<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> and/or Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>. Interlayer anions, e.g. water molecules and/or carbonates, compensate the positive charge and they may also be exchanged for catalytically active components [3,14,18–22]. Moreover, acid-base properties can be tailored, as reported e.g. for calcined NiMgAl-hydrotalcites by Pavel et al. [23] Basic properties, memory effect, and ability to exchange anions make them good catalysts and adsorbents [3,19]. Ni-containing double layered hydroxides were found to be active in the DRM [3,14,24–30]. After appropriate thermal treatment DLHs form nano-oxides whose strong interaction hinders Ni from sintering at high temperatures required for

\* Corresponding authors.

E-mail addresses: [magnus.ronning@ntnu.no](mailto:magnus.ronning@ntnu.no) (M. Rønning), [patrick.da\\_costa@upmc.fr](mailto:patrick.da_costa@upmc.fr) (P. Da Costa).

DRM [30]. It was also found that the stability of Ni-loaded hydrotalcite catalysts in DRM was enhanced by the addition of an appropriate promoter. Ce was reported to promote oxidation of carbon deposits through the Boudouard reaction [31,32], while Zr inhibited reactions leading to the formation of carbon deposits [14,25]. Lanthanum promotion contributed to carbon gasification which was assigned to the formation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [27].

Nevertheless, novel catalysts with enhanced selectivity and stability for DRM need to be developed, and promotion with metals may highly contribute to the improvement of catalytic properties. Yttrium is a rare-earth element that has recently attracted large interest for catalytic applications. As reported by Francis and Whitlow [33] yttrium oxides show high temperature oxidation resistance in the presence of carbon dioxide. Additionally, yttrium oxide has been studied as a support for DRM catalysts [34,35]. However, there are only a few literature reports describing the role of yttrium as a possible promoter in the DRM reaction [36–39]. Li et al. [36] observed high resistance towards carbon deposition for Y-promoted Ni-SBA-15 catalysts, which was attributed to high dispersion of yttrium with nickel nanoparticles, and the ability of yttrium to create oxygen vacancies. Similar properties were also observed in Y-Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalysts [37]. Taherian et al. [39] reported a positive influence on controlling the nickel size and its dispersion into the mesopores of Ni/SBA-15 catalyst after modification with Y<sub>2</sub>O<sub>3</sub>. Moreover, in our previous study Ni-Y/KIT-6 catalyst exhibited better dispersion of nano-sized Ni particles inside the pores of the support as compared to Ni/KIT-6 material [38]. Also, the formation of coke was lower for Y-modified catalyst in the initial stability test at 700 °C. Furthermore, B. Li et al. [40] studied Ni/Y/Al<sub>2</sub>O<sub>3</sub> catalyst with yttrium introduced via different types of impregnation, and observed improved stability of the modified samples. However, in a recent study by Huang et al. [41] the impregnated NiO-Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> mesoporous catalysts were reported to be less stable than the samples prepared with a one-pot evaporation-induced self-assembly method. The former resulted in the creation of loosely attached Ni particles on the support, which was the reason for fast deactivation of the catalyst due to graphitic carbon formation. The second method revealed the presence of Ni particles strongly anchored to the Al<sub>2</sub>O<sub>3</sub> support. This resulted in an improvement of catalytic activity and stability. Additionally, the best results were obtained for a catalyst containing ca. 2 wt % of yttrium, which was attributed to the high surface area, small nickel particles and very high nickel dispersion.

To the best of our knowledge, no studies concerning the influence of yttrium on Ni-Mg-Al double-layered hydroxides have been reported in the literature. Only a few studies have dealt with Mg-Al hydrotalcites modified with Y for exoxidation [42], cyanoethylation [43] and aldol condensation [44].

The aim of this work was to prepare novel double-layered hydroxide-derived catalysts containing yttrium (0.6 and 1.5 wt %), and to examine the influence of Y promotion on the final physico-chemical properties of the resulting catalysts, their structure and performance in DRM in comparison to the corresponding thermodynamic equilibrium.

## 2. Thermodynamic equilibrium analysis

### 2.1. Minimization of Gibbs free energy

The Gibbs free energy analysis was used to study the equilibrium of the system containing several species. The total Gibbs free energy is expressed as [45–47]:

$$G_{total} = \sum_{i=1}^N n_i \left[ G_i^0 + RT \ln \left( \frac{f_i}{f_i^0} \right) \right] \quad (1)$$

Where the  $G_i^0$  is standard Gibbs free energy of formation of species  $i$ ,  $R$  stands for molar gas constant,  $T$  is temperature of the system, and a number of moles is assigned to  $n_i$  of species  $i$ . Standard-state is

**Table 1**

The list of reactions of dry methane reforming process [42,45,46].

Number	Name	Reaction	$\Delta H^0$ [kJ/mol]
1	Dry reforming of CH <sub>4</sub>	CH <sub>4</sub> + CO <sub>2</sub> = 2CO + 2H <sub>2</sub>	247
2	Reverse water gas shift	CO <sub>2</sub> + H <sub>2</sub> = H <sub>2</sub> O + CO	41
3	Methanation of CO <sub>2</sub>	CO <sub>2</sub> + 4H <sub>2</sub> = CH <sub>4</sub> + 2H <sub>2</sub> O	-165
4	Methanation of CO	CO + 3H <sub>2</sub> = CH <sub>4</sub> + H <sub>2</sub> O	-206
5	Hydrogenation of CO <sub>2</sub>	CO <sub>2</sub> + H <sub>2</sub> = HCOOH	15
6	Hydrogenation of CO <sub>2</sub>	CO <sub>2</sub> + 3H <sub>2</sub> = CH <sub>3</sub> OH + H <sub>2</sub> O	-49
7	Hydrogenation of CO	CO + 2H <sub>2</sub> = CH <sub>3</sub> OH	-91
8	Dehydration of CH <sub>3</sub> OH to CH <sub>3</sub> OCH <sub>3</sub>	2CH <sub>3</sub> OH = CH <sub>3</sub> OCH <sub>3</sub> + H <sub>2</sub> O	-37
9	Reforming of CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub> + H <sub>2</sub> O = 2CO + 4H <sub>2</sub>	205
10	Reforming of CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub> + CO <sub>2</sub> = 3CO + 3H <sub>2</sub>	258
11	Oxidative coupling of CH <sub>4</sub>	2CH <sub>4</sub> + CO <sub>2</sub> = C <sub>2</sub> H <sub>6</sub> + CO + H <sub>2</sub> O	106
12	Reforming of C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub> + 2CO <sub>2</sub> = 4CO + 3H <sub>2</sub>	430
13	Oxidative coupling of CH <sub>4</sub>	2CH <sub>4</sub> + 2CO <sub>2</sub> = C <sub>2</sub> H <sub>4</sub> + 2CO + 2H <sub>2</sub> O	284
14	Reforming of C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> + 2CO <sub>2</sub> = 4CO + 2H <sub>2</sub>	290
Reactions of coke			
15	Methane decomposition	CH <sub>4</sub> = C <sub>(s)</sub> + 2H <sub>2</sub>	75
16	Boudouard reaction	2CO = C <sub>(s)</sub> + CO <sub>2</sub>	-172
17	Hydrogenation of CO <sub>2</sub>	CO <sub>2</sub> + 2H <sub>2</sub> = C <sub>(s)</sub> + 2H <sub>2</sub> O	-90
18	Hydrogenation of CO	CO + H <sub>2</sub> = C + H <sub>2</sub> O	-131
19	Steam on C	C <sub>(s)</sub> + H <sub>2</sub> O = CO + H <sub>2</sub>	131

expressed as 25 °C and 1 atm, while  $f_i^0$  is a fugacity at this state of species  $i$ , and  $f_i$  refers to operating state. In view of Eq. (1),  $n_i$  moles of species has to fulfill the following relation:

$$\sum_{i=1}^N a_{ji} n = b_j \quad (2)$$

Where the number of element  $j$  expressed in grams or atoms of molecule  $i$  is assigned to  $a_{ji}$ .  $b_j$  is a total number of moles of element  $j$  in the feed. Additionally, the following equality:  $1 \leq j \leq M$ , where  $M$  is the number of elements in the mixture, has to be fulfilled.

### 2.2. Calculation method

Thermodynamic calculations were carried out by HSC Chemistry 5 software. The minimization of Gibbs free energy method was used. The influence of temperature and feed gas composition were examined in an isobaric system in order to calculate the equilibrium amount of CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, C, and equilibrium conversions of CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>/CO molar ratio.

For the calculations, the chemical reactions in methane reforming processes were considered (Table 1) [45,48,49]. The following reactants were taken into account: Ar<sub>(g)</sub>, CH<sub>4(g)</sub>, CO<sub>2(g)</sub>, CO<sub>(g)</sub>, H<sub>2(g)</sub>, H<sub>2</sub>O<sub>(g)</sub>, C<sub>(s)</sub>, C<sub>2</sub>H<sub>2(g)</sub>, C<sub>2</sub>H<sub>4(g)</sub>, C<sub>2</sub>H<sub>6(g)</sub>, CH<sub>3</sub>OCH<sub>3(g)</sub>, CH<sub>3</sub>OH<sub>(g)</sub>, HCOOH<sub>(g)</sub>, while the substrates were assumed as: CH<sub>4(g)</sub>, CO<sub>2(g)</sub> and Ar<sub>(g)</sub>. All calculations were performed with constant pressure of 1 bar.

### 2.3. Equilibrium plots

Fig. 1 presents equilibrium amount of reactants as a function of temperature for dry methane reforming (CO<sub>2</sub>/CH<sub>4</sub>/Ar = 1/1/8,  $p = 1$  bar). The results are in good agreement with other authors' work [50,51]. Due to the endothermic nature of the process, and accompanied by parallel reactions, a large variation in the quantity of components while temperature increase (from 0 to 1000 °C) is observed. In the middle of the temperature range (at 500 °C) a large amount of carbon is formed, together with water, and greater amount of H<sub>2</sub> with respect to CO. The CO<sub>2</sub> equilibrium reaches a maximum peak at 500 °C, which refers to the lowest conversion of this gas in the entire

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