From Biogas To Syngas Over Ni Incorporated Ca and Mg Based Hydrotalcite-Like Catalysts

S. Yasyerli, G. Topaloglu, G. Dogu

Department of Chemical Engineering, Gazi University
Maltepe Ankara Turkey; e-mail: syasyerli@gazi.edu.tr ; gdogu@gazi.edu.tr

ABSTRACT

Dry reforming of methane with carbon dioxide is a promising route for the conversion of biogas to syngas, which may then be converted to non-petroleum transportation fuels and valuable chemicals. In this study Ni incorporated Mg and Ca based hydrotalcite-like materials (Ni-MgAlO and Ni-CaAlO, respectively) were synthesized following a one-pot procedure. Results proved that the materials containing Ni/Mg or Ni/Ca molar ratios of 0.2 were highly stable. Dry reforming reactions performed at 600°C showed that the catalytic performance of Ni-CaAlO was better than the performance of Ni-MgAlO, in terms of product distribution and hydrogen yield. However, in terms of coke formation, the performance of Ni-MgAlO was much better, yielding very small coke formation and negligible catalyst deactivation during time-on stream experiments extending upto 50 hours.

***Keywords*:** Synthesis gas, biogas, hydrotalcite, nickel, catalyst

1 INTRODUCTION

Catalytic transformation of methane-carbon dioxide mixture, produced through anaerobic digestion of organic waste, to synthesis gas is an attractive pathway for the production of chemicals and fuels from biogas. Catalytic processes for further conversion of syngas to chemicals through Fischer-Tropsch and methanol synthesis routes is available. Dimethyl ether, which is a promising diesel fuel alternate, may also be produced from syngas using bi-functional catalytic systems. Another attractive property of this process is the utilization of two of the most abundant greenhouse gases in the production of chemicals and fuels, thus contribution to the completion of carbon cycle. This process is also called dry reforming of methane and involves the following catalytic reaction as the main reaction [1-3]:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1)$$

According to the stoichiometry of this reaction, a synthesis gas mixture containing a H_2/CO mole ratio of one is expected. However, occurance of reverse water gas shift reaction (RWGS), together with dry reforming, cause reduction in the hydrogen yield

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

.

Coke formation and catalyst instability are some of the problems of this process. Depending upon the reaction temperature, coke formation may take place through methane decomposition or CO disproportionation reactions. Development of active and stable catalysts with coke minimization are major challenges in conversion of biogas to syngas. Due to its low cost and availability, Ni based catalysts are generally preferred for this reaction. However, significant coke formation was reported with these caralysts [1,4,5]. Positive effects of Ru and Rh and Mg addition into Ni incorporated silicate structured mesoporous catalysts on coke formation was illustrated in our recent studies [5,6]. The type of support was also reported to have significant influence on coke formation. Coke formation and catalyst deactivation were reported to take place faster in microporous and more acidic supports.

Hydrotalcites are basic clay type materials, composed of positively charged brucite-like layers. A typical composition of a hydrotalcite is $Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$. Water and CO_2 are removed from its structure as result of activation of these materials by calcination. Calcined hydrotalcite is a highly active mesoporous material for sorption of CO_2 [7]. Considering these attractive properties of hydrotalcites [8,9], in the present study, Ni incorporated Mg and Ca based hydrotalcite-like materials were synthesized following one-pot procedures. These materials are (denoted as Ni-MgAlO and Ni-CaAlO, respectively. Catalytic performances of these materials were then tested in transpormation of methane-carbon dioxide mixture to synthesis gas.

2 EXPERIMENTAL

Catalyst synthesis and characterization:

Synthesis of Ni incorporated Mg and Ca based hydrotalcite-like materials were made following a one-pot co-precipitation procedure keeping the Mg/Al or Ca/Al ratio as 3 in the synthesis solution. Pre-determined amout of nickel nitrate hexahydrate was added to this solution to achieve products containing different ratios of Ni/Mg or Ni/Ca. Precipitation was achieved by adding the solution containing Mg^{+2}, Al^{+3} and nickel ions, to a Na_2CO_3 solution, by adjusting the final pH as 10 [10]. After the

aging process, the final product was filtered, washed, dried and calcined at 600°C. Synthesized materials were characterized by XRD, ICP, TGA-DTA, N_2 adsorption/desorption, H_2 TPR and SEM techniques. Characterization of the used catalysts by similar techniques gave information about the amount and type of coke formed on these catalysts during reaction.

Dry reforming reaction tests:

Dry reforming reactions were performed in a tubular reactor at 600°C. Catalyst pellets (0.1 g) of about 1-2 mm were packed into the reactor by supporting from both ends. Total flow rate of the feed gas, which was composed of $CH_4/CO_2/Ar$=1/1/1, was adjusted as 30 ml/min, measured at room temperature. Before the dry reforming tests, the catalyst was reduced in a flowing hydrogen stream at 550°C. Composition of the reactor outlet stream was analyzed by a gas chromatograph, connected on-line to the reactor.

3 RESULTS AND DISCUSSIONS

XRD analysis of the synthesized materials indicated formation of characteristic structures of hydrotalcites. Most of the Ni and Ca were found to be in the oxidation state of +2 in the calcined materials. ICP-MS analysis proved incorporation of Ni into the structure of hydrotalcite in the respective ratio of the synthesis solution. TPR analyis of Ni-MgAlO3 (containing a Ni/Mg ratio of 0.2) showed two small reduction peaks at 380°C and 460°C, and another large peak in the 700-850°C range. Small peaks at lower temperatures were identified to correspond to the reduction of extraframework NiO and/or NiO present close to the external surface of the catalyst. However, the large peak at high temperature indicated the presence of most of the nickel within the framework of the synthesized materials with strong interaction of NiO-MgO. Similar results were obtained with Ni-CaAlO having a similar ratio of Ni/Ca. However, in this case the TPR peak observed at low temperature (440°C) was much stronger than the peak observed for Ni-MgAlO3, indicating higher amount of extraframework NiO in this material. Also, increase of Ni/Mg ratio of the Ni-MgAlO type materials with Ni/Mg ratios of 2.0, 0.5 and 0.2 (Ni-MgAlO1, Ni-MgAlO2 and Ni-MgAlO3, respectively) is expected to increase the amount of extraframework nickel in the synthesized materials.

N_2 adsorption/desorption isotherms of the synthesized materials proved the occurrence of a mesoporous structure (Fig. 1) with most of the pores ranging between 5-50 nm for the materials contaaining Ni/Mg and Ni/Ca ratios of 0.2. Average pore diameters of Ni-CaAlO and Ni-MgAlO3 were about 21 and 22 nm respectively.

Activity test results obtained with Ni incorporated Mg based materials containing different Ni/Mg ratios clearly indicated that the materials with high Ni/Mg ratios were highly unstable (Fig. 2). XRD, TGA-DTA and SEM analysis proved increase of coke formation with an increase in Ni/Mg ratio. The peak at a 2θ of 26° corresponds to carbon due to coke formed on the catalyst (Fig. 3). This was considered to be due to increase of extraframework nickel in the structure of synthesized materials with an increase in Ni/Mg ratio. However, the material containing a NiMg ratio of 0.2 was highly stable (Fig. 2). In fact, time on-stream experiments performed with this catalyst extending upto 50 hours showed continuation of stable performance.

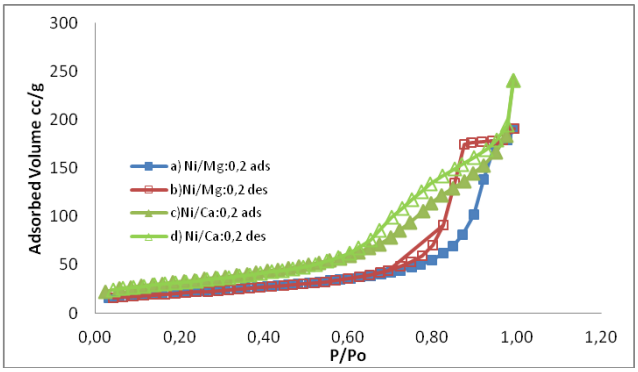

Fig. 1. N_2 adsorption/desorption isotherms of Ni_CaAlO and NiMgAlO3.

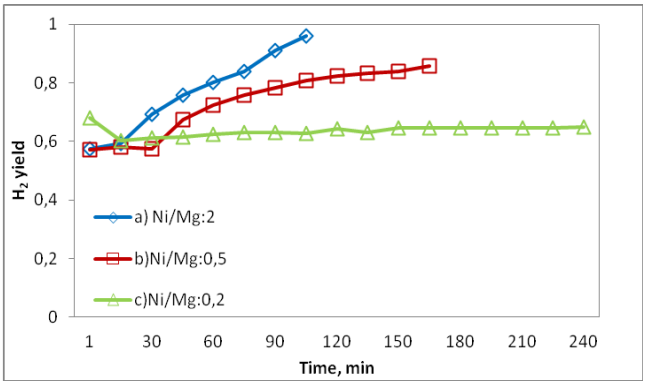

Fig.2. Hydrogen yield values (defined as the ratio of moles of hydrogen produced per mole of methane introduced to the reactor) of Ni-MgAlO1, Mi-MgAlO2 and NiMgAlO3.

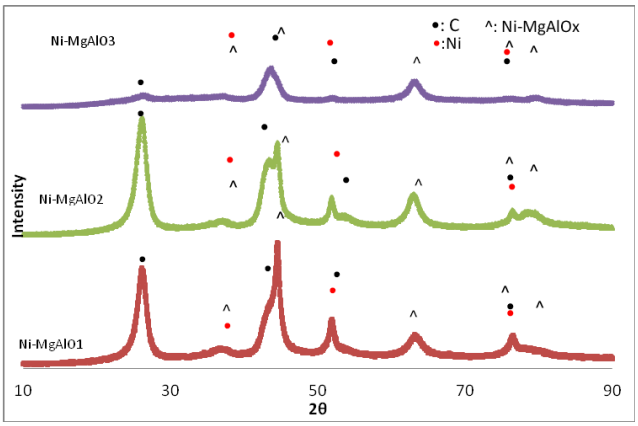

Fig.3. XRD patterns of Ni-MgAlO1, Ni-MgAlO2 and Ni-MgAlO3 after reaction.

Following these results, dry reforming experiments were continued with Ni-MgAlO3 and Ni-CaAlO materials containing Ni/Mg and Ni/Ca ratios of 0.2. Results proved that, these materials were highly active and stable in dry reforming reaction. Methane conversion values approached to the equilibrium conversion value at 600°C. As indicated by the XRD analysis, no change in the crystal structures of the catalysts was observed after reaction and decrease of surface area was less than 5% for Ni-MgAlO3 (Table 1).

Table 1. Changes in surface area due to coke formation during dry reforming at 600°C. (Reaction period: 240 min)

Catalyst	Surface Area (m^2/g)	
	Before Reaction	After Reaction
Ni-MgAlO	156.9	149.1
Ni-CaAlO	100.2	79.2

The catalytic performance of novel Ni-CaAlO was found to be much better than Ni-MgAlO, in terms of product distribution and hydrogen yield. It was shown that with Ni-CaAlO, hydrogen and CO selectivities were both very close to 2, while with Ni-MgAlO3 hydrogen selectivity was less than CO selectivity due to occurance of RWGS reaction (Figures 1,2). However, in terms of coke formation, performance of Ni-MgAlO3 was much better, yielding smaller coke formation and negligible catalyst deactivation during time on stream reaction tests, extending upto 50 hours.

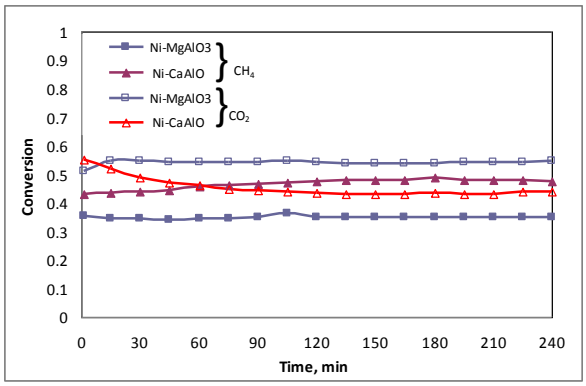

Fig. 4. CH_4 and CO_2 conversions with Ni-MgAlO3 and Ni-CaAlO.

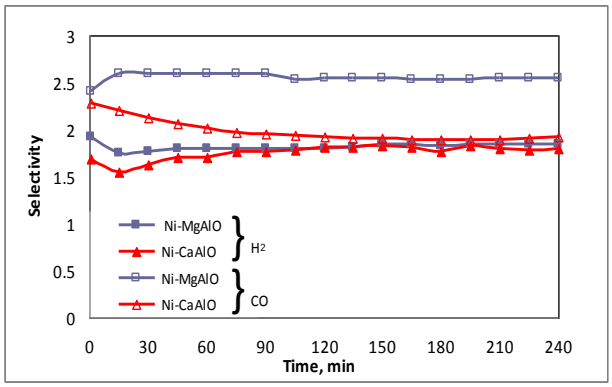

Fig. 5. H_2 and CO selectivites with respect to CH_4 with Ni-MgAlO3 and Ni-CaAlO.

SEM analysis of the used catalysts indicated formation of filamentous carbon on the active sites of the catalysts. Formation of filamentous carbon was much higher on used Ni-CaAlO than on Ni-MgAlO3 at the end of a reaction period of 4 hours (Fig. 6.).

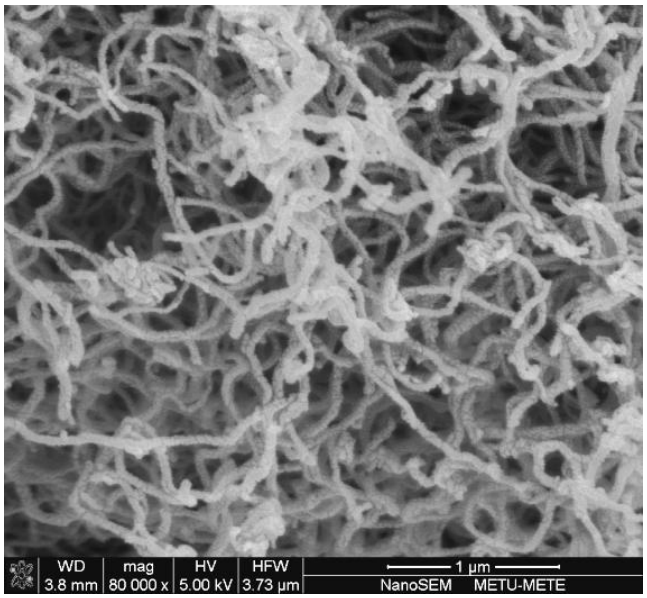

Fig. 6. Filamentous carbon formed on Ni-CaMgAlO after a reaction period of 4 hours.

4 CONCLUDING REMARKS

It was concluded that, catalytic performance of Ni incorporated MgAlO type hydrotalcite, which was synthesized by the one-pot route, was highly stable with small coke formation, while with Ni incorporated Ca based hydrotalcite, coke formation was much higher due to presence of higher amount of extra-framework nickel. Increase of Ni/Mg ratio in Ni-MgAlO type materials also increased coke formation, having best performance with the material containing Ni/Mg=0.2. On the other hand, the Ca based material Ni-CaAlO is better in terms of hydrogen yield, minimizing RWGS reaction.

5 ACKNOWLEDGEMENT

TUBITAK and Gazi University Research Funds (BAP 06/2011-44) and contributions of Prof. Timur Dogu of METU are gratefully acknowledged.

REFERENCES

[1] Nimwattanakul W., Luengnaruemitchai A. and Jitkarnka S, Int.J.HydrogenEnergy 31, 93-100 2006.
[2] Cheng Z.X., Zhao X.G., Li J.L. and Zhu Q.M., Appl. Catal A:Gen 205, 31-33, 2001.
[3] Juan-Juan J., Roman-Martinez M.C. and Illan-Gomez M.J., Appl. Catal. A: Gen 359, 27-32, 2009.

[4] Corthals S., Nederkassel J.V., Geboers J., Winne H.D. et al., Catal. Today 138, 28-32, 2008.
[5] Arbag H., Yasyerli S., Yasyerli N., Dogu G., Int. J. Hydrogen Energy 35, 2296-2304, 2010.
[6] Yasyerli S., Filixgok S., Arbag H., Yasyerli N., Dogu G., Int.J.Hydrogen Energy 36, 4863-74, 2011.
[7] Ficicilar B., Dogu T., Catal Today 115, 274-279, 2006.
[8] Tsyganok A.I., Inaba M., Tsunodo T. and Tekehira K, Appl. Catal. A:Gen. 292, 328-343, 2005.
[9] Daza C.D., Gallego J., Moreno J.A., Mondragon F., Moreno S. and Molina R, Catal. Today 133-135, 357-366, 2008.
[10] Topaloglu G, "Development of Catalysts for Dry Reforming of Methane", M.S. Thesis, Gazi University, Ankara-Turkey, Sept. 2012.