Low temperature dry reforming of methane over hydrotalcite derived Ni/Mg/Al and Cu/Mg/Al mixed oxides

Radosław Dębek[1,2*], Katarzyna Zubek[1], Małgorzata Adamowska[2], Monika Motak[1], Patrick Da Costa[2], Teresa Grzybek[1]

[1]*AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A.Mickiewicza 30, 30-059 Cracow, Poland*

[2]*Sorbonne Universités, UPMC Paris 6, Institut Jean le Rond D'Alembert, UMR CNRS 7190, Saint-Cyr l'Ecole, 78210, France*

**corresponding author:debek@agh.edu.pl*

Introduction

The dry methane reforming (DRM) reaction is one of the most promising ways of CO_2 utilization with huge potential of future application. The latest research is focused on obtaining efficient, robust and stable catalyst, since in case of CO_2/CH_4 reforming there is a considerable problem of catalyst deactivation by coke formation. In the presented work catalysts based on hydrotalcite materials were tested. Mixed oxides derived from hydrotalcites were chosen, because of their unique properties (basic characteristics, memory effect, high specific surface area). Moreover this type of materials were already reported to show high CO_2 and CH_4 conversions and considerable stability [1].

Materials and Methods

The hydrotalcites (LDH - Layered Double Hydroxides) were synthesized by standard co-precipitation method (60°C and pH=10) [1]. In this way samples HT1 (comp.: 37 wt.% Mg, 14.2 wt.% Al), HT2 (comp.: 63.5 wt.% Ni, 7.7 wt.% Al) and HT5 (comp.:19.1 wt.% Mg, 4.9 wt.% Cu, 8.0 wt.% Al) were synthesized. A part of sample HT1 underwent ion-exchange modification with $Ni(EDTA)^{2-}$ complexes or $Ni(EDTA)^{2-}$and $Ce(EDTA)^{-}$ complex, resulting in samples HT3 and HT4, respectively [2]. Sample HT5 was also loaded with cerium species using ion-exchange procedure. Such method was sufficient to introduce ca.1wt.% of both nickel and cerium species onto catalysts surface. The prepared catalysts were characterized by XRD, low temperature nitrogen sorption, TPR, FTIR, TEM and elemental analysis. The catalytic tests were performed in a fixed-bed reactor for 1h at 550°C with GHSV equal to $20000h^{-1}$ and total feed gas flow 100 cm^3/min (CH_4/CO_2/Ar=1/1/8). Prior to each experiment, the catalyst sample was activated in the stream of H_2 at 900°C for 1h. The products of the reaction were analyzed by online gas chromatograph (Varian Micro-GC).

Results and Discussion

The characterization of the synthesized catalysts confirmed that the prepared materials had typical hydrotalcite structure before calcination and periclase structure of mixed oxides after calcination (XRD), and high surface area 100-120 m^2/g (N_2 sorption). The results of TPR experiments showed reduction peaks arising from reduction of NiO to metallic nickel (catalysts HT2 ca. 550°C, HT3 and HT4 ca. 890°C) and reduction peaks arising from reduction of copper species (sample HT5 ca. 280°C). FTIR measurements confirmed successful incorporation of metal-EDTA complexes into hydrotalcites structure.

Figure 1 presents the results of the catalytic tests. At 550°C high CH_4 and CO_2 conversions was shown only by nickel-containing samples. Of those HT2 showed the best catalytic performance. For the two samples modified with ion-exchange method, the better catalytic performance was observed for sample HT4, loaded with cerium compounds. Support alone (HT1) did not show any activity. In case of copper containing sample very low conversions were observed. The obtained values of H_2/CO molar ratios for nickel samples were higher then 1, which suggests the occurrence of side reactions, such as methane decomposition. This hypothesis was confirmed for sample HT2 by performing an additional catalytic test. The catalysts did not show significant deactivation during one-hour tests.

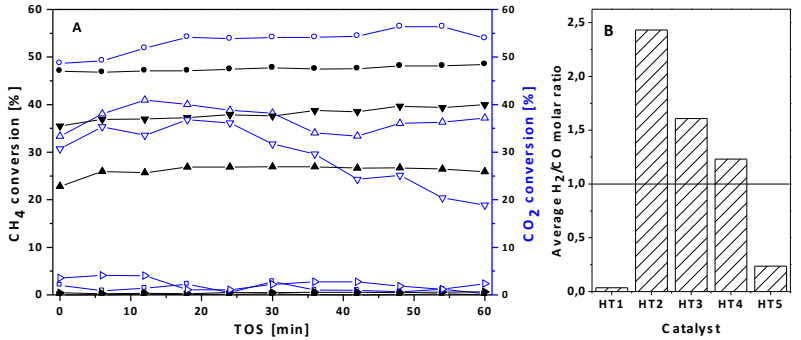

Figure 1. The results of catalytic tests: (A) CH_4 and CO_2 conversions HT1(■), HT2 (●), HT3(▲), HT4(▼), HT5(►); (B) average H_2/CO molar ratio;

Significance

Mixed oxides containing nickel showed high CH_4 and CO_2 conversions at 550°C. The best performance was observed for the sample with nickel introduced into hydrotalcite layers (HT2). Catalysts HT3 and HT4, ion-exchanged nickel samples, were also active in DRM reaction. For this two samples promoting effect of cerium addition was observed. H_2/CO values suggest the occurrence of side reactions, mainly methane decomposition. Copper containing sample, as well as the support were inactive in the tested reaction.

Acknowledgement

The work was financed within NCBR strategic research project 'Technologies supporting development of safe nuclear energy', research task no. 1 'Development of high temperature reactors for industrial applications', agreement no. SP/J/1/166183/12, step task no. 15 'Preparation and physicochemical characterization of catalysts for dry reforming of methane'

References

1. Daza, C.E.; Gallego, J.; Moreno, J.A.; Mondragon; F.; Moreno, S.; Molina R. *Catalysis Today* **2008**, 133-135, 357-366
2. Tsyganok A.I.; Suzuki K.; Hamakawa S.; Takehira K.; Hayakawa T. *Catalysis Letters* **2001** 77, 75-86