# Hydrotalcite derived catalysts with different Ni/Mg/Al molar ratios as a catalyst for low temperature dry reforming of methane

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## Introduction

DRM process is a highly endothermic reaction, which may be applied as one of the methods of $CO_2$ utilization. Hydrotalcites based catalysts containing nickel have been reported to be active catalyst and showed considerable activity for the reaction of $CO_2$ reforming of methane (DRM) [1]. In this work a series of hydrotalcite based catalysts with different Ni/Mg molar ratios were tested in order to determine optimal ratio of Ni/Mg cations in hydrotalcite brucite-like layers.

## Materials and Methods

The prepared catalysts were synthesized by co-precipitation method [1]. The series of hydrotalcites HT1, HT2, HT3, HT4, HT5 catalysts were obtained with $Ni^{2+}/Mg^{2+}$ molar ratio equal to 0/1, 1/3, 1/1, 3/1 and the sample without any $Mg^{2+}$ cations, respectively. The materials were characterized by XRD, low temp. $N_2$ sorption, $H_2$–TPR, FTIR and elemental analysis.

The catalysts were tested in DRM reaction at 550°C with the feed gas composition of $CH_4/CO_2/Ar=1/1/8$ (100 $cm^3$/min) and GHSV=20000$h^{-1}$. The samples were activated for 1h in stream of 3% $H_2$ in Ar at 900°C, prior to each experiment.

## Results and Discussion

The designation of the samples together with the results of elemental analysis and their textural parameters are presented in **Table 1**. The elemental analysis showed that the composition of synthesized samples is consistent with the assumed values of $M^{2+}/M^{3+}$ and Ni/Mg molar ratios at the step of catalyst preparation. The low temp. $N_2$ sorption experiments revealed that the values of specific surface area were increasing with the amount of nickel in the brucite-like layers. The opposite trend was observed for the values of total pore volume. The XRD diffractograms of uncalcined samples showed reflections typical for hydrotalcite structure at 2θ equal to 11, 24 and 35° indicating layered structure. The catalysts after calcination exhibited periclase-like structure typical for mixed oxides obtained from hydrotalcites [2]. The TPR-$H_2$ profiles of all nickel containing samples showed wide asymmetric peaks, which indicates different interactions of nickel species with the support. The maximum of temperature was shifted to the higher values with the increasing magnesium content, indicating the NiO species with strong interaction with the support, resulting from the formation of highly stable NiO-MgO solid solution [2].

**Figure 1** and **Figure 2** present the results of catalytic tests. Sample HT1 was completely inactive in DRM reaction. The nickel containing catalysts showed visible increase in activity with the increase in Ni content in terms of $CH_4$ conversion, while the obtained values of $CO_2$ conversion were similar for all tested catalysts. The reason for increase in $CH_4$ conversion is the reaction of methane decomposition at 550°C, which is reflected in the values of $H_2$/CO molar ratio.

**Table 1.** Designation of samples, results of elemental analysis and their textural parameters.

| Sample | Ni (wt.%) | Mg (wt.%) | Al (wt.%) | $M^{2+}/M^{3+}$ measured | Ni/Mg measured | $S_{BET}$ ($m^2$/g) | $V_{tot.}$ ($cm^3$/g) |
|---|---|---|---|---|---|---|---|
| HT1 | - | 35.1 | 13.2 | 2.96 | - | 95 | 0.84 |
| HT2 | 19.6 | 23.9 | 11.8 | 3.02 | 0.34 | 115 | 0.41 |
| HT3 | 36.6 | 14.8 | 11.1 | 3 | 1.02 | 126 | 0.35 |
| HT4 | 49.1 | 6.6 | 10.9 | 2.74 | 3.09 | 127 | 0.29 |
| HT5 | 58.7 | - | 8.9 | 3.02 | - | 121 | 0.24 |

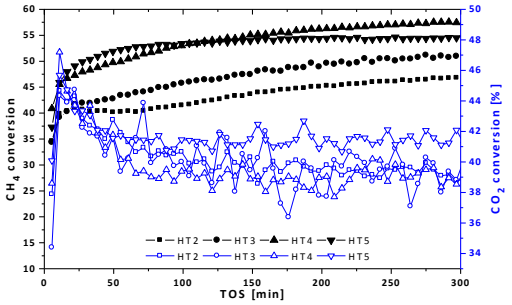


**Figure 1.** The results of catalytic tests.

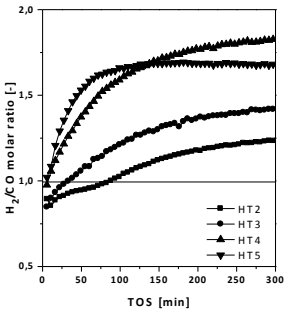


**Figure 2.** The obtained values of $H_2$/CO molar ratio.

## Significance

The synthesized materials exhibited properties characteristic for mixed oxides obtained from hydrotalcite calcination. The best catalytic performance was observed in case of HT5 sample. However, its good catalytic performance might be due to the occurrence of side reactions ($CH_4$ decomposition). So in order to determine the best catalyst additional tests at higher temperatures and characterization of samples after reaction need to be performed.

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## References

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2. Gonzalez, A.R.; Asencios Y.J.O.; Assaf, M.A.; Assaf, J.M. *Applied Surface Science* **2013**, 280, 87.