

CATALYTIC REACTION OF CARBON DIOXIDE WITH METHANE ON SUPPORTED Co/Mo CATALYSTS

Ghazaleh Khoshroo, Marietta Ábel, András Sápi, Anastasiia Efremova, Ákos Kukovecz, Zoltán Kónya

*Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
e-mail : khoshroo.ghazaleh@stud.u-szeged.hu*

Abstract

In this work the reforming of methane with carbon dioxide has been investigated at 773 K on supported Mo-Co/ Al₂O₃ catalysts with different loading 1%, 5% and 10 % of Mo. The catalysts were characterized by XRD and TEM methods before and after the reaction. The results revealed that 10%Co/Al₂O₃ had the highest conversion of CH₄ and CO₂ and highest syngas formation rate among the mentioned catalysts. In addition, the mentioned catalysts characterization before and after the reaction showed no differences.

Introduction

Some carbon-containing fossil fuel combustions, such as coal, natural (stranded or shale) gas, and petroleum, have emitted significant amounts of greenhouse gases, which can cause global climate change as well as environmentally hazardous pollutant emissions. [1]. Renewable energy development and greenhouse gas emissions reduction have become increasingly crucial global issues in recent years [2]. The conversion of CH₄ and CO₂, the two primary components of biogas and the principal greenhouse gases into synthesis gas is in the focus of academic and industrial research. Reacting the CH₄ and CO₂ is one option for achieving this goal [3]. The CH₄ can react with CO₂ as a reductant - by the techniques including Dry reforming (DR), Steam Reforming (SR) and Combining SR and DR -to produce the industrially important syngas (CO+H₂ mixture) [4]. From the CO+H₂ mixture both fuel and methanol or a variety of other products can be produced using currently available technologies [5].

Experimental

In this research, the DR reforming of methane with carbon dioxide has been investigated atmospheric pressure, at 773 K, using 10%Co/Al₂O₃, 1% Mo+10% Co/Al₂O₃, 5% Mo+10% Co/Al₂O₃ and 10% Mo+10% Co/Al₂O₃ catalysts, which were prepared by incipient wetness method and calcined at 773 K. The experiments were carried out in a fixed-bed continuous flow reactor. The amount of the catalysts used were 150 mg. The flow rate of the reactants was 30 ml/min. The catalysts were oxidized for 30 minutes and reduced for 60 minutes at 773 K and the catalytic tests were carried out at 573- 873K. The catalysts were characterized by XRD and TEM methods before and after the reaction.



Gas Chromatograph (Agilent 6890)



MiniFlex II
DESKTOP X-ray
DIFFRACTOMETER
(Rigaku)



FEI TECNAI G2 20 X-Twin high-resolution
transmission electron microscope
(HR-TEM)

Results and discussion

The results indicate that 10%Co/Al₂O₃ had the highest conversion of CH₄ and CO₂ and highest syngas formation rate among the mentioned catalysts. Furthermore, Mo promoted 10%Co/Al₂O₃ was found to be more active in 1% amount than the 5% or 10% Mo/Al₂O₃.

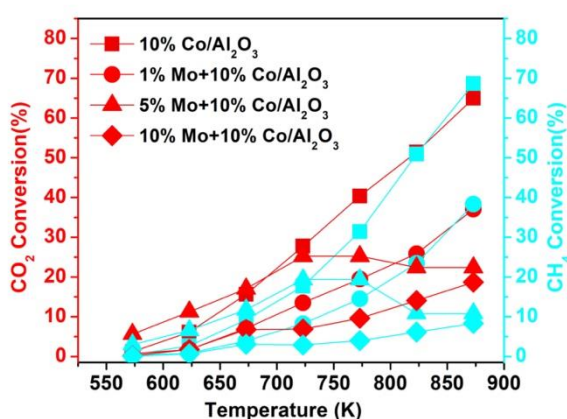


Fig.1. CO₂ and CH₄ Conversion in heating phase

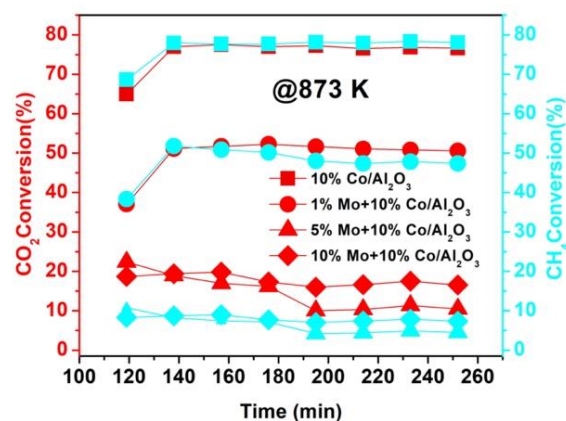


Fig2.CO₂ and CH₄ Conversion in isotherm phase

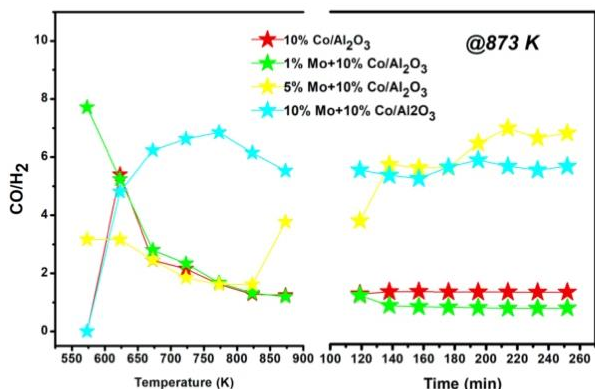


Fig.3. CO/H₂ in heating phase and isotherm phase

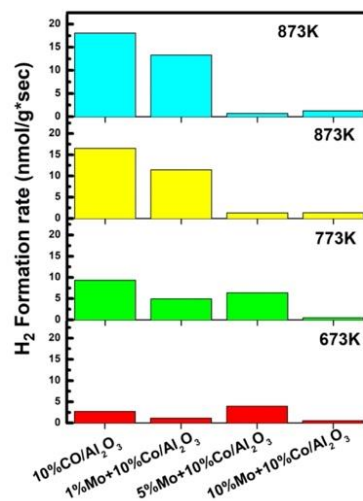


Fig.4. H₂ Formation rate in different temperatures

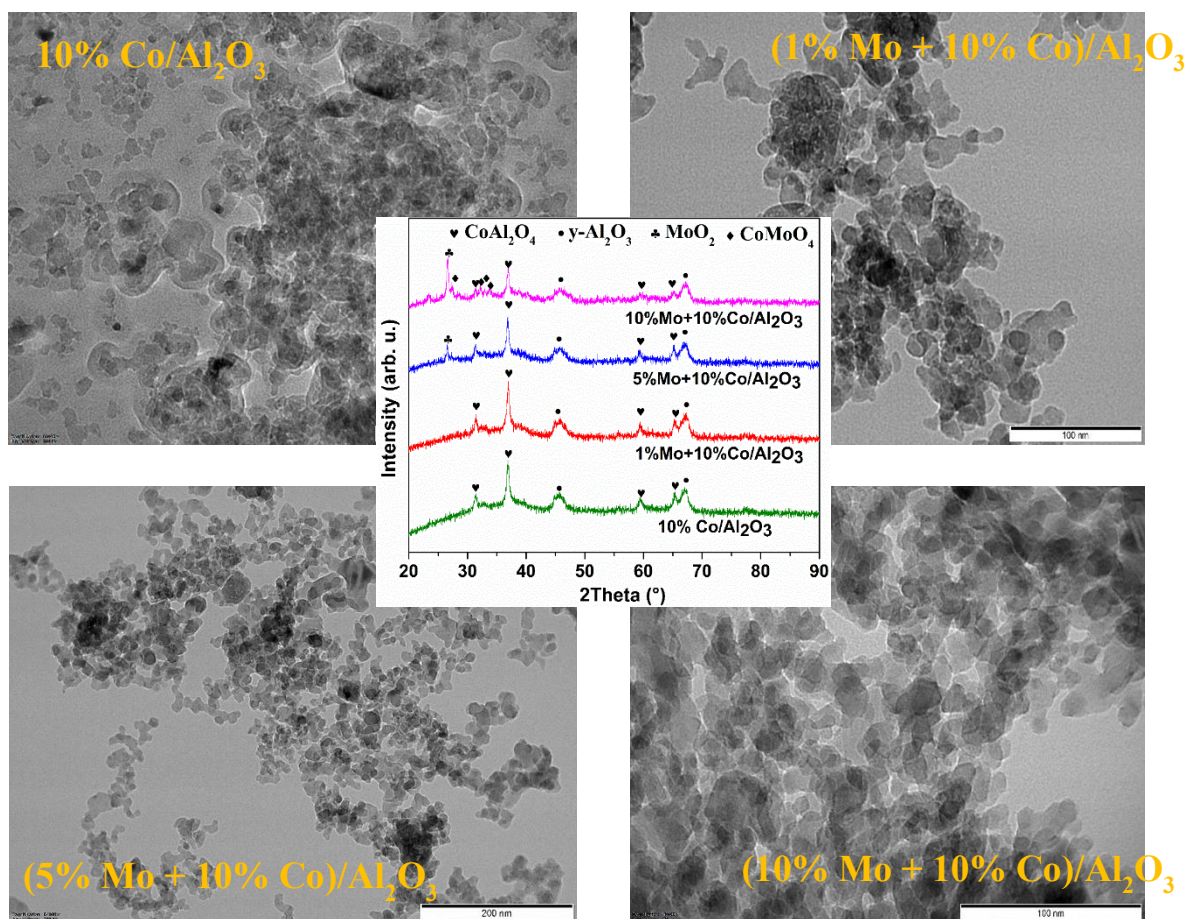


Fig.5. TEM pictures & XRD graph

Conclusion

- The 10%Co/Al₂O₃ reforming catalyst had the best performance in terms of CH₄ and CO₂ Conversion. In addition, among the promoted catalysts by Mo, 1% Mo+10%Co/Al₂O₃ was more active (Fig.1-2.)

- The main products of the reaction were H₂ and CO. The 10%Co+1%Mo/Al₂O₃ showed the highest ratio of CO/H₂ in heating phase, while the 5%Mo+10%Co/Al₂O₃ showed the highest ratio in isotherm phase. (Fig.3.)
- The 10%Mo+10%Co/Al₂O₃ had the fast-increasing CO/H₂ ratio in the heating phase and had the steady trend in the isotherm phase. (Fig.3.)
- The catalysts were characterized before and after the reaction with XRD and TEM which no differences were found before and after the reaction (Fig.5.).

Acknowledgements

- University of Szeged, Interdisciplinary Excellence Centre, Department of Applied and Environmental Chemistry.
- Stipendium Hungaricum Scholarship Programme.

References

- [1] A.R.Kim, H.Y.Lee, J.M.Cho, J-H.Choi, J.W.Bae, Ni/M-Al₂O₃ (M=Sm,Ce or Mg) for combined steam and CO₂ reforming of CH₄ from coke oven gas, *J.CO₂.Utl.* (2017) 21.211-218.
- [2] Y.Xia, Na.Lu, J.Li, N.Jiang, K.Shang, Y.Wu, Combined steam and CO₂ reforming of CH₄ for syngas production in a gliding arc discharge plasma, *J.CO₂.Utl.* (2020) 37.248-259.
- [3] É.Horváth, K.Baán, E.Varga, A.Oszkó, Á.Vágó, M.Tőro, A.Erdőhelyi, Dry reforming of CH₄ on Co/Al₂O₃ catalysts reduced at different temperatures, *J.Catal.T.* (2017) 281. 233-240.
- [4] N.Schiaroli, C.Lucarelli, M.C.Iapalucci, G.Fornadari, A.Crimaldi, A.Vaccari, Combined Reforming of Clean Biogas over Nanosized Ni–Rh Bimetallic Clusters, *J.Catal.* (2020) 10,1345.
- [5] A. Erdőhelyi, Catalytic Reaction of Carbon Dioxide with Methane on Supported Noble Metal Catalysts, *J. Ctal.* (2021) 11,159.