Effect of Ni, Ce, Y, Zr and Fe promoters on CO_2 methanation with $Co/\gamma Al_2O_3$ catalyst

Nomin Battulga, Manlaibaatar Purevsuren, Enkhsaruul Byambajav*

Laboratory of Clean Energy Technology Development, Department of Chemistry, National University of Mongolia

**Corresponding author: enkhsaruul_b@num.edu.mn*

Highlights

- Zr promoter in Co/Al catalyst makes easier the reduction of cobalt active species.
- Co-Zr/Al catalyst produces the highest yield of methane at lower temperatures (<300°C).
- Optimal amount of Zr promoter is 2 wt.% in Co/Al catalyst to convert CO_2 into methane.

1. Introduction

Carbon dioxide (CO_2) is largely emitted from burning processes of the world main energy resources – fossil fuels. It has led to global warming and climate change. The use of carbon dioxide is one of the important methods for mitigating its environmental impact. Significant progress has been made in converting CO_2 to various high-value synthetic fuels and chemicals [1-2]. Among the processes, the hydrogenation of CO_2 to methane (1) is considered a candidate for an alternative, renewable energy process.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ кЖ/моль} \qquad (1)$$

In this research work, we obtained methane as a product of the modified Fischer-Tropsch synthesis (FT-CO_2) by converting CO_2 using 15%Co/γ-Al_2O_3 catalysts. The catalysts were enhanced with 2% Ni, Y, Fe, Ce, or 1-3% Zr promoters, respectively. The effects of different promoter metals on CO_2 conversion and methane selectivity during FT-CO2 synthesis over a Co/Al_2O_3 catalyst were investigated.

2. Methods

The catalysts are prepared using the incipient wetness impregnation method, and characterized by X-ray diffraction analysis and Temperature-programmed hydrogen reduction (H2-TPR) measurements. The catalyst contains 15% Co, noted as Co/Al. Based on this catalyst, 2% (wt.) of a metal promoter (Ni, Y, Fe, Ce, or Zr) is added. Catalytic activity of the catalysts is evaluated in a fixed-bed reactor at 50-400°C, under atmospheric pressure, and H_2:CO_2=4:1 molar ratio with a total volume rate of 3000 h^{-1}.

3. Results and discussion

Figure 1 shows the methane yield during CO_2 hydrogenation with the different metal-promoted Co/Al_2O_3 catalysts between the temperatures of 100 – 400°C under atmospheric pressure. It is suggested that Y, Ce, and Fe metals depress methane formation over the Co/Al2O3 catalyst, whereas Ni metal has little effect on CH_4 yield. However, the Zr significantly promotes the methane formation from CO_2 at lower temperatures (<300°C). Based on catalyst characterization results, zirconium facilitates the activation of the main cobalt species on the alumina support. TPR analysis indicates no strong interaction between cobalt and the alumina support in the presence of the zirconium promoter. Additionally, XRD and TPR methods identify larger peaks for metal cobalt (Co^0) species after H_2 treatment or the programmed reduction in the presence of a Zr promoter. On the contrary, a reduction of the γ-peak around the temperature of >500°C, perhaps due to cobalt aluminate inactive species, is detected for the non-promoted Co/Al and Co-Fe/Al catalysts.

To assess the effect of Zr content in Co/Al catalysts, the Zr promoter content is varied between 1% and 3% (wt.). The optimal Zr promoter loading is 2 wt.%, yielding the highest CO_2 conversion (74.6%) and the highest CH_4 selectivity (98.9%) at an equilibrium temperature of 400°C.

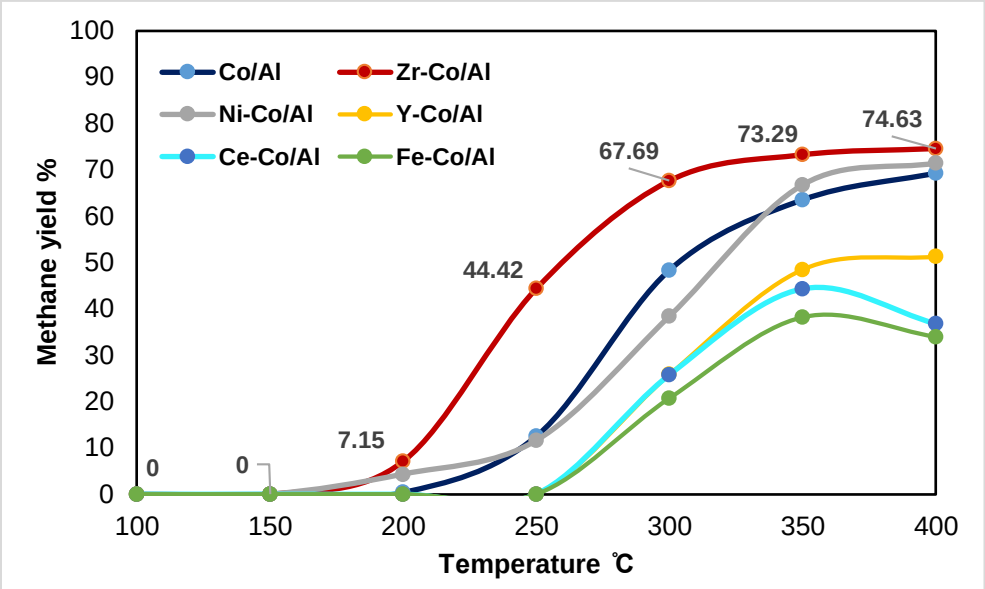

Figure 1. Methane yield with different metal-promoted Co/Al catalysts during CO_2 hydrogenation

4. Conclusion

Cobalt catalyst promoted by zirconium produces the highest yield of methane during CO_2 hydrogenation at a lower temperature under atmospheric pressure. The Zr promoter facilitates the activation of the main cobalt species on the alumina support and does not generate inactive cobalt aluminate species due to their suitable interaction strength.

References

[1] Nyamsuren Battumur, Nomuunaa Sergelenbaatar, Tungalagtamir Bold, Enkhsaruul Byambajav, "Cerium-promoted nickel catalysts supported on yttrium-doped alumina for carbon dioxide methanation", *Journal of CO2 Utilization*, 2023, 68, 102380

[2] Buyan-Ulzii Battulga, Tungalagtamir Bold, Enkhsaruul Byambajav, "Effect of Fe and Co promoters on CO methanation activity of nickel catalyst prepared by impregnation-co-precipitation method", *International Journal of Chemical Reaction Engineering*, 2020, 18 (5-6), 20200076

Keywords

CO_2 hydrogenation, cobalt aluminate, low temperature methanation, temperature programmed reduction