

CO, NI AND K AS PROMOTERS IN CO₂ HYDROGENATION ON MoS₂ BASED CATALYSTS

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INTRODUCTION

CO₂ is a well known greenhouse gas and the amount in the atmosphere is still rising. The goal of this work was to study recycling and utilization of carbon dioxide in flue gas by catalytic reduction. Flue gas contains about 10 – 15 vol.% CO₂, oxygen, water and traces of sulfur containing substances like H₂S. There are several ways to convert CO₂ into valuable compounds using different catalysts. For example: Ni based catalysts for CH₄ formation, Cu/ZnO/Al₂O₃ for methanol production or MoS₂ based catalysts for alcohol synthesis. However, the sulfur contamination in the flue gas leads to deactivation of many catalysts. MoS₂ based catalysts should not be affected by sulfur containing feed gas. Co-Mo-S materials are known as hydrodesulfurization catalysts and are also active for CO₂ hydrogenation.^[1] Therefore, in this work, we have studied MoS₂ based catalysts in order to learn about correlations between synthesis and composition, structural and catalytic properties.

EXPERIMENTS

In this work different formulations of Co-Mo-S and Ni-Mo-S catalysts were prepared hydrothermally^{[2], [3]} and by precipitation^[4] and compared to each other. Different supports (activated carbon and alumina) were used. Catalysts with and without potassium promoter were synthesized. Catalytic properties were tested in a plug flow reactor up to 20 bar. Reaction orders of the reactants and apparent activation energies of the product formation were calculated. A long-term test was done to ensure the stability of the catalyst.

The catalysts were characterized by TPD (temperature programmed desorption), TPR (temperature programmed reduction), TPO (temperature programmed oxidation), XRD (X-ray diffraction) and N₂ physisorption and the changes of the catalyst during the reaction were investigated.

RESULTS AND DISCUSSION

Products were mainly CO, methane and traces of methanol. Fig. 1 shows the yield of CO and CH₄ over different Co-Mo-S catalysts. The effect of potassium as promoter was investigated. Catalysts with potassium promoter produced much less CH₄ and more CO under the given conditions. There was no dependence on the support.

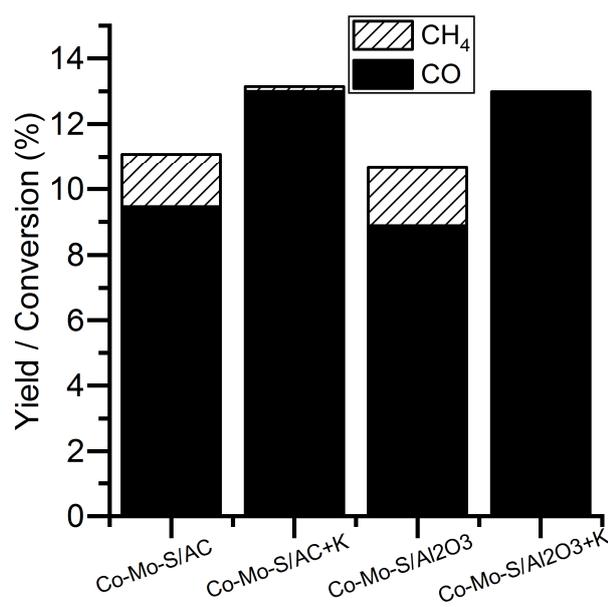


Fig. 1: Yield of CO and CH₄ at 330 °C, 21 bar, 3000 mlN/(g_{catalyst}*h)

Fig. 2 shows the conversion of a $\text{MoS}_2 + \text{K}$ catalyst compared to a $\text{Co-Mo-S} + \text{K}$ catalyst. The conversion of the $\text{Co-Mo-S} + \text{K}$ catalyst was higher at the given conditions. The $\text{Co-Mo-S} + \text{K}$ catalyst showed a lower selectivity to CH_4 .

A long-term test over 200 hours showed a constant conversion of CO_2 over the catalyst.

Under reducing conditions, the catalyst was stable below 500°C , whereas under oxidizing condition above 300°C SO_2 was formed.

XRD showed a change of the cobalt sulfide phase during the reaction.

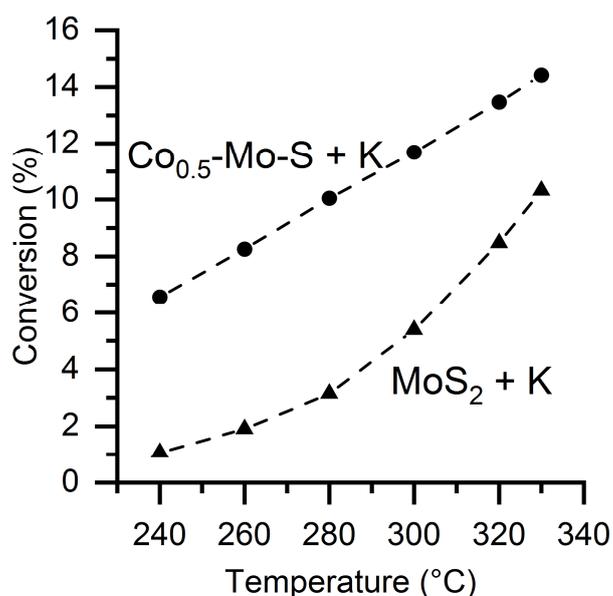


Fig. 2: Conversion of CO_2 over $\text{MoS}_2 + \text{K}$ and $\text{Co-Mo-S} + \text{K}$, 21 bar, $300 \text{ mL}/(\text{g}_{\text{catalyst}} \cdot \text{h})$

CONSLUSION

Co, Ni and K are efficient promoters of MoS_2 based catalysts to increase the formation of CO and inhibit the CH_4 production. The catalyst was stable under working conditions.

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REFERENCES

- [1] M. D. Porosoff, B. Yan, and J. G. Chen, "Catalytic reduction of CO_2 by H_2 for synthesis of CO, methanol and hydrocarbons: challenges and opportunities," *Energy Environ. Sci.*, vol. 9, pp. 62–73, 2016.
- [2] H. Li et al., "Nanosheet-structured K–Co– MoS_2 catalyst for the higher alcohol synthesis from syngas: Synthesis and activation," *J. Energy Chem.*, 2018.
- [3] D. Li et al., "The performances of higher alcohol synthesis over nickel modified $\text{K}_2\text{CO}_3/\text{MoS}_2$ catalyst" *Fuel Process. Technol.*, vol. 88, no. 2, pp. 125–127, 2007.
- [4] S. Liu, H. Zhou, Q. Song, and Z. Ma, "Synthesis of higher alcohols from CO_2 hydrogenation over Mo–Co–K sulfide-based catalysts" *J. Taiwan Inst. Chem. Eng.*, vol. 76, pp. 18–26, 2017.