Revealing the effect of Pd on Co-based catalysts in dry and bi-reforming of methane

Kuralay T. TILEGEN[1, 2], Sholpan S. ITKULOVA[*1,2], Yerzhan A. BOLEUBAYEV[1], Aidana K. AITZHANOVA[1], Makpal A. ZHUMASH[1]

[1]D.V. Sokolsky Institute of Fuel, Catalysis, and Electrochemistry, 142, Kunaev str., Almaty, 050010, Kazakhstan
[2]Kazakh British Technical University, 59, Tole bi str., Almaty, 050000, Kazakhstan
* s.itkulova@kbtu.kz, sholpan.itkulova@gmail.com

Significance and Relevance
The modification of Co-based catalysts with a small amount of Pd (0.05-0.1 wt. %) significantly improves the performance of catalysts in dry and bi-reforming of methane (DRM, BRM) in terms of high activity and stability. The conversion degree of feed gases (CH_4, CO_2) varied within 61-99% for DRM and BRM depending on temperature, feed composition, amount of Pd dopant, and method of preparation. The addition of water to feedstock for DRM increases the methane conversion and the H_2/CO ratio in produced syngas.

Preferred and 2nd choice for the topic: …………………….
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The dry and bi-reforming of methane can be considered as a promising technology to realize a low-carbon economy by utilizing greenhouse gases (CH_4, CO_2) and directly generating synthesis gas with a balanced ratio of H2 and CO for high-value chemicals. The biggest stumbling blocks for the large-scale industrial application of these processes are the catalysts' coke formation and stability problems. Adding noble metals as promoters to the catalysts substantially increases the catalyst's resistance to carbon deposition and their durability without loss in activity[1, 2]. This work's main objective is to study Pd's promotional effects on Co-based catalysts with a small content of Pd during dry and bi-reforming of methane.

Materials and Methods

The bimetallic Co-Pd catalysts were prepared by wet co-impregnation and sol-gel methods. The alumina was co-impregnated with Co and Pd-based precursors. For the preparation of catalysts by sol-gel (modified Pechini method), citric acid was used as a gelling agent. The performance of catalysts was studied in DRM and BRM at an equimolar feed ratio of $CH_4:CO_2$. The 5%Co-Pd/Al_2O_3 catalysts were characterized by XRD analysis, TPR-H_2, SEM, TEM, and BET.

Results and Discussion

Since DRM is a highly endothermic process the effect of temperature is significant. As shown in Figure 1, increasing the temperature leads to higher conversion degree of methane and greater product yields, exceeding 92% and 14 µmol/(g·s), respectively. When 20 vol.% steam is introduced to the DRM process using a 5%(Co-Pd(99:1))/Al_2O_3 catalyst, the H_2/CO ratio increases from 1.01 to 1.34. Furthermore, this yields substantial amounts of hydrogen and carbon monoxide. This indicates that varying the steam volume in the feed allows the production of synthesis gas with desirable ratios of H_2/CO, making it suitable for further applications, such as Fischer-Tropsch synthesis. The bimetallic Co-Pd catalysts demonstrate exceptional effectiveness, largely due to the synergistic interactions between cobalt and palladium, which enhance the dispersion and reducibility of cobalt. Even minimal quantities of palladium (ranging from 0.05-0.1 wt. %) significantly influence cobalt's performance, maintaining high activity and selectivity over a long time, which confirmed by stability test for 100 hours.

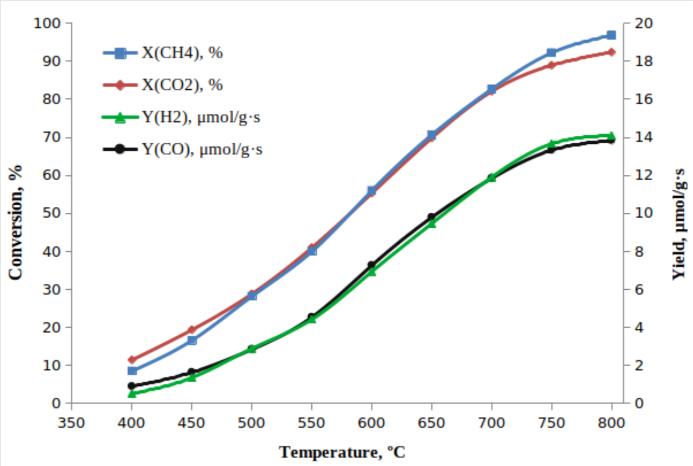

Figure 1 The dependence of reactant's conversion (CH_4, CO_2) and yield of products (H_2, CO) on temperature in DRM over 5%(Co-Pd(99:1))/Al_2O_3 at CH_4:CO_2(1:1), P=1 atm, GHSV=1000h^{-1}

References

1. W. Jang, J. Shim, H. Kim, S. Yoo, H. Roh, *Catalysis Today* **2019**, *324*, 15–26.
2. S. Bhattar, Md. Abedin, S. Kanitkar, J. Spivey, *Catalysis Today* **2021**, *365*, 2–23.

Acknowledgements

The authors wish to thank the Ministry of Education and Science of the Republic of Kazakhstan for funding this research (Grant No AP19679439).