Dry reforming of methane over Ni-Al catalysts prepared by different methods

Alua Manabayeva[1]*, Svetlana Tungatarova[1,2], Tolkyn Baizhumanova[1,2], Dmitry Murzin[3], Dinmukhamed Shoganbek[2]

1 D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan; 2 Al-Farabi Kazakh National University, Almaty, Kazakhstan; 3 Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Turku/Åbo, Finland
*Corresponding author:manabaeva_2018@mail.ru

Highlights

- The surface areas of Ni/α-Al_2O_3 and 15Ni-35Al are low.
- $NiAl_2O_4$ was found only in 15Ni-35Al.
- Presence of $NiAl_2O_4$heighten the catalytic activity of 15Ni-35Al.
- Compared to Ni/α-Al_2O_3catalyst 15Ni-35Al catalyst exhibited better catalytic performance.

1. Introduction

There is growing interest in finding other applications of raw biogas, for example, its use as a feedstock for the production of alternative, sustainable and ecofriendly biofuels, as well as valuable chemicals of industrial importance. Synthesis gas ($CO+H_2$) is produced through dry reforming of methane (DRM), which has been widely proposed in the literature due to the direct use of both main components of raw biogas (CH_4 and CO_2) [1]. The advancement of catalyst for DRM is directed to the employment of transition metals (Ni) based catalysts. It has been discovered that Ni-based catalysts display very good catalytic effectiveness. But they often tend to deactivation by agglomeration of metal particles and carbon alluvium [2]. The application of appropriate support can substantially heighten the catalytic activity and reduce carbon accumulation of catalysts. In the current work Ni-Al catalysts were prepared by solution combustion synthesis and wet impregnation. Solution combustion synthesis is known for its simplicity, cost-effectiveness, and the ability to produce catalysts with unique properties due to the rapid and controlled nature of the reaction. The other method is wet impregnation, which offers control over the metal loading on the support and allows for the incorporation of multiple metals, providing flexibility in tailoring the catalyst composition. This method is valued for its versatility and ability to produce catalysts with well-defined structures and controlled metal dispersion on the support [3].

2. Methods

The catalyst was prepared by solution combustion synthesis. The necessary amounts of $Ni(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$ and urea, were placed in a thermostable beaker and completely dissolved in 30 mL of deionized water, which was heated beforehand to 80 °C. The beaker containing the solution was placed in a muffle furnace preheated to 500 °C. The combustion of the solution occurred within 10 – 15 minutes. Thereafter, the beaker was cooled to room temperature.

A monometallic Ni/α-Al_2O_3 catalyst was prepared by impregnation to compare its performance with the catalysts synthesized by SCS. The α-Al_2O_3support with the grain size of 0.04-0.08 mm was obtained by calcination of γ-Al_2O_3 in the furnace at 1150 °C for 2 hours. Thereafter, a certain amount of $Ni(NO_3)_2·6H_2O$ was dissolved in water and mixed with α-Al_2O_3, followed by drying at 250 °C for 1.5 hand calcination at 650 °C for 3 h. The loading amount of Ni was fixed at 12 wt.%.

Catalytic performance was conducted in fixed-bed quartz tubular reactor.The gas mixture with the gas ratio of CH_4: CO_2: Ar equal to 1: 1: 1 (vol.) was used in DRM. The total flow rate of gases was 100 mL/min corresponding to gas hourly space velocity (GHSV) of 3000 h^{-1}.Prepared and spent catalysts were characterized by XRD, BET.

3. Results and discussion

Four catalysts were tested in DRM for 10 h stability. The results are depicted in Figure 1. Ni-Al catalysts synthesized by two different methods displayed almost same methane conversion and CO yield. However, CO_2 conversion of 15Ni-35Al was higher than that of 12 wt.% Ni/α-Al_2O_3. In addition, H_2 of the former catalyst was therefore greater. For 15Ni-35Al and 12 wt.% Ni/α-Al_2O_3 catalysts deactivation rates were 0.13 and 0.02, respectively, showing that Ni-Al catalyst prepared by wet impregnation underwent less coking during 10 h stability examination.For all catalysts H_2/CO ratio was equal or close to unity, indicating possible occurrence of RWGS reaction, especially for 15Ni-35Al.
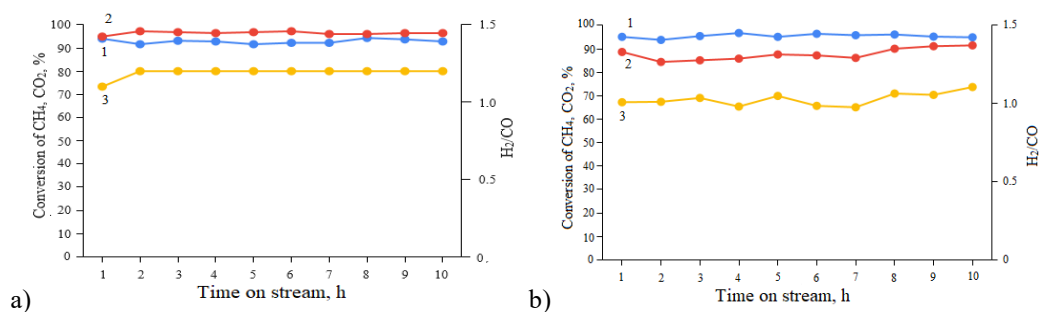

Figure 1. Long-term time-on-stream performance of the a) 15Ni-35Al and b) 12 wt.% Ni/α-Al_2O_3 catalysts in DRM at 850 °C. Notation: 1 – CH_4, 2 – CO_2, 3 – H_2/CO

The yield of hydrogen for 15Ni-35Al was higher than for 12 wt.% Ni/α-Al_2O_3. Moreover, after 10 h the values of parameters increased, and for 15Ni-35Al methane conversion and hydrogen yield were greater. Compared to 15Ni-35Al catalyst in 12 wt.% Ni/α-Al_2O_3catalyst spinel was not identified. In case of the former catalyst spinel phase heighten stability. The surface area of 15Ni-35Al and 12 wt.% Ni/α-Al_2O_3 catalysts are 12 m^2/g and 15 m^2/g, respectively. Moreover, the surface area of catalyst obtained from solution combustion synthesis is lower because it is distinguishing feature related to materials of this type, making it more active in DRM.

4. Conclusions

In this exploration of catalysts for the DRM, the comparative analysis has provided valuable insights into their stability and activity. Notably, the catalyst composition of 15Ni-35Al has demonstrated superior performance. This enhanced stability and activity can be attributed to the presence of the nickel aluminate spinel phase and a lower surface area, suggesting a favorable synergy between composition and structural characteristics. The distinct advantages of 15Ni-35Al, marked by its consistent and robust performance, position it as a promising candidate for further investigations and practical applications in DRM. While the 12 wt.% Ni/α-Al_2O_3 catalyst also exhibited commendable performance, with its own set of strengths, such as good activity, there were observed fluctuations and a decrease in activity over time. These nuances indicate the sensitivity of catalysts to variations in composition and structure, emphasizing the importance of understanding the intricate interplay between these factors.

References

[1] Q.Zhang,M. Akri,Y. Yang,B. Qiao, Cell Rep. Phys. Sci.4(2023) 101310.
[2] S.A. Al-Zahrani, A.S. Al-Fatesh, M.-N. Kaydouh, A. Al Otaibi, F. Francesco, A.H. Fakeeha, N. El Hassan, Alex. Eng.J. 74 (2023) 371-386.
[3] S. Ali, M.M. Khader, M.J. Almarri, A.G. Abdelmoneim, Catal. Tod. 343 (2020) 26-37.