Methane Reforming over Ni Catalysts – Understanding the Impact of Preparation Methods and Oxide Supports

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Highlights

- Ni supported on SiO_2, CeO_2, and La_2O_3 were evaluated for methane reforming reaction
- Preparation methods affect the performance greatly, with combustion methods showing high activity.
- Reducible of support e.g. CeO_2 and La_2O_3 shows better performance compared to non-reducible SiO_2.

1. Introduction

The growing global demand for energy, coupled with the rapid depletion of fossil fuel reserves, has intensified the pursuit of sustainable alternative energy sources. Among promising strategies to address these challenges is dry reforming of methane (DRM), a process that converts methane and carbon dioxide, two major greenhouse gases, into syngas. In this study, we examine how synthesis conditions and catalyst support characteristics influence the performance of nickel-based catalysts in DRM. Over recent decades, significant research has focused on greenhouse gas mitigation, with DRM emerging as an environmentally attractive route for converting CO_2 and CH_4 into valuable synthesis gas for the production of liquid fuels and a range of industrial chemicals. Despite its environmental and economic advantages, DRM has yet to achieve large-scale commercial deployment due to severe catalyst deactivation caused by high-temperature sintering and carbon deposition. Carbon formation is primarily driven by side reactions such as methane decomposition ($CH_4 \rightarrow C + 2H_2$) and the Boudouard reaction ($2CO \rightarrow CO_2 + C$). In this work, we introduce a novel catalyst synthesis approach to enhance the stability of established DRM catalysts. The findings demonstrate notable improvements in catalytic performance and resistance to deactivation under laboratory-scale conditions, highlighting the potential of this method for future DRM applications. Here, we have investigated the impact of the synthesis method and the support nature on DRM performance. Additionally, the catalytic activities were further evaluated for methane partial oxidation and methane tri-reforming reactions.

2. Methods

The catalysts were synthesized using wet impregnation, co-precipitation, combustion synthesis [1–4], and physical mixing methods to evaluate the effect of catalyst preparation technique on dry reforming performance. In the physically mixed method, the precursor metal-nitrate is dissolved in water and combusted in the presence of glycine, and the resulting powders are mixed with the support. In contrast, in the solution combustion synthesis, the precursors are dissolved in support-dispersed water and combusted to get the supported catalyst. The catalysts are then calcined at 600 °C for 1 h and used for MDR stability tests at 700 °C, where a CO_2:CH_4 ratio of 1:1 is maintained in a packed-bed reactor containing <0.5g of pelletized catalyst.

3. Results and discussion

A selected result on the performance of silica-supported NiCo catalyst is provided in Figure 1. This study demonstrates the impact of catalyst preparation on activity-stability relationships. The 10 wt.% NiCo/SiO_2-PM catalyst exhibits a moderate decline in performance over 20 h time-on-stream (TOS), with CH_4 conversion decreasing from 48% to 44% and CO_2 conversion falling from 61% to 56% (Fig. 1). In contrast, the combustion-synthesized (CM) catalyst demonstrates significantly superior stability and activity, maintaining exceptionally high conversion levels over 70 h TOS. For this catalyst, CH_4

conversion decreases only from 93% to 87%, while CO_2 conversion drops from 96% to 90%. Comprehensive characterization using SEM, TEM, NAP-XPS, and XAS (XANES and EXAFS; data not shown here) reveals a pronounced metal–support interaction in the CM catalyst [5,6]. NAP-XAS measurements, conducted under reactive gas environments, albeit at lower pressures than actual DRM conditions, further elucidate changes in surface composition and metal oxidation states, providing insight into the enhanced stability and resistance to deactivation observed for the CM catalyst. Results include CeO2 and La2O3 supports, which are planned to be presented during the conference.

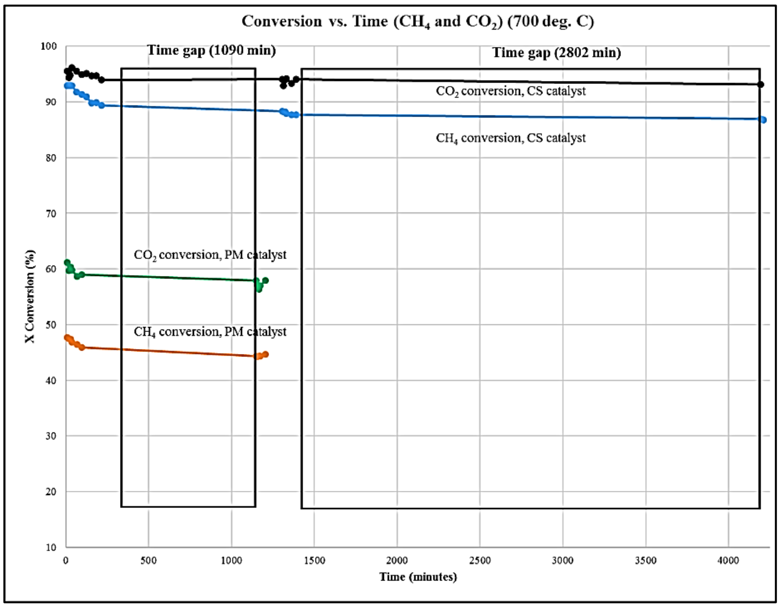

Figure 1. MDR stability tests performed on 10 wt.% NiCo/SiO_2 catalysts prepared by PM (physical mixing method) and CS (combustion synthesis method), at 700 °C

4. Conclusions

The results of this work show the impact of preparation methods and support nature on catalytic performance in methane reforming. Combustion techniques were found to be more favorable for promoting stronger metal-support interactions, whereas reducible supports, such as CeO2, were more resistant to coking and exhibited high CO2 and CH4 conversion. These results, along with the relevant characterization of catalysts, are planned to be presented in detail during the conference. Overall, this work contributes to the scientific effort to develop coke-resistant, stable catalysts for the dry reforming of methane to convert two predominant greenhouse gases (CH4 and CO2) into valuable products.

References

[1] A Kumar, EE Wolf, AS Mukasyan, AIChE J 2011;57:3473–3479.
[2] A Kumar, EE Wolf, AS Mukasyan, AIChE J 2011;57:2207-2214.
[3] A Kumar, EE Wolf, AS Mukasyan, Ind. Eng. Chem. Res. 2010, 49, 11001–11008
[4] A Ashok, A Kumar, J Ponraj, SA Mansour, F Tarlochan, Appl Catal B Environ 2019;254:300-311.
[5] AAA Mohammed, MAHS Saad, A Kumar, MJ Al-Marri, Greenh Gases Sci Technol 2020;10:715–24.
[6] A Kumar, AAA Mohammed, MAHS Saad, MJ Al-Marri., Int J Energy Res 2022; 46: 441– 451.

Keywords
Combustion synthesis of catalysts; Methane dry reforming, Reducible supports; Greenhouse gases conversion.

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