

Optimizing Ni-Based Catalysts for Dry Reforming of Methane: Impact of MgO Supports Doped with Fe, Cu, and Ce

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Significance and Relevance

This study explores the improvement of Ni-based catalysts supported on MgO and doped with Fe, Cu and Ce, focusing on the improvement of stability and catalytic efficiency in the dry reforming of methane (DRM). Comprehensive chemical and physical characterizations reveal a strong relationship between catalyst structural properties, activity and carbon deposition resistance, providing valuable insights to optimize syngas production and promote DRM as a sustainable fuel generation process.

Introduction and Motivations

Dry reforming of methane is an effective catalytic process for converting two significant greenhouse gases, methane (CH₄) and carbon dioxide (CO₂), into syngas (a mixture of CO and H₂), which serves as a valuable feedstock for synthetic fuels. This process not only offers a pathway for sustainable energy production but also addresses environmental challenges by mitigating greenhouse gas emissions.¹ Ni-based catalysts are commonly used for DRM due to their cost-effectiveness and high activity in CH₄ activation; however, their long-term stability is compromised by issues like carbon deposition, sintering, and deactivation at high temperatures. Improving the structural and chemical properties of the support can enhance the catalyst stability and reduce coke formation.^{2,3} In particular, this study investigates the role of magnesium oxide and MgO doped with metals such as Fe, Cu, and Ce in promoting catalyst durability and efficiency, with the goal of improving the applicability of DRM for sustainable syngas production (Figure 1).



Figure 1. Schematic representation of the DRM reaction carried out over Nickel catalysts supported on MgO and MgO doped with Fe, Cu and Ce.

Materials and Methods

Ni catalysts were supported on MgO and MgO doped with Fe, Cu, and Ce. The supports were synthesized via hydrothermal precipitation and then calcined at 600 °C. Ni was deposited onto the prepared magnesium oxide supports through wetness impregnation, followed by calcination at 600 °C. Before the DRM reaction, an in-situ reduction was performed at 800 °C for 1 hour under an H₂/Ar atmosphere. DRM reaction was carried out in a fixed-bed reactor by feeding a gas mixture of CH₄ and CO₂ (ratio 1:1). Catalytic performance in DRM was evaluated, and post-reaction characterization, including XRD and TGA-DSC, was carried out to investigate structural stability and carbon deposition behavior.



Results and Discussion

The influence of dopants on the reduction properties, structural phase composition and on the catalytic activity was investigated. Comparison of the catalytic performance of Ni-MgO catalysts, shown in Figure 2, with CH₄ and CO₂ conversion curves plotted against temperature, demonstrates the activity of these catalysts in DRM. All samples display strong overall catalytic performance. In the temperature range of 450–700 °C, the conversion of the reactants follows the trend Ni-FeMgO < Ni-CuMgO < Ni-CeMgO. The lower conversion observed with the Fe-doped catalyst is probably due to side reactions, such as the reverse water-gas shift, for which Fe-based catalysts are highly active. Above 700 °C, CH₄ and CO₂ conversions reach approximately 90% and 100%, respectively, for the Ni-MgO catalysts.

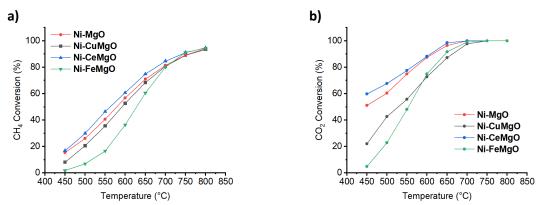


Figure 2. DRM results of Ni-MgO catalysts as a function a) CH_4 and b) CO_2 Conversion vs Temperature at 450–800 °C.

Characterization of the catalysts using XRD and TGA-DSC after the DRM reaction provided insights into structural stability, coke formation, and decomposition temperatures. These results offer valuable guidelines for optimizing Ni-based catalysts for sustainable syngas production, contributing to the broader application of DRM in environmental and energy solutions.

References

- 1. X. Cai, Y.H. Hu, Energy Sci Eng. 2019, 7, 4–29.
- 2. V. La Parola, L. F. Liotta, G. Pantaleo, M. L. Testa, A. M. Venezia, *Appl. Catal.A: Gen.* **2022**, *642*, 118704.
- 3. Huang, Y. Yan, S. Saqline, W. Liu, B. Liu, Appl. Catal. B: Environ. 2020, 275, 119109A.

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