Oxidative Sintering Behavior of Ni-Based Catalysts exemplified by CO_2 Methanation Reaction

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Introduction

The extensive combustion of fossil fuels has resulted in a substantial increase in CO_2 emissions, intensifying the greenhouse effect and accelerating climate change. In this context, CO_2 hydrogenation has emerged as a highly promising strategy for both mitigating emissions and enabling carbon recycling within a sustainable energy future. When combined with hydrogen produced from renewable energy sources (e.g., wind and solar), the Sabatier reaction ($CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$) provides an attractive pathway for renewable energy storage and transport in the form of methane, under the widely recognized Power-to-Gas (P2G) concept. The reaction is an exothermic process thermodynamically favored at high pressures and relatively low temperatures and can be described as the sequential combination of the Reverse Water–Gas Shift reaction followed by CO methanation. Efficient implementation of this process requires the development of highly active, selective, and thermally stable supported catalysts. Both noble metals (Ru, Rh, Pt, Pd, Ir) and non-precious metals (Ni, Fe, Co) have been investigated as active phases, with Ni-based catalysts attracting particular interest due to their low cost and natural abundance combined with high activity.

In the present work, the thermocatalytic CO_2 hydrogenation is investigated over Ni catalysts supported on ceria nanorods (CeO_2-NRs), with emphasis on optimizing catalytic activity, long-term stability, and resistance to oxidative thermal aging in comparison with conventional Ni/Al_2O_3 systems. The unique physicochemical properties of CeO_2-NRs —such as high oxygen storage capacity (OSC), enhanced lattice oxygen mobility, abundant oxygen vacancies, and strong metal–support interactions— render it a highly promising support for improving catalyst durability and mitigating sintering phenomena under demanding reaction conditions.

Materials and Methods

A hydrothermal synthesis method was applied to prepare nanorod-shaped CeO_2 supports (CeO_2-NRs), according to our previous study [1]. 10 wt.% Ni was deposited onto the CeO_2-NRs support via wet impregnation [1]. A reference 10 wt.% Ni/γ-Al_2O_3 catalyst was also prepared for comparison purposes. Evaluation of these Ni/CeO_2-NRs and Ni/γ-Al_2O_3 catalysts subjected to the same oxidative aging protocol, was exemplified by the CO_2 hydrogenation reaction in the temperature range of 100–600 °C. The reaction was performed under a feed mixture consisting of 20% H_2 and 5% CO_2 balanced with Ar, at a total flow rate of ~20 $cm^3\ min^{-1}$.The detailed experimental procedure for the Sabatier reaction, as well as the thermal sintering protocols applied to the Ni catalysts, are presented schematically in Figure 1.

A variety of characterization techniques, including X-ray diffraction (XRD), nitrogen physisorption (BET), scanning electron microscopy (SEM), elemental analysis and mapping by energy-dispersive X-ray spectroscopy (EDS), H_2 temperature-programmed reduction (H_2-TPR), and H_2 chemisorption, were employed. The physicochemical properties and thermal sintering behavior of the nanostructured materials were thoroughly investigated following the application of well-defined aging protocols.

Results and Discussion

It clearly emerges that the nature of the support plays a crucial role in determining the oxidative thermal sintering behavior of the metal nanoparticles and consequently their behavior on Sabatier reaction.

Specifically, by employing two supports with distinctly different oxygen storage capacities (OSCs), namely γ-Al_2O_3 and CeO_2-NRs, the following conclusions can be drawn:
(a) The Ni/Al_2O_3 catalyst exhibited a significant growth in the size of the metal nanoparticle after oxidative thermal aging, indicating pronounced sintering phenomena of the active phase unable to be restrained by metal-support interactions.
(b) In contrast, the Ni/CeO_2-NRs catalyst demonstrated remarkable resistance to sintering. Its structural and morphological characteristics remained almost unchanged even after 10 hours of oxidative thermal aging, evidencing strong anti-sintering behavior of the Ni particles via enhanced metal-support interactions.
The fresh Ni/CeO_2-NRs catalyst exhibits superior catalytic performance in Sabatier reaction compared to Ni/γ-Al_2O_3. It shows ignition temperature $T_{ign} \approx 200$ °C and reaches a maximum CO_2 conversion of approximately 92% at 350 °C, while maintaining nearly 100% CH_4 selectivity up to 450 °C. Notably, even after 10 h under oxidative sintering conditions Ni/CeO_2-NRs demonstrates only a ΔT_{50}=+10°C shift in the temperature corresponding to 50% CO_2 conversion (T_{50}), confirming its good resistance to sintering. Time-on-stream (TOS) experiments further verified the good stability of the Ni/CeO_2-NRs catalyst, during three consecutive oxidative aging cycles. In contrast, the Sabatier reaction activity of the Ni/γ-Al_2O_3 catalyst degrades significantly after 10 h of oxidative sintering (ΔT_{50}=+60°C).

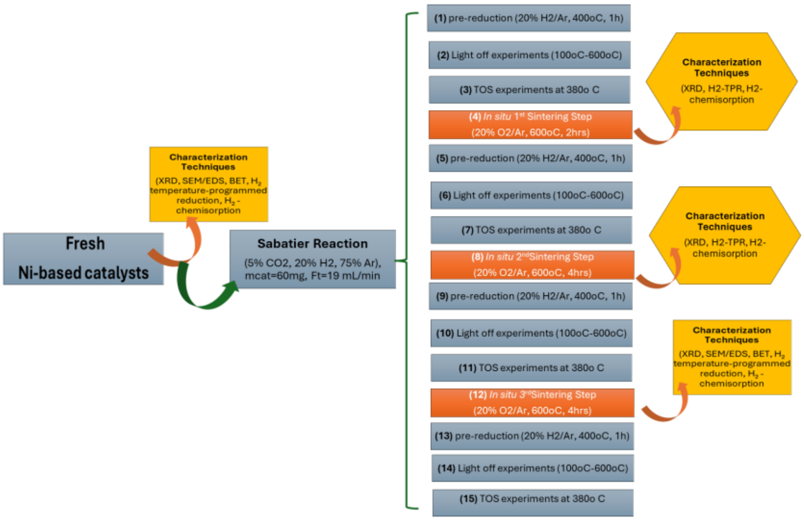

Figure 1. *Experimental procedure of Sabatier reaction on Ni-based catalysts*

Conclusions

Supports play a significant role in governing both catalytic activity and stability of the metal particles against sintering. The enhanced metal–support interactions and structural robustness of the Ni/CeO_2-NRs system effectively suppress sintering phenomena, leading to superior activity and durability in Sabatier reaction even after repeated oxidative aging cycles compared to the Ni/γ-Al_2O_3 catalyst. The results highlight nanostructured ceria supports as a highly promising strategy for the design of sinter-resistant and high-performance CO_2 methanation catalysts.

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References

[1] Nikolaraki, E., Drosou, C. Mytafides, C.K., Papazisi, K.M., Balomenou, S., Tsiplakides, D., Froudas, K.G., Trikalitis, P.N., Panagiotopoulou, P., Gournis, D.P., Yentekakis, I.V., 2025. Shape-controlled CeO_2 and GDC nanostructured supports turn iridium to an efficient and highly selective CO_2 methanation catalyst. J. Environ. Chem. Eng., 13, Issue 5,117434, https://doi.org/10.1016/j.jece.2025.117434.