

Catalytic Performance of Ni-based Catalysts Supported on γ -Al₂O₃-ZrO₂-TiO₂-CeO₂ Composite Oxide for CO₂ Methanation

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Introduction

Significant reductions in carbon dioxide (CO₂) emissions and the development of nonfossil fuel energy sources are critical to minimize the effects of CO₂ as a greenhouse gas in the atmosphere and reduce our dependence on nonrenewable energy sources, most notably crude oil.

Among the main challenges for the future electrical power supply from renewable energies such as solar and wind is the long term storage and transportation from remote areas. The Power-to-Gas (PtG) technology is a promising option to reduce the energy loss using the hydrogenation of CO₂. The hydrogenation of CO₂ into hydrocarbons have been the most investigated reactions to obtain fuels [1]. Among several hydrogenation reactions, methanation of CO₂ following the Sabatier reaction is the most advantageous one regarding thermodynamics.

Nickel based catalysts are the most studied materials for Sabatier reaction, because of their high activity and low price, but metal sintering at reaction conditions diminishes their industrial viability. The type of support used for heterogeneous catalysts is an important factor to consider on solving such problems [2]. In this work, we focused our attention on the selection of supports for Ni-based catalysts with low Ni content.

Experimental Method

Composite oxide supported Ni-based catalysts were prepared by wet impregnation technique and applied for the methanation of carbon dioxide. The composite oxide supports were prepared by impregnation-precipitation method using a commercial γ -Al₂O₃ powder as a host with variation of the percentage (5-15%) of loading ZrO₂, TiO₂ and CeO₂ promoters from their respective salt precursors. NH₄OH was used as precipitating agent.

The as prepared catalysts were characterized by AAS, XRD, BET and H₂-TPR. Catalytic activities of the newly synthesized catalysts (10 mg) were investigated towards hydrogenation of CO₂ at atmospheric pressure using a fixed bed reactor.

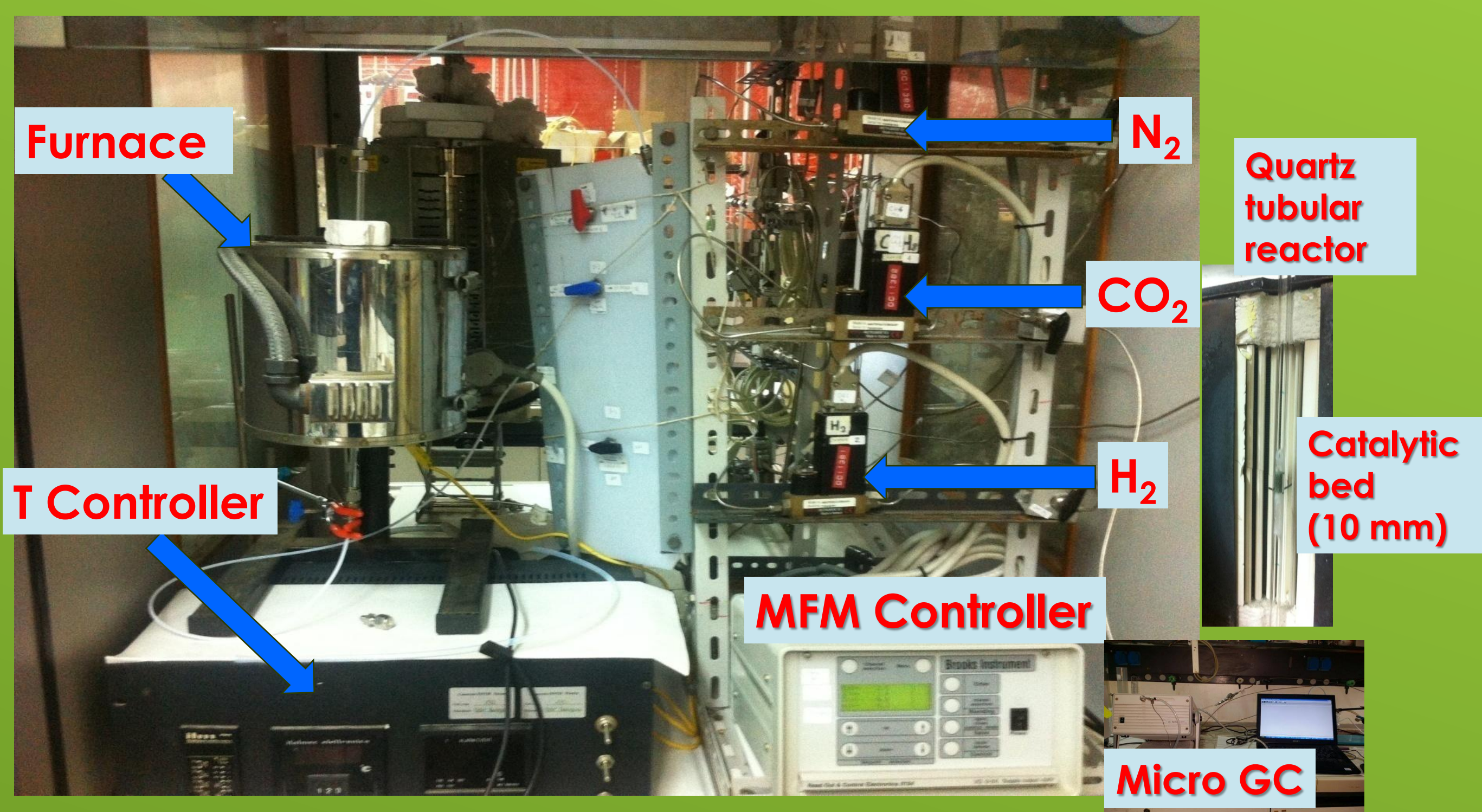


Figure 1. Laboratory scale fixed bed micro reactor.

Results and Discussion

A significant difference in XRD patterns (Fig 2) of the γ -Al₂O₃ support and the composites was observed that assures the successful loading of the promoters. Comparing the average crystallite size of NiO, calculated from measured values using the Scherrer formula ($d = k\lambda/\beta\cos\theta$) from Ni (220) at 2 theta = 62.8° diffraction peak broadening in Fig. 2 is increasing as the percentage of the loaded oxides increased Ni/C13 catalyst has relatively larger crystalline size.

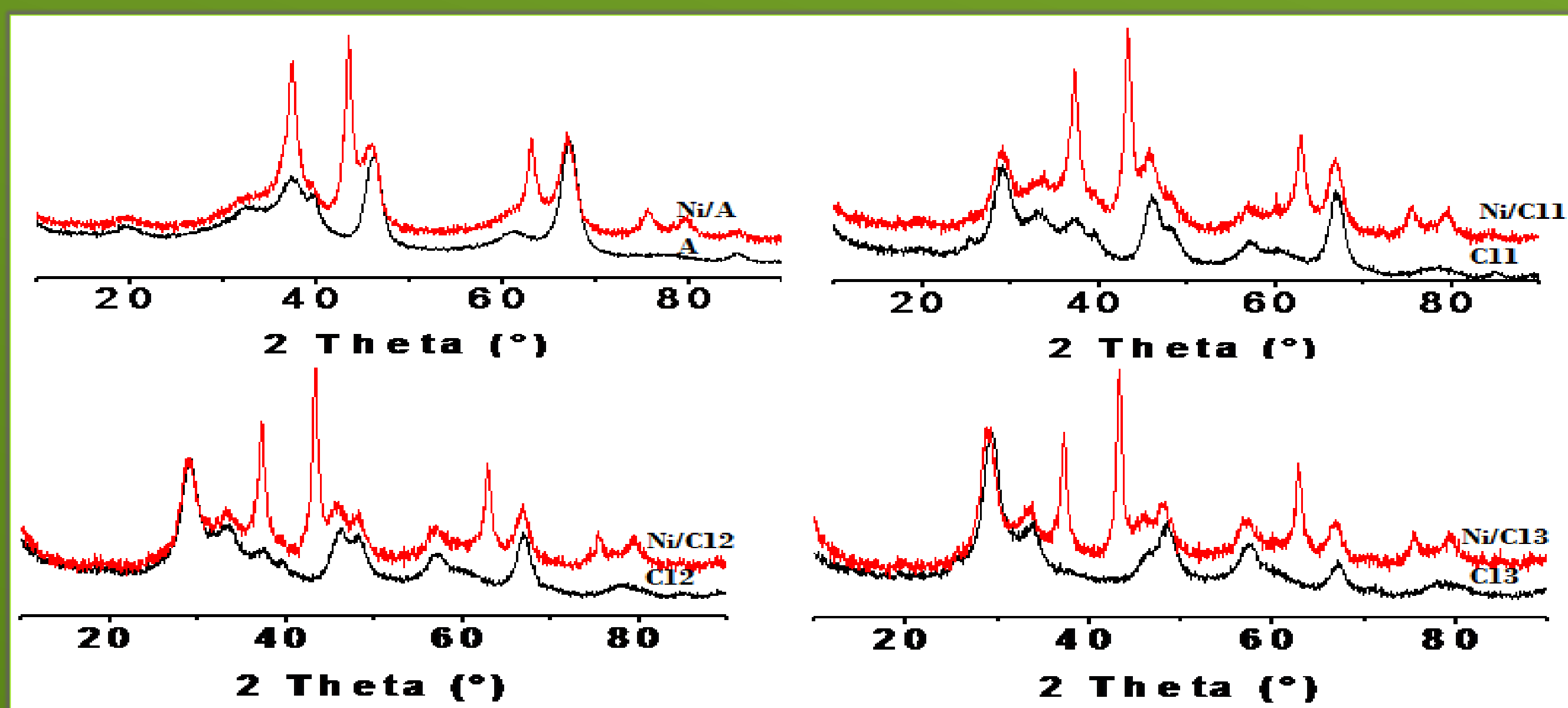


Figure 2. XRD Pattern of supports compared with the Ni/composite supported catalysts.

Table 1. CO Chemisorption and AAS Results.

Catalyst	Nickel dispersion (%) ^a	Nickel surface area (m ² /g-Ni) ^a	Ni (wt. %) ^b
Ni/A	2.33	15.74	15.42
Ni/C11	2.67	17.81	16.55
Ni/C12	2.17	14.50	17.20
Ni/C13	2.38	15.86	16.45

^a Calculated by assuming CO/Ni_{atom} = 1.

^b Determined by AAS analysis.

Conclusions

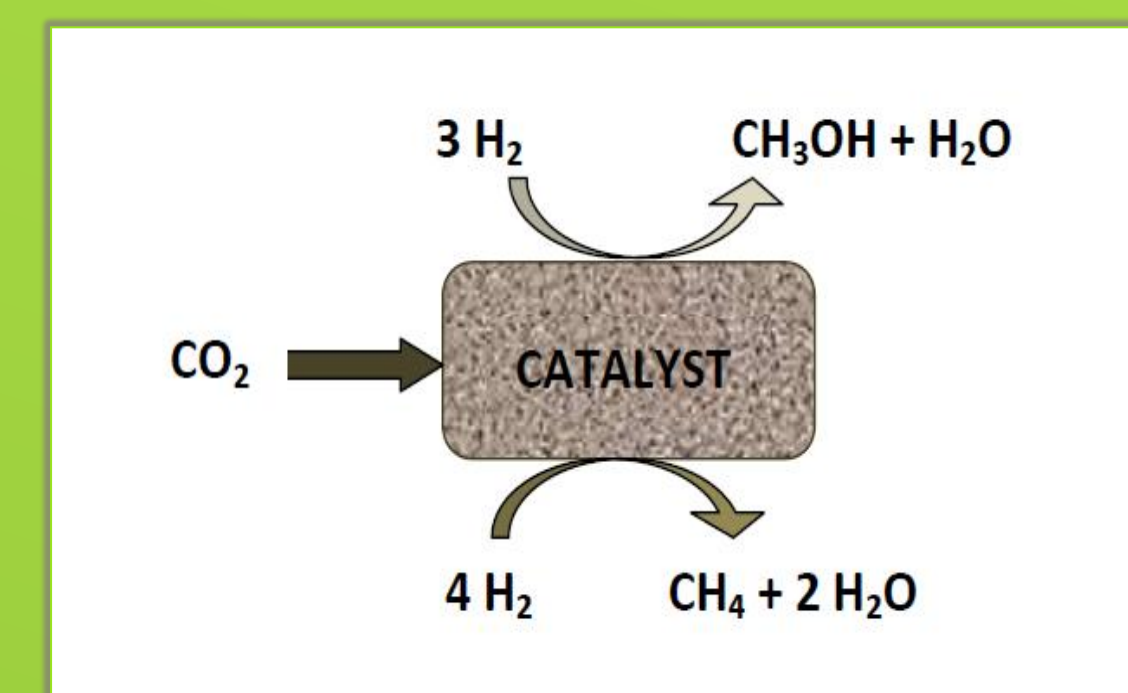
Composite oxide supported Ni-based catalysts were prepared by wet impregnation technique and applied for the methanation of carbon dioxide. Better performance of the composite oxide supported Ni-based catalysts were achieved due to the improvements in reducibility nature of the catalysts which was investigated using H₂-TPR.

Acknowledgements

The authors would like to thank The HELMETH EU project "Integrated High-Temperature ELectrolysis and Methanation for Effective Power to Gas Conversion" and SINCEM grant i.e. a Joint Doctorate program selected under the Erasmus Mundus Action 1 Program (FPA 2013-0037).

References

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- [2] X. Duan, G. Qian, X. Zhou, Z. Sui, D. Chen, W. Yuan. *Appl Catal B Environ.* 101 (2011) 189-196.



According to the H₂-TPR profiles (Fig 3) for all the catalysts, β -peak and γ -peak temperatures shifts downwards for the composite oxide supported Ni-based catalysts, suggesting a weaker interaction between NiO and the composite support.

These results to have more β -type NiO species which is active to the catalytic reaction at the temperature applied for the reduction pretreatment (i.e. 500°C).

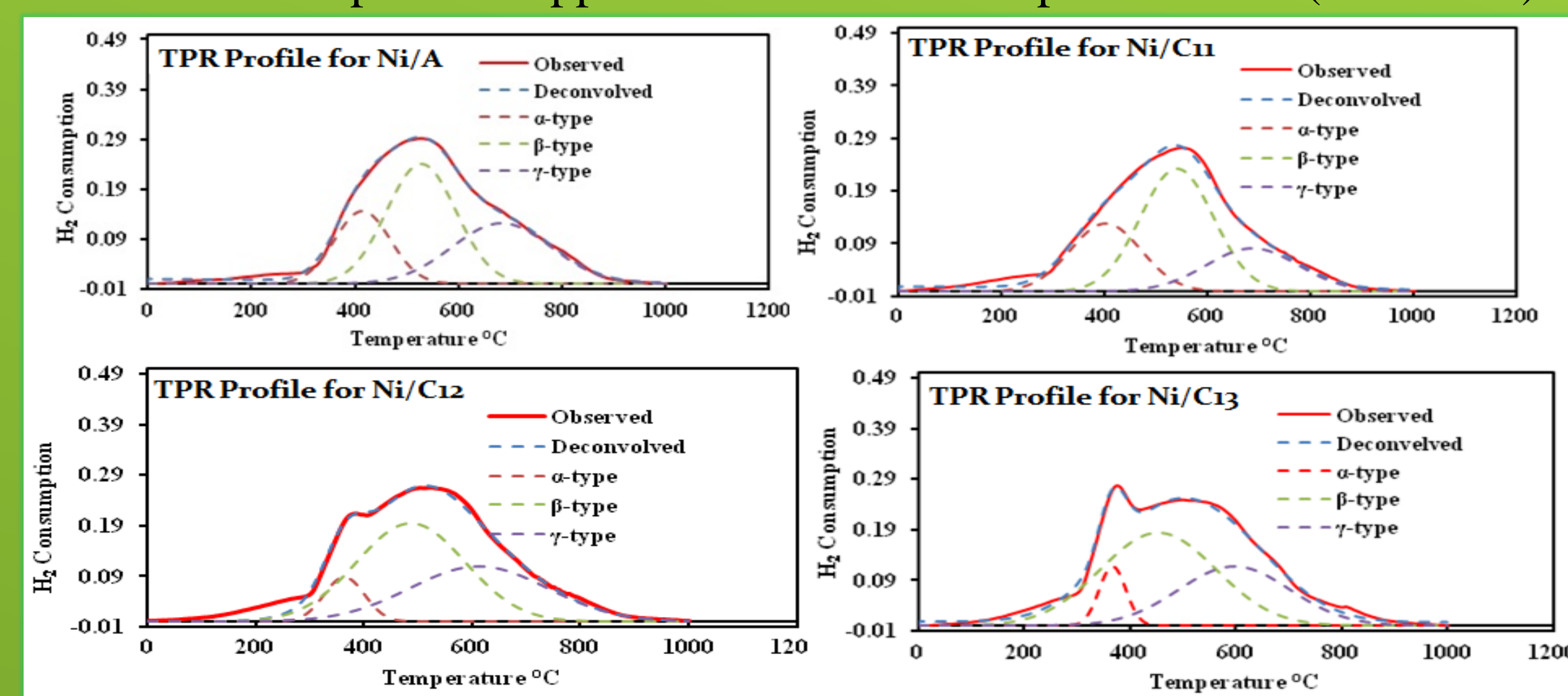


Figure 3. H₂-TPR Profiles of the Ni/composite oxide supported catalysts.

Fig. 4 shows the catalytic activity of the composite oxide supported Ni based catalysts for methane production from hydrogenation of CO₂ obtained at three reaction temperatures. Among the catalysts investigated the Ni/C13 catalyst which has 15% of each loading oxides shows better activity (62.24% conversion of CO₂ to CH₄ at 350°C).

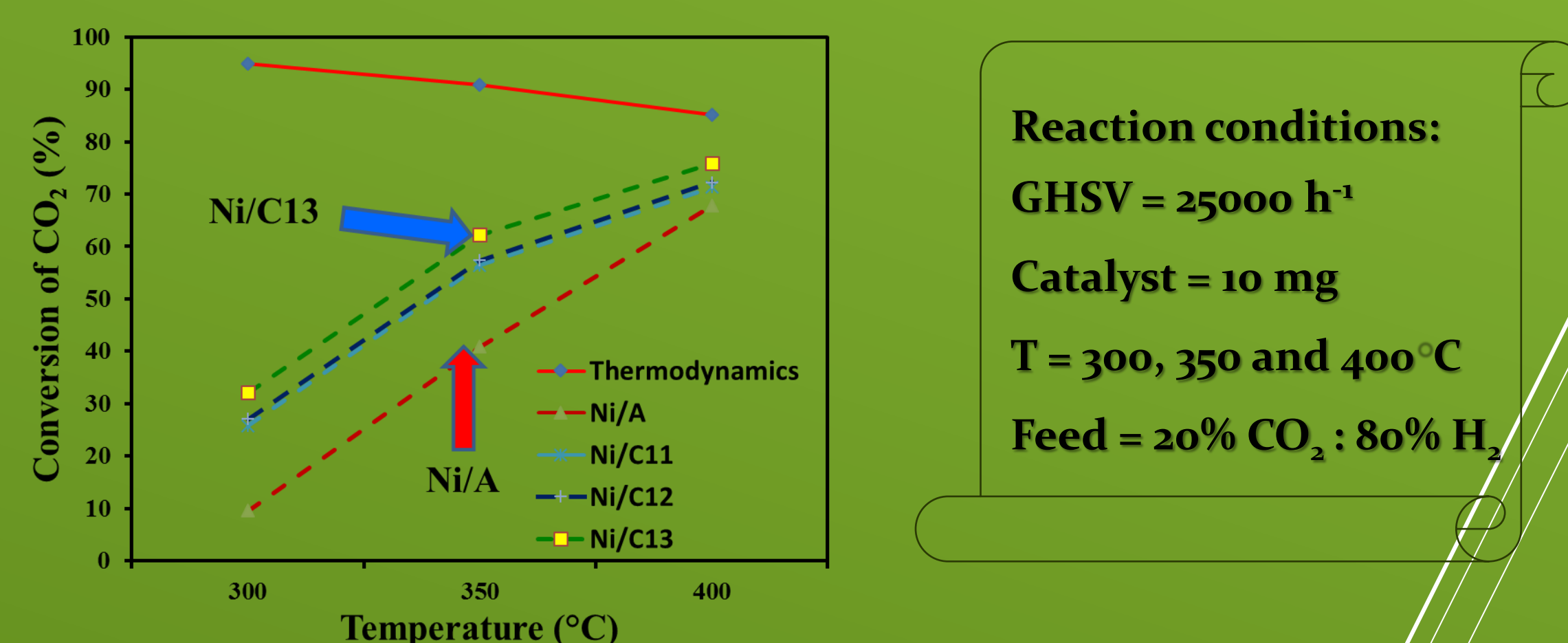


Figure 4. Effect of composite oxide supports on Ni-based catalysts for CO₂ methanation.