

Influence of Ni-Fe load in a bimetallic catalyst supported on Zeolite 13X for CO₂ methanation in a fixed bed reactor

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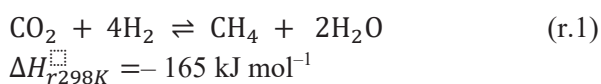
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Abstract

In this work three Ni-Fe catalysts supported on zeolite 13X were tested for CO₂ methanation at different temperatures. The study shows the influence of the active species load on the synthesized catalysts. In addition, the effect of Ni-Fe ratio present on the catalysts was observed.

Introduction

Power to Methane (P2M) technologies have shown their potential of contributing to the energy transition. P2M allows to store green hydrogen from surplus renewable energy into methane, which is a stable and easy to transport energy vector. The hydrogen methanation is conducted by the *Sabatier* reaction (r.1), where H₂ is combined with CO₂ to produce methane. If CO₂ comes from a biogas stream, the process constitutes a biogas upgrading. The resulting methane stream could achieve the normalized standards to be injected into the natural gas network [1].



Sabatier reaction is commonly catalyzed by nickel or ruthenium oxides, however both present important limitations to the methanation process scaleup [2]. Ruthenium is a highly expensive metal and nickel can exhibit coke deactivation during the methanation reaction. Previous studies have shown the potential of combining nickel and iron supported on gamma alumina to avoid nickel deactivation. Meanwhile, the cost of the resulting catalyst is reduced favorizing its industrial application [3].

In this work, the methanation behavior of three Ni-Fe catalyst supported on 13X zeolite has been experimentally analyzed in a fixed-bed reactor. These catalysts were synthesized by impregnation-evaporation in a vacuum rotary evaporator followed

by a calcination at 450-500 °C. That synthesis was performed at TU Delft (The Netherlands) as part of an international collaboration with the Catalysis and Reactor Engineering Group (CREG). The methanation experiments presented in this study relate the total load of active phase in the catalyst (10%^w vs 5%^w) with its effectivity to transform the CO₂ into CH₄. In addition, the influence of the mass ratio Ni:Fe (3:1 and 1:1) was examined at different temperatures by comparison with two catalysts with same total amount of active phase. The catalysts synthesized for both experiment series were: 7.5%^w Ni-2.5%^w Fe, 1.25%^w Ni-3.75%^w Fe and 2.5%^w Ni-2.5%^w Fe. The role of zeolite support is to remove *in situ* the water produced by reaction (r.1), shifting its thermodynamic equilibrium toward products (*Le Châtelier's* principle) [4].

Experimental

Firstly, the effect of diffusional constraints (internal and external) was studied, fixing a volumetric flow of 250 mL(STP)/min and a particle size (100 ≤ d_p ≤ 200 μm), enough to ensure kinetic regime. Experiments were carried out in a fixed bed reactor of approximately 12 cm length and 13 mm inner diameter, at atmospheric pressure. For the reaction experiments the mass of solids introduced in the bed (pre-mixed) was 0.5 g of catalyst and 10g of γ-Al₂O₃ as inert solid, to avoid *hot-spots*. Before starting a methanation experiment, the catalyst was activated at 500 °C for 2 h with a gas flow composition of 50% H₂, 45% Ar and 5% N₂ (by vol.). After the activation stage, the temperature was decreased to experimental conditions. These were 250-400 °C, a flow of 250 mL(STP)/min composed by 10%^v of inert gas and 90%^v reactants with 2:1, 4:1 or 6:1 H₂:CO₂ molar ratios. Concentration in the reactor outlet was monitored with a micro chromatograph (*Agilent 490*).

Influence of the active phase load was tested for stoichiometric conditions (4:1 H₂:CO₂) at the 250-

400 °C temperature interval, obtaining the highest conversion results for 7.5 %^wNi-2.5 %^wFe catalyst (Figure 1). Thus, 7.5 %^wNi-2.5 %^wFe catalyst was selected to study its behavior for over and under stoichiometric ratios (2:1 and 6:1) Figure 2.

Results and Discussion

Temperature showed a positive effect for all the methanation conditions as can be observed in both figures. The optimum catalyst load was found for 7.5 %^wNi-2.5 %^wFe, meanwhile for the same total amount of active phase (Ni+Fe=5%^w) the best performance mass ratio was also 3:1 Ni:Fe (Figure 1).

From the feeding ratio study of Figure 2, adding over-stoichiometric H₂ (6:1) maximizes the CO₂ conversion. The opposite behavior was found for under-stoichiometric H₂ conditions (2:1). Stoichiometric conditions (4:1) presented reasonable compromise of conversion results for both reactants.

Acknowledgments

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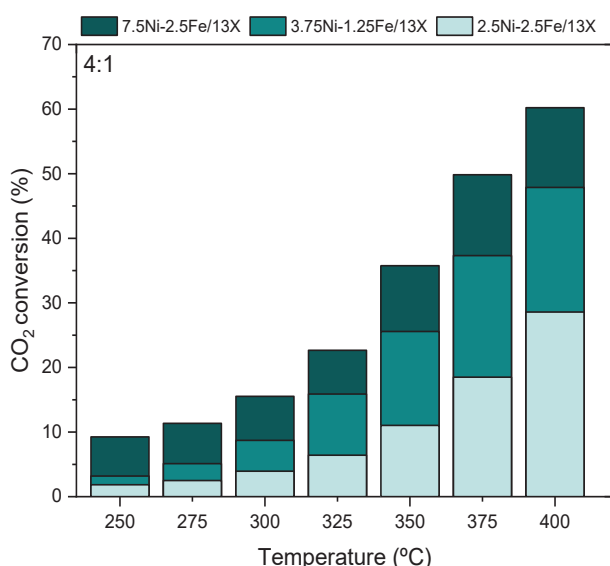


Figure 1. Active phase mass load influence at different temperatures

References

- [1]. DURÁN, P., ARAGÜÉS-ALDEA, P., GONZÁLEZ-PIZARRO, R., MERCADER, V.D., CAZAÑA, F., FRANCÉS, E., PEÑA, J.A. and HERGUIDO, J., 2024. Biogas upgrading through CO₂ methanation in a polytropic - distributed feed fixed bed reactor. *Catalysis Today*. 1 October 2024. Vol. 440, pp. 114849. DOI 10.1016/J.CATTOD.2024.114849.
- [2]. MERCADER, V.D., DURÁN, P., ARAGÜÉS-ALDEA, P., FRANCÉS, E., HERGUIDO, J. and PEÑA, J.A., 2024. Biogas upgrading by intensified methanation (SESaR): Reaction plus water adsorption - desorption cycles with Ni-Fe/Al₂O₃ catalyst and LTA 5A zeolite. *Catalysis Today*. 1 May 2024. Vol. 433, pp. 114667. DOI 10.1016/J.CATTOD.2024.114667.
- [3]. SANZ-MARTÍNEZ, A., DURÁN, P., MERCADER, V.D., FRANCÉS, E., PEÑA, J.A. and HERGUIDO, J., 2022. Biogas Upgrading by CO₂ Methanation with Ni-, Ni-Fe-, and Ru-Based Catalysts. *Catalysts 2022, Vol. 12, Page 1609*. Online. 8 December 2022. Vol. 12, no. 12, pp. 1609. [Accessed 17 February 2023]. DOI 10.3390/CATAL12121609.
- [4]. WEI, L., AZAD, H., HAIJE, W., GRENMAN, H. and DE JONG, W., 2021. Pure methane from CO₂ hydrogenation using a sorption enhanced process with catalyst/zeolite bifunctional materials. *Applied Catalysis B: Environmental*. 15 November 2021. Vol. 297, pp. 120399. DOI 10.1016/J.APCATB.2021.120399.

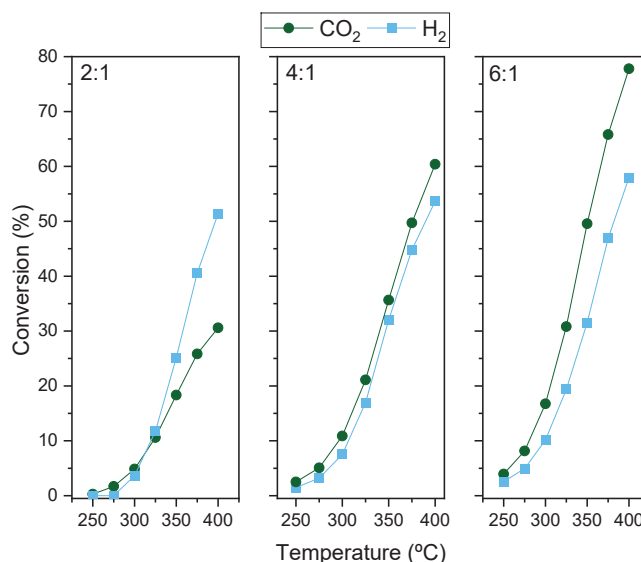


Figure 2. Effect of H₂:CO₂ feeding molar ratio at different temperatures for a catalyst with 7.5%Ni-2.5%Fe/13X