# Mechanical Mixture (MM) Materials for Cyclic CO₂ Power-to-Methane: Filler Influence and Stability

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## Abstract

This work explores the influence of active fillers (zeolites and alumina) in mechanical mixtures (MM) for cyclic CO₂ methanation using Ni-Fe based catalysts. Zeolites promote in situ water removal, enhancing CH₄ yield. The effect on temperature distribution and system stability was evaluated in a fixed-bed reactor under cyclic conditions.

## Introduction

The transition toward sustainable energy systems is a global priority, driven by the urgent need to reduce greenhouse gas emissions—particularly carbon dioxide ($CO_2$) and methane ($CH_4$)—and mitigate climate change. Despite significant progress in renewable energy deployment, especially solar and wind power, the intermittency and variability of these sources continue to hinder their full integration into the energy grid. Consequently, energy storage technologies that can buffer renewable fluctuations and stabilize supply-demand dynamics are critical to enabling deep decarbonization [1]. Power-to-Methane (PtM) is a promising strategy for storing excess renewable energy in the form of synthetic natural gas (SNG), via the *Sabatier* reaction (r.1).

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \text{(r.1)}$$
$$\Delta H_{r,298K} = -165.1 \text{ kJ mol}^{-1}$$
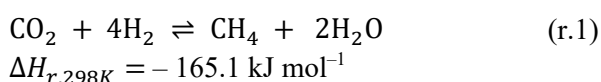
Cyclic CO₂ methanation with in situ adsorption is a potential route for intensifying PtM [2]. However, Dual-Function Materials (DFMs), which combine catalytic and adsorption sites in one solid, suffer from limitations such as site competition and progressive deactivation [3], especially with alkaline adsorbents. Mechanical Mixture (MM) systems could avoid this issue by physically separating the catalyst and adsorbent, allowing independent optimization of each function.

In this work, it is proposed to include a third solid ("filler"), which might provide an additional function to the MMs and at the same time improve the temperature distribution of the fixed bed, counteracting the tendency to hot spots formation due to the exothermicity of (r.1). In this context, zeolite 5A, 13X, and alumina were proposed as active fillers for cyclic CO₂ methanation. Zeolites have been reported in previous studies as a valid method to intensify the conversion of CO₂ in methanation [4], due to their capacity to in situ remove water. Consequently, the reaction is shifted towards the products due to *Le Châtelier's* principle. The catalyst selected is bimetallic Ni:Fe (7.5:2.5 wt%) supported on $\gamma$-Al₂O₃, while Na₂O is used as CO₂ adsorbent. The effectiveness of both has been studied in previous works of the CREG research group [4].

## Experimental

Firstly, the effect of diffusional constraints (internal and external) was studied, fixing a volumetric flow of 150 mL(SATP)/min, 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. The fixed-bed reactor was loaded with: (i) 2 g of 7.5 wt% Ni–2.5 wt% Fe/$\gamma$-Al₂O₃ as methanation catalyst, (ii) 2 g of 10 wt% Na₂O/$\gamma$-Al₂O₃ as CO₂ adsorbent, and (iii) 6.5 g of inert or structuring filler. The fillers tested included high-purity $\gamma$-Al₂O₃ (SASOL Puralox), zeolite LTA 5A, and zeolite 13X (Si/Al ≈ 1.2). The particles (100–200 μm) were homogenized by mechanical mixing.

Before starting a methanation experiment, the catalyst was activated at 500 ºC 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 the experimental conditions. Each methanation experiment (**Figure 1**) includes two steps: first the reactor is fed with CO₂ diluted in inert (adsorption step); after that, CO₂ is exchanged in the inlet by H₂ (hydrogenation) at a total volumetric flow rate of 150 mL min⁻¹ (SATP). The adsorption stage introduces a 12 vol% CO₂ stream (Ar balance), while

the methanation step was carried out with 5 vol% $H_2$ (Ar balance). The range of temperatures tested was 250 to 400 °C. Step durations were optimized by (i) interrupting the adsorption at 90% of the solid's maximum capacity and (ii) prolonging the methanation until the complete conversion of the retained $CO_2$, using the $CO_2 \rightarrow CH_4$ yield as the optimization variable
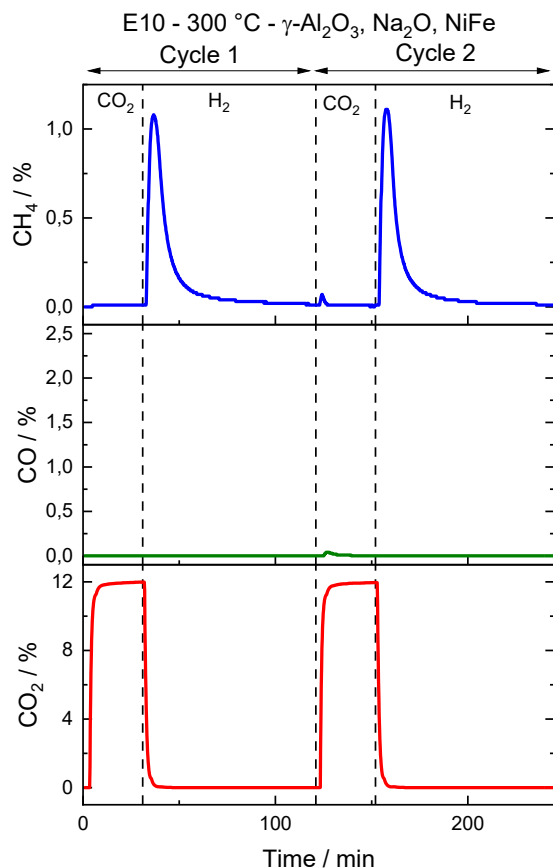


Figure 1. Example of cyclic $CO_2$ adsorption-methanation

# Results and Conclusions

The results (**Figure 2**) showed a balance between $CO_2$ adsorption capacity and methane production at 300 °C for both zeolite 13X and $\gamma$-$Al_2O_3$, identifying this temperature as optimal for cyclic methanation. Zeolite LTA 5A showed a higher methane production at elevated temperatures in comparison with the other filler materials, which was attributed to its lower affinity for $CO_2$ adsorption and its moderate hydrophilic nature. In general, among the MM materials studied, the catalyst/zeolite 13X mixture exhibited the highest methane production and relative stability during cyclic methanation (**Figure 2**). The functional separation achieved by MM systems eliminates the catalytic competition observed in DFMs and allows independent

optimization of the composition and microstructure of each active solid.

Additionally, as intended, all tested fillers—zeolites 13X and 5A, and alumina—resulted in significantly softer longitudinal temperature profiles in the solids bed (not shown), because they diluted the exothermic heat generated by reaction (r.1).
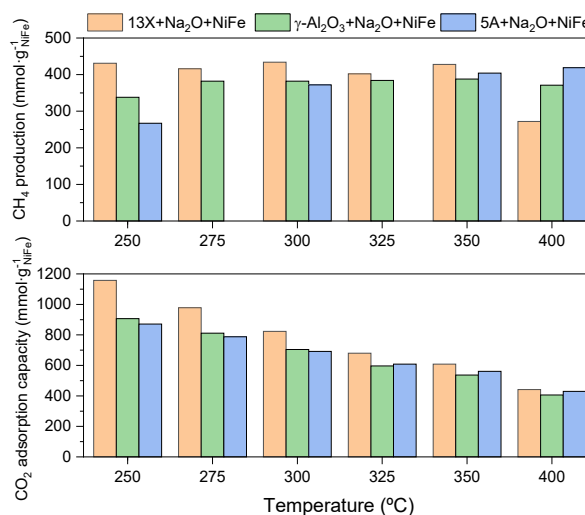


Figure 2. Temperature influence in methane production and $CO_2$ adsorption capacity

## Acknowledgements

## REFERENCES

[1]. KOUROUGIANNI, F. et al. A comprehensive review of green hydrogen energy systems. *Renewable Energy*. 231 (2024) 120911. doi: 10.1016/j.renene.2024.120911

[2]. FARIA, C. et al. Process intensification concepts for $CO_2$ methanation − A review. *Fuel*. 386 (2025) 134269. doi: 10.1016/J.FUEL.2024.134269.

[3]. LIU, K. et al. The distributions of alkaline earth metal oxides and their promotional effects on $Ni/CeO_2$ for $CO_2$ methanation. *Journal of $CO_2$ Utilization*. 38 (2020) 113–124. doi:10.1016/J.JCOU.2020.01.016.

[4]. MERCADER, V.D., ARAGÜÉS-ALDEA, P., DURÁN, P., FRANCÉS, E., HERGUIDO, J., PEÑA, J.A. Optimizing Sorption Enhanced Methanation (SEM) of $CO_2$ with Ni3Fe +LTA 5 A mixtures. *Catalysis Today*. 453 (2025) 115262. doi: 10.1016/J.CATTOD.2025.115262.