

# Sorption enhanced CO<sub>2</sub> methanation to obtain high purity methane

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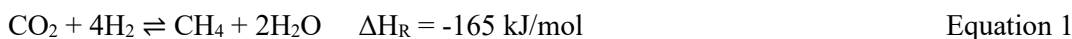
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## Highlights

- Bifunctional material with catalytic and water adsorbing sites
- Nickel on zeolite 13X catalyst
- Thermodynamic equilibrium shift to achieve high purity carbon neutral methane

## 1. Introduction

The urgent need to mitigate climate change has highlighted the interest in carbon dioxide (CO<sub>2</sub>) utilization technologies, particularly in processes that yield valuable products while reducing atmospheric CO<sub>2</sub> levels. One such promising approach is sorption-enhanced methanation (SEM) of CO<sub>2</sub> (**Equation 1**), aimed at producing high-purity methane (CH<sub>4</sub>) by overcoming the thermodynamic limitations of conventional methanation reactions. In this process, water, a key by-product of methanation, is continuously removed via sorption on a zeolite based catalyst, thereby shifting the equilibrium towards methane formation [1].



The bifunctional material is composed by zeolite 13X which acts as adsorbent for water and support for the metals, nickel provides the catalytic active sites and cerium increases CO<sub>2</sub> adsorption. This technique offers significant potential for improving both conversion efficiency and product purity in applications such as synthetic natural gas (SNG) production, compatible with the current natural gas infrastructure. Methane synthesis from renewable hydrogen and carbon dioxide collected from industrial flue gases represents a promising pathway towards fuel independence for countries lacking domestic fossil fuel resources. By converting excess renewable electricity into a storable and transportable synthetic fuel, long-term energy storage and CO<sub>2</sub> valorisation are achieved.

## 2. Methods

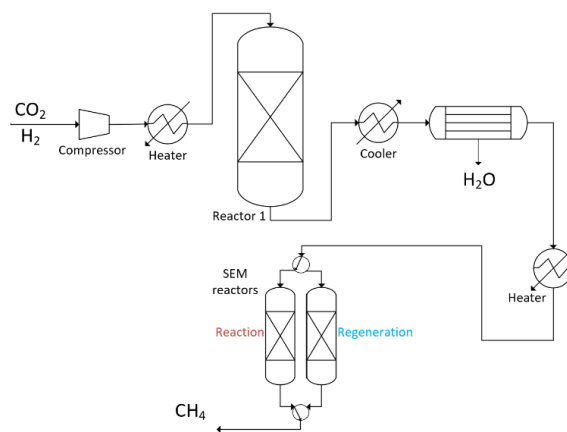
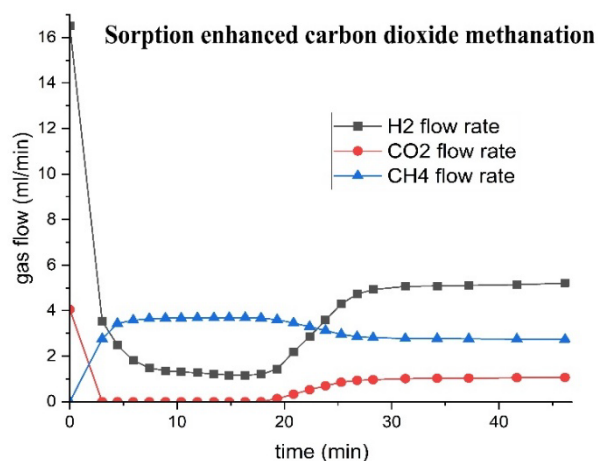
Sorption enhanced carbon dioxide methanation reaction is performed employing the catalyst 5%Ni2.5%Ce13X in a glass tubular laboratory reactor. The experiments were conducted at 240 °C and 1 atm, using a reacting gas stream composed of 16 ml/min of H<sub>2</sub>, 4 ml/min of CO<sub>2</sub> and 80 ml/min of He. Gas analysis was performed using an online microGC. Extensive catalyst characterization was performed using SEM, TEM, N<sub>2</sub>-physisorption, pyridine-FTIR, TGA, CO<sub>2</sub>-TPD and H<sub>2</sub>-TPR.

## 3. Results and discussion

The catalyst has displayed high activity in the sorption enhanced period (Figure 1), reaching a partial steady state where CO<sub>2</sub> conversion reached 100%, lasting about 18 minutes. 100% selectivity towards methane has been observed in the sorption enhancement period by performing an experiment with a mass spectrometer. After saturation of the zeolite with water produced during the reaction, no equilibrium shift was achieved and the conversion value reached steady state. The application of this bifunctional material is to be used only in the sorption enhancement period, where pure methane can be obtained. To conduct the process on a larger scale, in a continuous operation, multiple reactors in parallel could be used. In this configuration the reactors are operated alternating regeneration and reaction. An alternative is represented by a fluidized riser bed reactor which allows for the usage of smaller catalyst particles and continuous regeneration.

Figure 2, represents a simplified diagram of the process to obtain pure methane from carbon dioxide and hydrogen. In the inlet, the two reagents in stoichiometric amounts are sent to the first reactor which

operates at high temperatures and uses a commercial nickel-based catalyst. In this first reactor, high reaction rates are obtained, and the conversion is brought to 80-90%. The water formed is condensed away from the outlet stream and a dry gas mixture of CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub> is then sent to the sorption enhanced methanation reactors. In this unit, only 10 to 20% of the initial reagents need to be converted, allowing these reactors to be smaller and operate for longer time between regeneration. The heat produced in reactor one can be used to carry out the regeneration of the SEM reactors.



**Figure 1.** Sorption enhanced CO<sub>2</sub> methanation experiment. **Figure 2.** Sorption enhanced methanation plant diagram

## Conclusions

The experiments in sorption enhanced carbon dioxide methanation employing a bifunctional catalyst have demonstrated the possibility to obtain high purity methane already from the reactor outlet. This process takes advantage of the selective sorption of water on the zeolite surface to shift the thermodynamic equilibrium, eliminating the need for gas separation. A carbon neutral fuel produced with the presented method can help reach the aim of carbon neutrality and energy independence for countries without access to fossil fuel resources.

## References

The reference format is provided below [1 – 3]. [Times New Roman 10].

[1] E. Marchi, P. Gangotena, C. Frilund, T Salmi, P. Simell, H. Grénman. International Journal of Hydrogen Energy 177 (2025) 151628.

## Keywords

Carbon dioxide hydrogenation; Nickel based bifunctional material; High purity carbon neutral methane; Thermodynamic equilibrium shift.