

Process Intensification

Gas Phase Sorption Enhanced Reaction Processes

Pressure Swing Adsorption Reactor

KEYWORDS: CO₂ capture and utilization / Power-to-gas / CO₂ Methanation/ Syngas production / hydrotalcite-derived catalysts

This research topic is focused on the development of strategies for the mitigation of CO₂ emissions. Following the so-called power-to-gas concept, the catalytic methanation of CO₂ to produce synthetic natural gas is one of the strategies addressed. The other strategy studied is producing synthesis gas from CH₄, CO₂, and H₂O for further methanol production. The research involves the development of catalysts, adsorbents, and dual-function materials, and the implementation of integrated processes such as pressure swing adsorptive reactors.

Introduction

Among the many approaches explored for reducing CO₂ emissions into the environment, capturing and using it to produce fuels or other useful compounds appears to be a promising strategy, particularly methane production, in the so-called power-to-methane (PtM) concept. This concept relies on storing surplus renewable power as methane, which can be easily and safely distributed in huge quantities through the existing natural gas infrastructures. The methanation of CO₂ involves its catalytic conversion with renewable-based H₂ through the Sabatier reaction. However, the parallel reverse water gas shift (RWGS) reaction can occur, leading to undesired CO formation, especially at higher temperatures. Therefore, developing catalysts that can perform the methanation of CO₂ at relatively low temperatures is crucial. Moreover, some materials, such as hydrotalcite-derived Ni that combine the CO₂ sorbent capacity of hydrotalcite with a methanation Ni catalyst open the door for the integration of CO₂ capture and utilization in the same material with close active sites, which might be useful for integration in multifunctional reactors.

From the process point of view, a packed bed made of a selective CO₂ sorbent and a methanation catalyst can be cyclically operated like a pressure swing adsorptive reactor (PSAR), switching between sorption and reactive regeneration stages. The integrated concept takes advantage of the heat released from the reaction coupled with the endothermic CO₂ desorption, driving the migration of sorbed CO₂ to catalytic sites to react with H₂.

Turning synthesis gas (syngas) into methanol offers an additional appealing choice for CO₂ utilization since it may be utilized as a chemical feedstock to create other chemicals or products and as an energy carrier. Syngas can be produced

from CO₂, H₂O, and CH₄ via bi-reforming of methane (BRM), which is a combination of steam reforming of methane (SRM) and dry reforming of methane (DRM). The strongly endothermic BRM reaction requires an efficient catalyst. The material to support the active phases and promoters must show thermal stability, which a porous metallic ribbon structure can achieve. Another needed feature is high thermal conductivity to ensure efficient heat transfer into the reaction zone.

Current Development

Ruthenium, hydrotalcite-derived nickel (NiMgAl), and bimetallic nickel-ruthenium (Ru/NiMgAl) catalysts were synthesized and tested for the CO₂ methanation reaction. The catalysts were characterized by different physical-chemical techniques and screened based on their activity, selectivity, and stability. The catalysts with the best performance (i.e., the hydrotalcite-derived NiMgAl and Ru/NiMgAl) seem quite

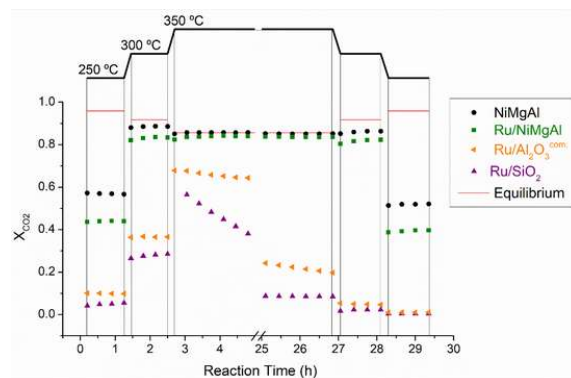


Fig 1. Evolution of CO₂ conversion with time and temperature for the methanation reaction catalyzed with different materials.

promising, even when compared with other methanation catalysts reported in the literature.

A hydroxy sodalite (H-SOD) membrane reactor was studied through modeling and simulation for in situ steam removal during the CO₂ methanation reaction. After model validation against experimental data. The effects of various operating conditions were studied, namely, the permeation zone conditions (e.g., changing the sweep gas composition, pressure, and flow rate), the reaction conditions (e.g., changing the temperature, pressure, and contact time), and the inlet gas

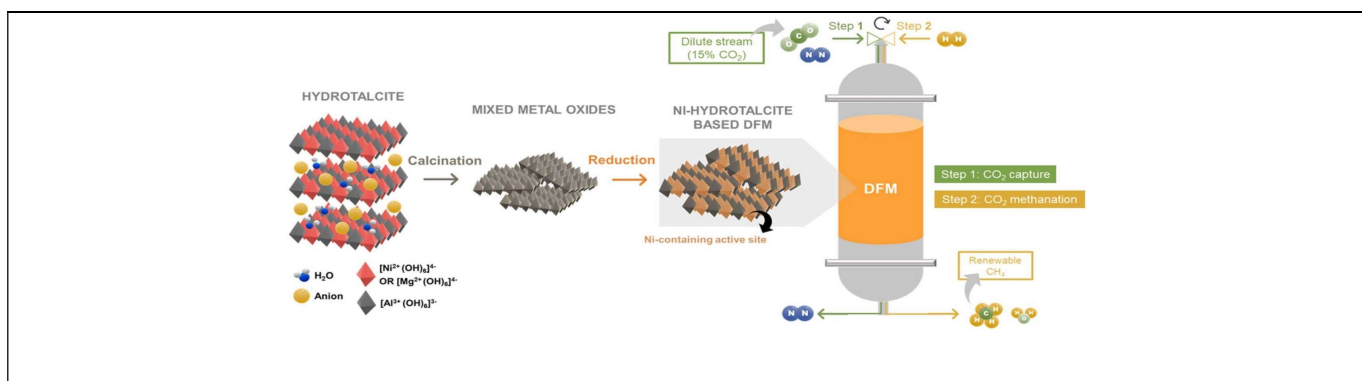


Fig 2. Cyclic operation of CO₂ capture and conversion into methane on Ni-hydrotalcite based dual function materials.

composition (e.g., ideal feed composition ($H_2/CO_2 = 4$) and biogas-based streams).

A cyclic unit of two parallel sorptive reactors filled with a mixture of a potassium-promoted hydrotalcite and a commercial methanation catalyst (Ru/Al_2O_3) was tested. The sorption and reactive regeneration stages were performed alternately on both sorptive reactors until a cyclic steady-state was achieved. Each experiment was evaluated by several process indicators, namely, CO_2 sorption capacity, CO_2 conversion, CH_4 productivity and purity, and moles of H_2 fed per mole of CH_4 produced.

Ni-hydrotalcite-based dual-function materials (DFMs) have been prepared and applied for the combined CO_2 capture and methanation in a single reactor. The materials have been synthesized with different chemical properties, and the effect of reduction temperature on their cyclic performance was studied. The cesium-promoted sample reduced at 450 °C featured a CO_2 sorption capacity of $0.48 \text{ mol}_{CO_2} \cdot \text{kg}_{DFM}^{-1}$ and produced ca. $0.33 \text{ mol}_{CH_4} \cdot \text{kg}_{DFM}^{-1}$. Its good performance was associated with a higher number of medium and strong basic sites.

Nickel-substituted hydrotalcites promoted with cesium were synthesized. After a materials screening stage, a detailed parametric study was carried out with the most promising sample to evaluate the effect on the dual-function capability of several operational conditions. Cesium-doped extrudates were selected and used in the parametric study. Under cyclic steady-state and operation at 350 °C and 1 bar, the reactor packed with this material allowed capturing ca. $0.24 \text{ mol}_{CO_2} \cdot \text{kg}_{DFM}^{-1}$ and the complete conversion of the captured CO_2 into CH_4 .

The bi-reforming of methane (BRM) reaction was studied to help identify the adequate conditions to perform it. Reaction studies were carried out over a nickel-based catalyst with varying temperatures (798–1123 K). The results obtained can be used to establish a reaction mechanism to determine a kinetic model and obtain the numerical values of the kinetic constants to describe the observed experimental behavior and support the future industrial implementation of the BRM reaction. The results show that syngas can be successfully produced using this process. For the range of operating conditions studied, the carbon dioxide and methane conversions increase with temperature, reaching 40% and 100% at the largest temperature studied.

A Ni catalyst supported on a layered double hydroxide (LDH) with potassium as a promoter was developed for catalytic BRM and compared to catalysts reported in the literature. The main focus was the modifications performed to obtain a material that can catalyze BRM at lower temperatures and get a hydrogen-to-carbon monoxide ratio close to two in the obtained syngas, a prerequisite for producing methanol. The influence of the operating conditions from 300 °C to 900 °C on the conversion of the reactants and product distribution was studied. Accordingly, it was concluded that it is only possible to

obtain molar ratios of hydrogen-to-carbon monoxide close to two at high temperatures.

Future Perspectives

Future developments on this topic involve implementing strategies to improve the efficiency of CO_2 capture and utilization processes. Achieving the goal of more efficient processes requires the development of research work on different areas, namely on the development of new materials such as catalysts able to operate at relatively low temperatures, suitable sorbents for CO_2 capture, materials able to work as both catalyst and sorbent, implementing and optimizing integrated processes such as pressure swing adsorptive reactor.

Related Sustainable Development Goals



Outputs

Master Dissertations

[1] Ricardo de Oliveira, Estudo da viabilidade técnica e económica na produção de gás natural sintético por metanação catalítica, MIEQ, FEUP, 2020

PhD Dissertations

[1] Ana Catarina Faria, Multifunctional reactors for CO_2 methanation: Power-to-Gas concept, PDEQB, FEUP, 2023

Selected Publications

- [1] J.A. Martins *et al.*, Catalysts 9, 1008 (2019)
- [2] A. F. Cunha *et al.*, Energy Reports 6, 74-79 (2020)
- [3] S. Najari *et al.*, Energy Conversion and Management 226, 113550 (2020)
- [4] A. C. Faria *et al.*, Ind. Eng. Chem. Res. 59, 16170–16184 (2020)
- [5] A. F. Cunha *et al.*, RSC Adv. 10, 21158-21173 (2020)
- [6] S. Saeidi *et al.*, Progress in Energy and Combustion Science 85, 100905 (2021)
- [7] J. A. Martins *et al.*, ACS Sustainable Chem. Eng. 10, 7833–7851 (2022)
- [8] S. Saeidi *et al.*, Renewable and Sustainable Energy Reviews 183, 113392 (2023)
- [9] A. C. Faria *et al.*, Journal of CO_2 Utilization 72, 102476 (2023)
- [10] A. C. Faria *et al.*, Chemical Engineering Journal 476, 146539 (2023)
- [11] J. Brito *et al.*, Fuel Processing Technology 250, 107859 (2023)

Team

Alírio E. Rodrigues, Emeritus Professor; **Ana C. Faria**, Ph.D. Student; **Alexandre Ferreira**, Assistant Professor / Group Leader; **José M. Loureiro**, Associated Professor.

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