Sustainable methane production by CO_2 hydrogenation on the Ni-Mn-modified mesoporous silicas obtained from rice husks

Grigoria Theochari*[1], Margarita Popova[1], Daniela Kovacheva[2], Daniela Karashanova[3]

[1] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
[3] Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria
Keywords: waste rice husks utilisation, Mn doped Ni SiO_2 catalysts, methane production, 3D printed catalysts
Presenting author email: grigoria.theochari@orgchm.bas.bg

The increasing emission of greenhouse gases and their severe effect on the climate has come into the spotlight as a major challenge to sustainable development. The European Green Deal is a new EU strategy aiming to combat climate change by no net emissions of GHGs by 2050. Carbon Capture, Utilization, and Storage (CCU) offers an optimistic strategy for addressing climate change while simultaneously addressing the global energy demand (Jangam et al., 2020). Among various catalytic processes of CO_2 valorization, the so-called Sabbatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$), is very promising due to its potential to recycle carbon and reduce the net greenhouse gas emissions. The development of an efficient catalyst is of key importance for the processes of CO_2 valorization. The use of catalysts based on transition metals such as: Ni, Co, Cu, Fe, could be a good alternative to substitute the noble metals due to their affordable prices and high activity. Nickel is the most extensively studied one due to its low cost, high availability, and favorable catalytic properties (Medina et al., 2025). To improve the performance of Ni-based catalysts at lower temperatures, secondary transition metals such as Mn are often used as dopants (Prabhakar et al., 2025). The catalytic support also influences the efficiency in the methanation process. A disadvantage of the usual supports (Al_2O_3, ZrO_2, CeO_2, MCM-41, SBA-15) is their high cost, which is due to the use of expensive reagents, incl. template, high temperature and longer procedure leading to higher energy consumption. A significantly more economical approach is the use of waste materials, low temperature and absence of expensive templates to obtain mesoporous silicas (Popova et al., 2024). Examples of raw materials for obtaining porous materials are most often agricultural waste, such as rice husks. Rice husk is one of the main wastes of the rice industry, generated in big quantities, it is rarely used as animal food because of its low nutritional value. More commonly it is used as a fertilizer additive. Hence, utilization of agricultural waste can serve as a low-cost precursor for obtaining catalysts carries used in CO_2 hydrogenation, at the same time addressing the issue of waste management.

In the present study, we have developed Ni-Mn-based mesoporous silica (MS) catalysts with high activity and selectivity for CO_2 conversion to methane. The produced catalysts were also 3D printed to simulate the feasibility of the process on a larger scale.

Materials and Methods

The initial and modified materials were characterized by XRD (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany), N_2 physisorption (Quantachrome instruments AUTOSORB iQ-MP-AG, Boynton Beach, FL 33426, USA), thermal analysis (STA449F5 Jupiter of NETZSCH Gerätebau GmbH (Netzsch, Germany), and solid-state NMR (Bruker Avance II+ 600 NMR spectrometer (Karlsruhe, Germany).

Samples were reduced in hydrogen (60 mL/min) up to 400 °C for 1h ex situ before the catalytic experiments. Hydrogenation of methane was performed at atmospheric pressure using a fixed-bed flow reactor. The amount of the catalyst which is used in the catalytic experiment is a 150 mg sample with particle size 0.25–0.5 mm. The CO_2 reactant was fed in the reactor with a flow rate of 30 ml/min H_2 and CO_2, GHSV= 12 000 $cm^3h^{-1}gcat^{-1}$, (H_2/CO_2 is 4/1) and catalytic experiments were carried out in the interval 250–400 °C. On-line analysis of the reaction products was performed using a NEXIS GC-2030 ATF with a VALCO Plot VPHS-D CFS-PD3053-200 (30 m × 0.53 mm × 20.0 μm) column.

Results and Discussion

The mesoporous silica was synthesized from rice husks without template by a simple procedure. Incipient wetness impregnation method was used for preparation of Ni-Mn-containing mesoporous silica catalysts. The XRD patterns of the reduced catalysts show the formation of finely dispersed nickel nanoparticles. Impregnation with nickel and manganese resulted in a decrease of the surface area but the shape of the isotherms is similar to

the parent silica. Therefore, the changes are due to the pore blocking effect of incorporated metal oxides and metal oxide deposition on the outer surface.

Catalytic activity of the obtained catalysts in CO_2 methanation reaction was studied with increasing reaction temperature (Figure 1).

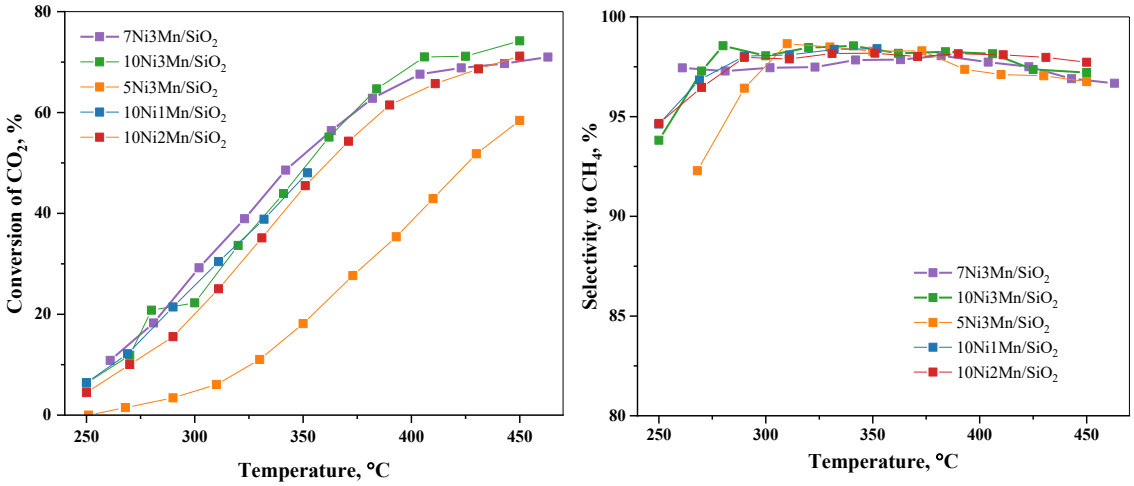

Figure 1. Catalytic activity of the studied catalysts as a function of reaction temperature (H_2:CO_2 = 4:1; GHSV = 12 000 mL $gcat^{-1}$ h^{-1}).

The catalysts show high catalytic activity and selectivity to methane. The presence of manganese facilitated the reduction of nickel during the reductive pretreatment and improved the nickel dispersion. Formation of Mn_xO_y has a positive effect on the catalytic performance because of the formation of basic sites with moderate strengths, enhancing the adsorption of slightly acidic CO_2. The basic sites promote the formation of monodentate formate species, that can be easily converted to methane. It was found that the presence of nickel nanoparticles and Mn_xO_y with the optimal ratio could result in higher activity and stability of the catalyst. Among the prepared catalysts, the 7 wt. % Ni- 3 wt. % Mn supported mesoporous silica catalysts showed the highest catalytic activity in CO_2 hydrogenation to methane. Our results suggest that addition of manganese, a cheap and abundant transition metal, holds significant potential for industrial application in sustainable power to gas technologies.

References

Frontera, P., Macario, A., Ferraro, M., & Antonucci, P. (2017). *Catalysts*, *7*(59). https://doi.org/10.3390/catal7020059

Jangam, A., Pati, S., Hongmanorom, P., Tianxi, Z., Junmei, C., & Kawi, S. (2020). A review of recent catalyst advances in CO_2 methanation processes. *Catalysis Today*, *356*, 471–489. https://doi.org/10.1016/j.cattod.2020.07.023

Medina, O. E., Amell, A. A., López, D., & Santamaría, A. (2025). Comprehensive review of nickel-based catalysts advancements for CO_2 methanation. *Renewable and Sustainable Energy Reviews*, *207*, 114926. https://doi.org/10.1016/j.rser.2024.114926

Prabhakar, J. K., Kumar, R., Ray, K., Apte, P. A., & Deo, G. (2025). Understanding the role of Mn in Ni-Mn/Al_2O_3 and Ni_3Fe-Mn/Al_2O_3 catalysts for enhanced CO_2 methanation activity. *Journal of Environmental Chemical Engineering*, *13*(1), 115233. https://doi.org/10.1016/j.jece.2024.115233

Vrijburg, W. L., Garbarino, G., Chen, W., Parastaev, A., Longo, A., Pidko, E. A., & Hensen, E. J. M. (2020). Ni-Mn catalysts on silica-modified alumina for CO_2 methanation. *Journal of Catalysis*, *382*, 358–371. https://doi.org/10.1016/j.jcat.2019.12.026

Popova, M., Mitova, V., Dimitrov, M., Rosmini, C., Tsacheva, I., Shestakova, P., Karashanova, D., Karadjova, I., & Koseva, N. (2024). *Molecules*, *29*(3540). https://doi.org/10.3390/molecules29093540

Acknowledgements

This work was supported by the Bulgarian National Science Fund with the project КП-06 Н59/12.