

Renewable CH₄ production via CO₂ hydrogenation over mono- and bi-metallic Ru-Ni/MCM-41 catalysts.

A. Rontogianni¹, N. Chalmpe², E. Nikolaraki¹, G. Botzolaki¹, G. Goula¹, P. Zygouri², N.D. Charisiou³, M.A. Goula³, D. Moschovas², A. Avgeropoulos², M.A. Karakassides² *, D. Gournis^{2,*}, I.V. Yentekakis^{1,*}

¹ Laboratory of Physical Chemistry & Chemical Processes, School of Environmental Engineering, Technical University of Crete, 73100 Chania, Crete, Greece

² Dept. of Materials Science and Engineering, University of Ioannina, Greece.

³ Dept. of Chemical Engineering, University of Western Macedonia, GR-50100 Koila, Greece

* Correspondence: yentek@isc.tuc.gr (I.V. Yentekakis); dgourni@uoi.gr (D. Gournis); mkarakassides@uoi.gr (M.A. Karakassides)

TOPIC: Greenhouse gases mitigation by H₂

ABSTRACT

Since fossil fuels still remain the dominant source of energy in the industrial, commercial, residential, and transportation sectors, tremendous quantities of CO₂, the major greenhouse gas, are emitted into the atmosphere, raising its concentration from ~280 ppm before the industrial revolution to ~410 ppm nowadays. Predictions indicate a concentration of CO₂ ~570 ppm by the end of the century with the concomitant global warming and climate change to seem threatening, if no urgent mitigating actions implemented. Therefore, control of CO₂ emissions is a critical and urgent environmental issue. A possible solution for moderating CO₂ emissions can be provided by energy models with a reduced environmental footprint that can also be combined with the so-called *cyclic economy* strategies. CO₂ capture and utilization (recycling), through its conversion to added-value products and fuels, are nowadays among the approaches that receive intense research and technological interest. To this purpose, CO₂ hydrogenation toward methane production, the well-known Sabatier reaction, is a major topic, especially when the hydrogen demands for CO₂ methanation can be provided via a solar- or wind-powered water-splitting system, thus further expanding the eco-friendly and sustainability character the concept, often called the *power-to-gas* (P2G) process. P2G is also considered as a promising method for the storage of hydrogen, overcoming the safety difficulties of direct storage and transport of hydrogen. Here we report on CO₂ hydrogenation toward methane, investigated at 200–600 °C and H₂/CO₂ = 4/1 v/v, over mono- and bi-metallic Rh-Ni based catalysts supported on mesoporous silica MCM-41. Nickel was incorporated in-situ into the MCM-41 lattice (denoted as Ni-MCM-41 support), while the wet impregnation method was used as a second step for adding Ru on the Ni-MCM-41, using two different Ru precursors, namely RuCl₃ and Ru(III)-acetylacetonate. This enabled us to investigate in detail the effect of catalyst's design aspects (i.e., Ru precursor used, Ru/Ni molar ratio, the pre-incorporation of Ni into MCM-41 lattice), as well as reaction operational parameters (i.e., temperature, gas hourly space velocity, time-on-stream stability) on CO₂ methanation activity and selectivity performance. A plethora of characterization techniques, such as N₂ adsorption-desorption methods, isothermal H₂-chemisorption, hydrogen temperature programmed reduction (H₂-TPR), powder X-ray diffraction (pXRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and Fourier-transform infrared spectroscopy (FTIR), were applied in order to obtain well-documented structure-activity correlations for the investigated (CO₂+H₂)/Ru-Ni-MCM-41 catalytic system.

Acknowledgements: This research was co-funded by the European Union and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", under the call "RESEARCH-CREATE-INNOVATE" (project code: T1EAK-00782).