Activity Report for the implementation of the Postdoctoral Project

PD – PN-III-P1-1.1-PD-2016-1228

Phase 2 (January – December 2019)

Acronim: **MOFReCat**

"From nanoreactor to a high-performance fixed bed reactor using hierarchical MOF based catalysts"

Summary

The second phase of the project (January – December 2019) included activities regarding: (a) synthesis of catalysts of the type Ni/MOF-Al_2O_3, either by the wet impregnation method (IMP), either by the double solvent method with uses two solvents with different polarities (DS); (b) characterization of the prepared catalysts from the structural, morphological and functional point of view (specific surface area, pore volume and pore size distribution – BET, X ray diffraction – XRD, scanning and transmission electron microscopy – SEM/TEM, thermogravimetric analysis – TGA, diffuse reflectance IR spectroscopy – DRIFTS; (c) thermodynamic study of the methanation reaction; (d) design of experiments by statistical methods (DoE) using 3 factors (reaction temperature – T, gas hourly space velocity – GHSV, molar ratio of reactants – H_2/CO_2); (e) evaluation of catalytic performance of the synthesized Ni/MOF-Al_2O_3 catalysts by temperature programmed reactions (TPRea) and comparison with Ni/Al_2O_3 homologues catalysts.

Contents of the scientific and technical report (RST)

Conclusions

Thermodynamic analysis of the methanation reaction evidenced that a better equilibrium conversion may be obtained if hydrogen excess is used in the reaction feed. On the other hand, design of the experiments by statistical methods showed that the operating temperature is the most influential among the investigated factors upon the catalytic performance, while among the possible interactions between these factors, the one given by the reaction temperature and reactants molar ratio is more significant.

Synthesis of tipul Ni(10%)/MOF-Al_2O_3 catalysts was done following 2 strategies: (1) wet impregnation method followed by the reduction with sodium borohydride at ambient temperature (IMP method); (2) the double solvent method, ollowed by the reduction with sodium borohydride at ambient temperature (DS method). Among the prepared catalysts, Ni(10%)/MIL-101-Al_2O_3 (DS) shows the best catalytic activity, considering both CO_2 conversion, and methane selectivity, besides showing the best characteristics from the structural (high surface area, good pore size distribution, comparable crystalinity with the starting MIL-101-Al_2O_3 composite, superior thermal stability to MIL-101), morphological (goof dispersion of very small Ni nanoparticles on the catalyst surface, as well as in the pores of the superficial MIL-101), and functional (good CO_2 chemisorption capacity) point of view.

Results obtained during this phase are: (1) ***Products*** – samples of catalysts Ni(10%)/MIL-101-Al_2O_3 (IMP), Ni(10%)/MIL-101-Al_2O_3 (DS) and Ni(10%)/MIL-53-Al_2O_3 (DS), characterized from the structural, morphological and functional point of view; (2) ***Methods*** – (a) preparation method for Ni(10%)/MOF-Al_2O_3 catalysts by the wet impregnation method followed by the reduction at ambient temperature with sodium borohydride (IMP method); (b) preparation method for Ni(10%)/MOF-Al_2O_3 catalysts by the double solvent method followed by the reduction at ambient temperature with sodium borohydride (DS method); (c) laboratory method for the methanation of CO_2 using Ni(10%)/MOF-Al_2O_3 catalysts; (3) ***Thermodynamic study*** of the methanation reaction; (4) ***Statistical model*** for the design of experiments (DoE) for the methanation of CO_2; (5) ***Scientific and technical report (RST)*** which includes the complete synthesis and characterization procedures for the Ni(10%)/MOF-Al_2O_3 catalysts, results of the thermodynamic study, of the design of experiments and of the catalytic activity tests in the methanation of CO_2.

Dissemination of the results obtained during this phase was done by:

(1) ***project website*** (http://www.itim-cj.ro/PNCDI/pd92/index.htm);

(2) papers presented at ***international conferences***:

1. M. Mihet, O. Grad, G. Blanita, L. Barbu-Tudoran, M. D. Lazar – *Effective deposition of Ni nanoparticles on MIL-101 and MIL-101/Al_2O_3: catalytic performance in the methanation of CO_2,* 12th International Symposium of the Romanian Catalysis Society, Bucharest, Roamnia, 5-7 June, 2019 (oral presentation).
2. M. Mihet, O. Grad, G. Blanita, M.D. Lazar – *Synthesis and characterization of MIL-101 based catalysts: bulk MIL-101 and immobilized MIL-101 on γ-Al_2O_3 as catalytic supports,* 14th European Congress on Catalysis (EuropaCat 2019), Aachen, Germany, 18-23 August, 2019 (poster presentation).
3. M. Mihet, O. Grad, G. Blanita, L. Barbu-Tudoran, M.D. Lazar – *Ni@MIL-53 and Ni@MIL-53/Al_2O_3 catalysts: comparative performance in the methanation of CO_2,* 12th International Conference on Processes in Isotopes and Molecules (PIM 2019), Cluj-Napoca, Romania, 25-27 September, 2019 (poster presentation).
4. O. Grad, M. Mihet, M.D. Lazar, G. Blanita – *Hierarchical MOF/γ-Al_2O_3 composites: preparation and characterization,* 12th International Conference on Processes in Isotopes and Molecules (PIM 2019), Cluj-Napoca, Romania, 25-27 September, 2019 (poster presentation).

(3) ***article*** under review

O. Grad, M. Mihet*, G. Blanita, M. Dan, L. Barbu-Tudoran, M.D. Lazar – *MIL-101-Al_2O_3 as catalytic support in the methanation of CO_2 – comparative study between Ni/MIL-101 and Ni/MIL-101-Al_2O_3 catalysts,* Catalysis Today (FI = 4.888) (*corresponding author)

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Project Coordinator

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