Activity Report for the implementation of the Postdoctoral Project

PD – PN-III-P1-1.1-PD-2016-1228

Phase 1 (May – December 2018)

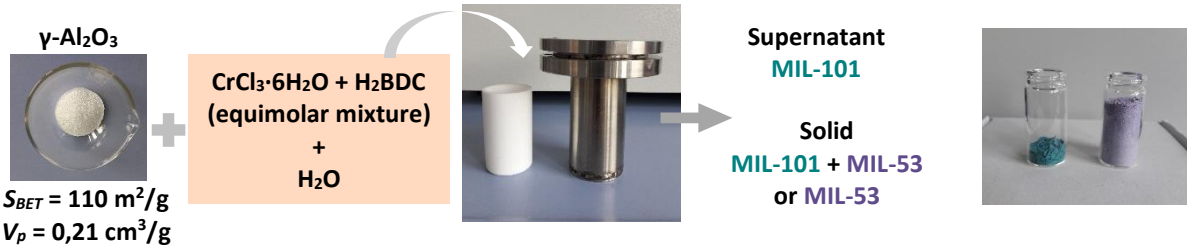
Acronim: **MOFReCat**

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

Summary

The first phase of the project (May – December 2018) included activities regarding: (1) the synthesis of MOF/Al_2O_3 hierarchical composites by macrostructural templating or impregnation method followed by solid phase synthesis, using 8 alumina samples with different properties regarding porosity, specific surface area, particle dimensions, surface properties, etc; (2) structural, morphological and functional characterization of the synthesized composites. The influence of several parameters on the MOF immobilization process was investigated; these parameters are: alumina/reactants ratio, reaction temperature, synthesis duration, support granulation, surface properties of the support. Moreover, successive deposition of MOF was pursued in order to increase the quality of the deposited MOF on the alumina pellets. The capacity of the synthesized MOF/Al_2O_3 composites to activate CO_2 (the main reactant in the CO_2 methanation process envisaged by this project) was investigated by temperature programmed desorption of molecularly or dissociatively chemisorbed CO_2.

Contents of the scientific and technical report (RST)



Scheme of the solvothermal synthesis procedure for MIL-101/MIL-53@Al_2O_3 composites.

Conclusions

Deposition of MOFs on different alumina supports was pursued following two strategies:

(1) ***solvothermal synthesis*** of the metal-organic framework on the selected alumina support, which leads to the immobilization of MOF on the outer surface of the alumina pellets;

(2) ***successive impregnation*** of the constituent reactants of the metal-organic framework on the selected alumina support, which leads to the immobilization of MOF in the pores of the alumina pellets.

In case of the **first strategy**, starting from the equimolar reactants' mixture (4,35 mmol $CrCl_3$ and terephthalic acid-H_2BDC) suspended in 40 mL distilled water, without added acid, and considering the surface properties of the selected alumina support, either MIL-53 (thermodynamic product), or MIL-101 (kinetic product) was deposited on the alumina pellets. The influence of the alumina /reactants ratio, reaction temperature and time, or of the alumina type on the type and quality of the deposited MOF was investigated. Investigation of the surface properties of the selected alumina samples and their correlation with the resulted products has evidenced that formation of MIL-101 on alumina is favored by the enhanced presence of the weak basic sites on the alumina surface. Therefore, the synthesis conditions for the following composites were established:

- **MIL-53/Al_2O_3**: commercial alumina with low number of weak basic sites (spherical granules), temperature of 150°C, 12 h reaction time, activation in DMF for 48 h (in order to remove the remaining terephthalic acid inside the pores of MIL-53).
- **MIL-101/Al_2O_3**: „in house" prepared alumina by the precipitation method (granules of irregular shape), with enhanced number of weak basic sites, temperature of 150°C, 12 h reaction time, activation in DMF for 48 h (in order to remove the remaining terephthalic acid inside the pores of MIL-101).

The **second synthesis strategy** leads to the formation of MIL-101 inside the pores of the commercial alumina sample, which under solvothermal synthesis resulted only in the formation of MIL-53, irrespective of the working conditions. Thus, the synthesis conditions for **MIL-101/Al_2O_3 (IMP)** are:

successive impregnation with aqueous solutions of the reactants in volumes equal to the pore volume of the selected alumina amount to be impregnated, commercial alumina with low number of weak basic sites, temperature of 190°C, 12 h reaction time, activation in ethanol for 24 h.

The successive deposition of MIL-53 or MIL-101 on alumina under solvothermal conditions gives crystalline composites up to the third deposition, the fourth one leading to the amorphization of the deposited MOF. In case of MIL-53/Al_2O_3 obtained by successive depositions, the specific surface areas of the resulted composites are by several tens of m^2/g larger than the starting alumina support (110 m^2/g), while the adsorption – desorption isotherms are similar to those corresponding to alumina (type IV, with hysteresis loop). In case of MIL-101/Al_2O_3 the successive depositions lead to the decrease of the specific surface area from 1032 m^2/g for the first deposition, up to 776 m^2/g for the third one. The adsorption – desorption isotherms are similar to the ones corresponding to pristine MIL-101.

From the functional point of view, each composite obtained using either of the investigated alumina supports shows a good CO_2 chemisorption capacity, either molecularly or dissociatively, which indicates good premises for the design of efficient CO_2 methanation catalysts starting from these MOF/Al_2O_3 composites.

Results obtained during this phase are: (1) ***Products*** – samples of MIL-53/Al_2O_3, MIL-101/Al_2O_3 and MIL-101/Al_2O_3 (IMP) characterized from the structural, morphological and functional point of view; (2) ***Methods*** – (a) solvothermal synthesis method for MIL-53/Al_2O_3; (b) solvothermal synthesis method for MIL-101/Al_2O_3; (c) synthesis method by impregnation for MIL-101/Al_2O_3 (IMP); (3) ***Scientific and technical report (RST)*** which includes the complete synthesis and characterization procedures for the MOF/Al_2O_3 composites.

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***:

O. Grad, **M. Miheț,** M.D. Lazăr, G. Blăniță – *Hierarchical MOF@Al_2O_3 composites – influence of synthesis conditions on the growth of benzenedicarboxylate-based MOFs on γ-Al_2O_3*, 14th Pannonian International Symposium on Catalysis, Stary Smokovec, Slovak Republic, 03 – 07 September **2018** (poster presentation).

M. Miheț, O. Grad, G. Blăniță, M.D. Lazăr – *MOF structuring by immobilization on γ-Al_2O_3 – synthesis and characterization of MOF@Al_2O_3 composites*, 7th European Congress on Chemistry – EuCheMS, Liverpool, 26 – 30 August **2018** (poster presentation).

03.12.2018

Project Coordinator

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