Activity Report for the implementation of the Postdoctoral Project

PD – PN-III-P1-1.1-PD-2016-1228

Phase 3 (January – April 2020)

Acronym: **MOFReCat**

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

Summary

The third phase of the project (January – April 2020) included activities regarding: (a) stability tests for the Ni/MOF-Al_2O_3 catalysts in the methanation of CO_2; (b) structural and morphological characterization of spent catalysts under prolonged exposure time (powder X-ray diffraction – XRD, scanning and tunneling electronic microscopy – SEM/TEM); (c) correlation of catalytic properties with catalytic performances in the methanation process.

Contents of the scientific and technical report (RST)

Conclusions

During the third phase of the project, Ni/MOF-Al_2O_3 catalysts with best catalytic performances exhibited during temperature programmed CO_2 methanation (TPRea) were subjected to stability tests at 280°C, while spent catalysts were characterized by X-ray powder diffraction and electronic microscopy in order to establish whether prolonged exposure to the reaction medium affects the structure, crystallinity and morphology of the catalysts. Moreover, catalyst deactivation due to possible C deposition on the catalytic surface was investigated.

Following the CO_2 methanation stability tests performed at 280°C under the same reaction conditions such as flow (4650 h^{-1}), feed composition ([CO_2] = 6.6 %, CO_2:H_2=1:5.2), or pressure (1 atm), as for the temperature programmed reactions (TPRea) performed during the second phase of

the project, it can be concluded that both Ni/MIL-101-Al_2O_3, and Ni/MIL-53-Al_2O_3 show stable CO_2 conversion and methane selectivity values for at least 7 h time on stream (TOS). For both catalysts, powder X-ray diffraction evidenced that the structure and crystallinity of the MOF-Al_2O_3 composites used as catalytic supports were preserved, while transmission electron microscopy (TEM) did not reveal any Ni nanoparticle agglomeration, or formation and deposition of filamentous C as a consequence of prolonged exposure to the reaction medium. All these facts lead to the conclusion that both Ni/MIL-101-Al_2O_3 and Ni/MIL-53-Al_2O_3 show a good stability under the proposed reaction conditions.

Among these catalysts, Ni/MIL-101-Al_2O_3 is particularly evidenced due to its superior catalytic performances proven in the methanation of CO_2, both in TPRea and stability tests. Thus, maximum CO_2 conversion of 86% is attained at 350°C, with a corresponding methane selectivity of 95%, while stable catalytic activity values determined at 280°C, are CO_2 conversion of 55%, with a corresponding methane selectivity of 90%.

Considering the catalytic activity results in the methanation of CO_2, in correlation with the structural, morphological and functional characteristics of the synthesized Ni/MOF-Al_2O_3 catalysts, Ni(10%)/MIL-101-Al_2O_3 (DS) catalyst is recommended as viable alternative for the methanation of CO_2. This catalyst is prepared using the double solvent approach for the deposition of Ni nanoparticles on MIL-101-Al_2O_3, while the catalytic support is synthesized by two successive depositions of MIL-101 on the starting alumina pellets.

The recommended reaction conditions are:

Temperature range: 250 – 350°C

Pressure: atmospheric

Flow regime: plug flow, GHSV of 4650 h^{-1}

Molar feed ratio: H_2/CO_2 = 5,3.

Results obtained during this phase are:

(1) Report containing the conclusions of catalytic activity, the recommended catalyst and reaction conditions for the CO_2 methanation reaction.

(2) *Scientific and technical report (RST)* which includes the complete experimental details, results and discussions for the stability tests in the methanation of CO_2 for Ni(10%)/MOF-Al_2O_3 catalysts, in correlation with the characterization results of spent catalysts.

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

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

(2) ***published papers***

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 = 5.825) (*corresponding author)
https://doi.org/10.1016/j.cattod.2020.05.003

M.D. Lazar, **M. Mihet**, M. Dan – *Hydrogen to Methane—An Important Step in the Power-to-Gas Concept,* in Comprehensive Renewable Energy, 2nd Edition, https://doi.org/10.1016/B978-0-12-819727-1.00032-7

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