Activity Report for the implementation of the project

TE – PN-III-P1-1.1-TE-2019-1447

CO_2 methanation by MOF based / derived ordered mesoporous catalysts

Acronym: **CO_2-OMC**

Phase 1 & 2 - Synthesis and characterization of MOF(Al) structures and of MOF(Al) based / derived Ni catalysts

Summary

During the first phase of the project **(Phase 1: November – December 2020)**, a thorough literature survey regarding the synthesis and characterization of Al based metal-organic frameworks (MOF(Al)) was performed. Three types of MOF(Al) form the MIL class (Materiaux de l'Institute Lavoisier) were selected: (a) 1 microporous structure, MIL-53, and (b) 2 mesoporous structures, MIL-100(Al) and MIL-101-NH_2(Al), in order to be synthesized individually, or to be used to obtain composite of the type MOF-Al_2O_3, or to obtain structured alumina by their derivation in air.

The second phase of the project **(Phase 2: January – December 2021)** involved activities regarding: (a) synthesis and characterization of Al-based metal-organic frameworks – MOF(Al) selected during the first phase of the project (MIL-53(Al), MIL-101-NH_2(Al) and MIL-100(Al); (b) synthesis and characterization of MIL-53(Al)-Al_2O_3 composites; (c) synthesis and characterization of structured alumina obtained by thermolysis of synthesized MOF(Al) structures (derivation of MOF(Al)); (d) synthesis and characterization of Ni catalysts by Ni nanoparticle deposition either on the synthesized MOF(Al) structures, either by derivation of Ni@MOF(Al) samples, either by incorporation of Ni onto the MOF(Al)-derived alumina. Well-defined MOF(Al) structures were thus obtained, while MOF-based and MOF-derived Ni catalysts show promising characteristics for their efficient use in the methanation of CO_2.

Contents of the scientific and technical report (RST)

Conclusions

Considering the objective of this phase to obtain MOF(Al) based and derived Ni catalysts, the following directions were pursued: (a) synthesis of MOF(Al) structures with good structural and textural properties; (b) synthesis of MOF-Al_2O_3 composites with enhanced thermal stability; (c) synthesis of MOF(Al) derived structures by thermolysis in air, for these materials to be further used as catalytic supports for the efficient dispersion of Ni nanoparticles.

The synthesized MOF(Al) structures belong to the MIL family, being either microporous metal-organic frameworks – MIL-53(Al), either mesoporous structures – MIL-101-NH_2(Al), fie MIL-100(Al). Among these structures, **MIL-53(Al)** synthesized by the classical method at 220°C for 72 h, either at 190°C, with a synthesis time reduced by 6 (12 h), or **MIL-100(Al)** were obtained with a very good quality, as confirmed by XRD and N_2 adsorption-desorption isotherms. Moreover, **MIL-53(Al)-Al_2O_3** composites with different amounts of deposited MIL-53(Al) on the alumina particles were obtained by use of different ratios between the reactants (different alumina:H_2BDC ratios).

By derivation at 600°C of the synthesized MOF(Al), alumina samples with different textural properties were obtained, which preserve to a great extent the specific pore volume of the starting MOF(Al). From the porosity point of view, MOF(Al) derived structures show a broader pore size distribution as compared to the starting metal-organic frameworks, 2 regions being distinguishable: small mesopores region (pores below 6 nm), and medium to large mesopores (10 – 50 nm). Compared to the commercial alumina, the porosity of the MOF(Al) derived alumina is significantly enhanced. Among the $Al_2O_{3[MOF(Al)]}$ samples, the ones obtained by derivation of MIL-53(Al) synthesized from aluminum nitrate at 190°C, for 12 h, **$Al_2O_{3[MIL-53(Al).190.12]}$**, are particularly evidenced due to their textural properties.

In order to obtain MOF(Al) based and derived Ni catalysts, three strategies were followed: (a) Ni deposition by the classical wet impregnation method on MIL-53(Al) and MIL-53(Al)-Al_2O_3 structures in order to obtain **Ni@MOF(Al) catalysts**; (b) derivation of Ni@MOF(Al) obtained either by impregnation, either by the double solvent method, in order to obtain **Ni@$Al_2O_{3[Ni@MOF(Al)]}$ catalysts;** (c) derivation of MOF(Al) and subsequent deposition of Ni nanoparticles by the impregnation method, followed by reduction in H_2 at 650°C, to obtain **Ni/$Al_2O_{3[MOF(Al)]}$ catalysts.** Catalysts with a very good Ni dispersion were obtained in each case, especially in the case of the MOF(Al) derived Ni catalysts which show a very narrow Ni nanoparticle distribution (around 5 nm). Functional characterization of catalysts reveals a good activation of either CO_2, or H_2, the reactants in the methanation process, which make these catalysts as promising candidates for the methanation of CO_2.

Results obtained:

(1) ***Methods*** – (a) synthesis method for MOF(Al) structures: MIL-53(Al), MIL-100(Al), MIL-101-NH_2(Al); (b) synthesis method for MIL-53-Al_2O_3 composites; (c) synthesis method for Ni@$Al_2O_{3[Ni@MOF(Al)]}$ catalysts obtained by thermolysis of Ni@MOF(Al); (d) synthesis method for Ni/$Al_2O_{3[MOF(Al)]}$ catalysts obtained by thermolysis of MOF(Al), followed by Ni nanoparticle incorporation.

(2) ***Products*** – samples of (a) MOF(Al) structures: MIL-53(Al), MIL-100(Al), MIL-101-NH_2(Al); (b) MIL-53-Al_2O_3 composites; (c) Ni@$Al_2O_{3[Ni@MOF(Al)]}$ and Ni/$Al_2O_{3[MOF(Al)]}$ catalysts, characterized from the structural, morphological and/or functional point of view.

(3) ***Scientific and technical report*** which includes the complete synthesis and characterization procedures for MOF(Al) structures, MIL-53-Al_2O_3 composites, and of Ni@$Al_2O_{3[Ni@MOF(Al)]}$ and Ni/$Al_2O_{3[MOF(Al)]}$ catalysts.

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

(1) ***project website*** (https://www.itim-cj.ro/PNCDI/co2omc/en/co2-omc-english/);

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

- M. Mihet, O. Grad, A. Turza, M. Dan, M. Suciu, M.D. Lazar – MIL-53-alumina composites as alternative in the methanation of CO_2, 13th International Conference on Physics of Advanced Materials (ICPAM-13), Sant Feliu de Guixols, Spain, 24-30 September, **2021** (oral presentation).
- O. Grad, A. Turza, M. Suciu, M.D. Lazar, M. Mihet **–** MOF(Al) based catalysts for CO_2 methanation, 13th International Conference on Processes in Isotopes and Molecules (PIM 2021), Cluj-Napoca, Romania, 22-24 September, **2021** (oral presentation).
- A. Sonica, O. Grad, A. Turza, S. Porav, M. Mihet **–** MOF-Al_2O_3 composites for catalytic applications, 9th European Young Engineers Conference, Warsaw, Poland, 19-21 April **2021** (oral presentation).

(3) ***published article***:

- O. Grad, G. Blanita, M.D. Lazar, M. Mihet* – „Methanation of CO_2 Using MIL-53-Based Catalysts: Ni/MIL-53–Al_2O_3 versus Ni/MIL-53", *Catalysts*, **2021**, 11(11) 1142. https://doi.org/10.3390/catal11111412

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