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 3 – Catalytic activity performance of MOF(Al) based / derived Ni catalysts in CO_2 methanation

Summary

The third phase of the project (January – October 2022) involved activities regarding: (a) evaluation of catalytic activity performance in the methanation of CO_2 for the MOF-based Ni catalysts: Ni@MOF(Al) or Ni@MOF(Al)-Al_2O_3; (b) evaluation of catalytic activity performance in the methanation of CO_2 for the MOF-derived Ni catalysts, such as Ni@$Al_2O_{3[Ni@MOF(Al)]}$, or Ni/$Al_2O_{3[MOF(Al)]}$; (c) stability tests for 24 h time on stream for the most active catalysts from the two series; (d) correlation of catalytic activity with structural, textural and functional properties of catalysts; (e) selection of optimal reaction conditions in the methanation of CO_2.

Contents of the scientific and technical report (RST)

Conclusions

The aim of this phase being the evaluation of catalytic activity performance of the MOF-based and MOF-derived Ni catalysts (experimental set-up, catalytic test under differential and integral conditions, stability tests, deactivation, etc.), the influence of the reaction temperature on the catalytic performance (CO_2 conversion and CH_4 selectivity) was investigated. The correlation of catalytic performance with catalysts' structural, textural, and functional properties was also targeted. The following conclusions were evidenced:

1. MOF-derived catalysts reveal the best catalytic performances in CO_2 methanation. Among these, those obtained by deriving Ni@MOF(Al) are more active than those prepared by impregnation of the mesoporous alumina obtained by calcination of MIL-53(Al), Ni/Al_{MIL-53}.
2. Among the MOF-based catalysts, those obtained by Ni impregnation on MIL-53(Al)-Al_2O_3 composites show the best catalytic performance over the entire investigated timeframe. Moreso, all investigated MOF-based catalysts are stable for 24 h time on stream.
3. MIL-53(Al) synthesized hydrothermally at 190°C and 12h, compared to 220°C, 72 h (classical procedure) is more advantageous to obtain MOF-derived catalysts, due to their structural, but more so, functional properties, with important contribution on the enhancement of the catalytic performance in CO_2 methanation.

4. Use of MIL-53(Al)(as) to obtain Ni/$Al_{MIL-53(as)}$ is very advantageous for two reasons: (a) this catalyst shows the best catalytic performance among the catalysts prepared by impregnation of the MIL-53(Al)-derived alumina, and (b) not only the synthesis procedure for MIL-53(Al) is more advantageous, but calcination of the as-synthesized MOF, avoiding thus the long and energy consuming activation step, brings about an additional economic benefit.
5. In order to obtain MOF-based catalysts, MIL-53(Al) synthesized by the classical method is more suitable, since these catalysts show better catalytic performance compared to those obtained by use of MIL-53$(Al)_{190.12}$.

Results obtained:

(1) ***Scientific and technical report*** which includes the catalytic activity results for the MOF-based catalysts (Ni@MIL-53$(Al)_{190.12}$, Ni@MIL-53$(Al)_{220.72}$, Ni@MIL-53(Al)-$Al_2O_{3-(1-1)}$, Ni@MIL-53(Al)-$Al_2O_{3-(2-1)}$, Ni@MIL-53(Al)-$Al_2O_{3-(4-1)}$) and MOF-derived catalysts (Ni@$Al_2O_{3-[D-Ni@M53-190.12]}$, Ni@$Al_2O_{3-[D-Ni@M53-220.72]}$, Ni@$Al_2O_{3-[D-Ni@MIL-100]}$, Ni/$Al_{MIL-53(as)}$, Ni/$Al_{MIL-53(lt)}$) tested in CO_2 methanation (temperature influence, stability, etc.)

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:***

- Oana Grad, Angela M. Kasza, Alexandru I. Turza, Monica Dan, Lucian Barbu-Tudoran, Mihaela D. Lazar, and Maria Mihet*, on CO_2 methanation by MIL-53(Al)-derived catalysts, under evaluation at *J. Environ. Chem. Eng.* (FI = 7.968)

(3) **patents:**

- Patent application A/00639 from 17.10.2022 - *Procedeu de obținere a compozitelor MIL-53(Al)-alumină cu diferite grade de depunere a structurii metal-organice MIL-53(Al)*, autori: Oana Grad, Alexandru I. Turza, Angela M. Kasza, Monica Dan, Mihaela D. Lazar, Maria Mihet

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

- Oana Grad, Angela M. Kasza, Alexandru Turza, Lucian Barbu-Tudoran, Mihaela D. Lazar, Maria Mihet* – *MOF derived Ni catalysts for CO_2 methanation*, 13th International Symposium of the Romanian Catalysis Society, RomCat2022, 20-24 Iunie, 2022, Băile Govora, România (**oral presentation**).
- Angela M. Kasza*, Oana Grad, Alexandru Turza, Monica Dan, Maria Suciu, Mihaela D. Lazar, Maria Mihet* – *MIL-53(Al)-alumina composites with different structural properties – CO_2 methanation as case study*, 13th International Symposium of the Romanian Catalysis Society, RomCat2022, 20-24 June, 2022, Băile Govora, Romania (**poster presentation**).
- Oana Grad*, Angela Kasza, Alexandru Turza, Mihaela D. Lazar, Maria Mihet – *Synthesis of MIL-53(Al)-based catalysts for the methanation of CO_2*, 1st Forum of Young Researchers on Heterogeneous Catalysis, YOURHETCAT2022, 11-13 July, Szeged, Hungary (**oral presentation**).

- Angela M. Kasza*, Oana Grad, Alexandru Turza, Maria Suciu, Maria Mihet* – *Methanation of CO_2 using MOF(Al)-derived Ni catalysts*, 1st Forum of Young Researchers on Heterogeneous Catalysis, YOURHETCAT2022, 11-13 July, Szeged, Hungary (poster presentation)
- Maria Mihet*, Angela M. Kasza, Oana Grad, Alexandru I. Turza, Mihaela D. Lazar – *CO_2 methanation using MOF(Al)-based / -derived Ni catalysts*, 8thEuChemS Chemistry Congress (ECC8), 28 August – 01 Septembrie, 2022, Lisbon, Portugal (poster presentation).

28.10.2022

Project Coordinator

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