Syngas generation via pyrolysis-dry reforming of plastics over Ni-Mo_2C/γ-Al_2O_3 catalyst - the effect of amine on structural and catalytic properties

Ewelina Pawelczyk[1,*], Izabela Wysocka[1], Antonio Gil[2], Jakub Karczewski[3], Michał Maciejewski[3], Jacek Gębicki[1]

[1]Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdansk University of Technology, Narutowicza 11/12 St., 80-233 Gdansk, Poland
[2]INAMAT, Science Department, Los Acebos Building, Public University of Navarra, Campus of Arrosadia, E-31006 Pamplona, Spain
[3]Faculty of Applied Physics and Mathematics, Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology, Narutowicza 11/12 St., 80-233 Gdansk, Poland

Keywords: catalysts, hydrogen, plastic waste, CO_2 utilization.

*Presenting author email: ewelina.pawelczyk@pg.edu.pl

In response to pressing global challenges, such as climate change, unmanaged plastic waste, and dwindling fossil resources, prioritizing sustainable development is imperative (Evode et al., 2021; Höök and Tang, 2013; Li et al., 2021). Introducing innovative, eco-friendly technologies to industries is key to securing a brighter future for the next generations. Particular attention should be paid to sustainable technologies that would allow the recovery of resources or energy from waste. Among these, pyrolysis combined with dry reforming (PCDR) of plastic waste stands out, garnering increasing interest (Olazar et al., 2024; Pawelczyk et al., 2022; Saad and Williams, 2017). PCDR involves decomposing plastic feedstock thermally under inert gas, followed by reforming the resulting volatiles to produce value-added products, e.g. synthesis gas. This approach not only tackles plastic waste management, but also offers an alternative to non-renewable resources for hydrogen production. Compared to conventional plastic waste management methods - incineration or landfilling, which emit toxic gases and leach harmful substances into the environment, PCDR emerges as a highly competitive and sustainable solution. Additionally, PCDR presents an opportunity to utilize carbon dioxide, aiding in climate change mitigation and promoting circular economy principles.

However, despite its potential, the technology is still in its early stages and requires further research before industrial-scale implementation. Key research area include suitable catalysts to ensure appropriate efficiency and stability of the process. Ni- or Co- based oxide catalysts commonly used in reforming processes are not sufficiently active or stable (Chen et al., 2020; Pawar et al., 2015; Pawelczyk et al., 2022). Transition metal carbides, in particular Mo_2C, have emerged as promising alternatives, exhibiting favorable activity in hydrocarbon reforming, and enhanced stability due to their characteristic oxidation-recarburization cycles (Czaplicka et al., 2021; Ma et al., 2017; Wang et al., 2022). Moreover, Mo_2C exhibits high catalytic activity in reforming of hydrocarbons with longer carbon chains, which is a promising prospect considering that the diverse hydrocarbon mixture is reformed in the PCDR process, not limited to methane (Czaplicka et al., 2021; Pawelczyk et al., 2022). Therefore, combining Ni or Co with carbide phase may result in beneficial effects on the catalyst performance.

The published research in the field of catalysts for PCDR is narrow, mostly limited to the conventional Ni or Co supported on oxides catalysts (Pawelczyk et al., 2022). Therefore, this work reveals novel Ni-Mo_2C/γ-Al_2O_3 catalysts. In order to obtain Mo_2C, the temperature-programmed carburization of organic-inorganic precursor method was used, offering a safer and more energy-efficient alternative to conventional methods that require utilization of gas hydrocarbons and hydrogen. Various amines (aliphatic, cyclic, aromatic) were used to synthesize the catalyst, demonstrating their influence on structural properties and activity. Catalyst characterization included BET surface area, XRD, CO_2-TPD, H_2-TPR, SEM and TGA. Catalytic activity was examined in PCDR of model mixture of polymers (LDPE, HDPE, PP, PS and PET) representing municipal waste plastics. The setup comprised a pyrolysis reactor followed by a fixed bed reforming reactor. Catalyst-to-plastic mass ratio was 0.5. The catalytic testing comprises the catalytic dry reforming of gases generated during pyrolysis-gasification step. The reforming was performed at 800°C, while the pyrolysis step was conducted from room temperature to 500°C. Output gases were chilled to capture condensable products, while remaining gases were analysed using gas chromatography. Non-catalytic PCDR served as a reference. Catalyst performance was evaluated based on synthesis gas yield, H_2:CO ratio, product distribution, CO_2 conversion, and catalyst stability. XRD, SEM, and TG analyses were also conducted post-reaction to assess structural changes and catalysts deactivation.

As presented in Fig. 1a, Ni-Mo_2C/γ-Al_2O_3_A, Ni-Mo_2C/γ-Al_2O_3_C, and Ni-Mo_2C/γ-Al_2O_3_H catalysts, synthesized using different amines (aniline, cyclohexylamine and hexylamine, respectively) showed high activity, resulting in notable improvements in syngas yields compared to non-catalytic process. The addition of catalysts enabled a syngas yield increase of over three times and a hydrogen yield boost of roughly tenfold. Moreover, different amines used for synthesis, influenced obtained syngas yield and composition, with Ni-Mo_2C/γ-Al_2O_3_H exhibiting the highest yields and H_2/CO ratio. In addition, obtained product distributions varied for different catalysts, indicating that variety of value-added products can be recovered from waste, depending on the catalyst

used. The investigation has shown that amine, besides carbon source, is a structure-forming factor that has a significant impact on the properties of the catalyst and, consequently, on its activity and stability. Catalyst properties, including surface area, pore size, basicity, and structure were affected. Catalysts also varied in crystallite size and Mo phase presence (Fig. 1b).

The obtained results indicate that catalysts based on metal carbides are promising candidates as catalysts for syngas generation from waste plastics. A significant influence of amine choice for catalyst synthesis was demonstrated. It was revealed that Ni-Mo_2C/γ-Al_2O_3 synthesized using hexylamine is the most promising catalyst among tested catalysts. Moreover, the carbide synthesis method is competitive to conventional methods in terms of cost and safety. Therefore, this work constitutes an important contribution to the field regarding pyrolysis combined with dry reforming as a sustainable method of plastic waste management.

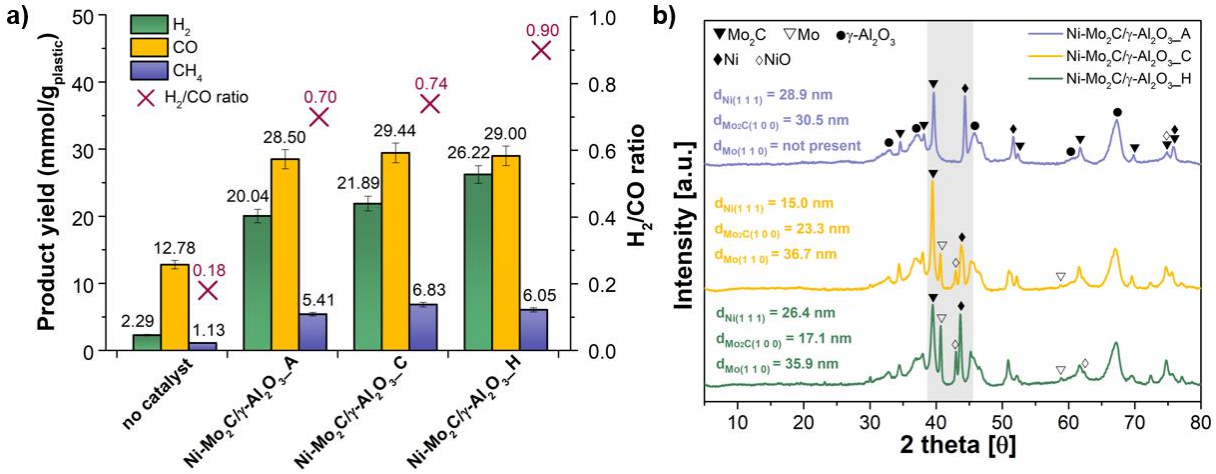

Fig. 1 a) Product yields and H_2/CO molar ratio obtained in PCDR of model mixture of plastics carried out without catalyst and over Ni-Mo_2C/γ-Al_2O_3 catalysts, b) XRD patterns and crystallite sizes for the synthesized Ni-Mo_2C/γ-Al_2O_3 catalysts.

References

Chen, S., Zaffran, J., Yang, B., 2020. Dry reforming of methane over the cobalt catalyst: Theoretical insights into the reaction kinetics and mechanism for catalyst deactivation. Appl Catal B 270, 118859. https://doi.org/10.1016/J.APCATB.2020.118859

Czaplicka, N., Rogala, A., Wysocka, I., 2021. Metal (Mo, W, Ti) carbide catalysts: Synthesis and application as alternative catalysts for dry reforming of hydrocarbons—a review. Int J Mol Sci 22. https://doi.org/10.3390/ijms222212337

Evode, N., Qamar, S.A., Bilal, M., Barceló, D., Iqbal, H.M.N., 2021. Plastic waste and its management strategies for environmental sustainability. Case Studies in Chemical and Environmental Engineering 4, 100142. https://doi.org/10.1016/J.CSCEE.2021.100142

Höök, M., Tang, X., 2013. Depletion of fossil fuels and anthropogenic climate change—A review. Energy Policy 52, 797–809. https://doi.org/10.1016/J.ENPOL.2012.10.046

Li, L., Zuo, J., Duan, X., Wang, S., Hu, K., Chang, R., 2021. Impacts and mitigation measures of plastic waste: A critical review. Environ Impact Assess Rev 90, 106642. https://doi.org/10.1016/J.EIAR.2021.106642

Ma, Y., Guan, G., Hao, X., Cao, J., Abudula, A., 2017. Molybdenum carbide as alternative catalyst for hydrogen production – A review. Renewable and Sustainable Energy Reviews 75, 1101–1129. https://doi.org/10.1016/j.rser.2016.11.092

Olazar, L., Saldarriaga, J.F., Lopez, G., Santamaria, L., Amutio, M., Olazar, M., Artetxe, M., 2024. Insight into the joint valorization of CO2 and waste plastics by pyrolysis and in line dry reforming for syngas production. Fuel Processing Technology 253, 108024. https://doi.org/10.1016/J.FUPROC.2023.108024

Pawar, V., Ray, D., Subrahmanyam, C., Janardhanan, V.M., 2015. Study of Short-Term Catalyst Deactivation Due to Carbon Deposition during Biogas Dry Reforming on Supported Ni Catalyst. Energy and Fuels 29, 8047–8052. https://doi.org/https://doi.org/10.1021/acs.energyfuels.5b01862

Pawelczyk, E., Wysocka, I., Gębicki, J., 2022. Pyrolysis Combined with the Dry Reforming of Waste Plastics as a Potential Method for Resource Recovery—A Review of Process Parameters and Catalysts. Catalysts 12, 362. https://doi.org/https://doi.org/10.3390/catal12040362

Saad, J.M., Williams, P.T., 2017. Pyrolysis-catalytic dry (CO2) reforming of waste plastics for syngas production: Influence of process parameters. Fuel 193, 7–14. https://doi.org/10.1016/J.FUEL.2016.12.014

Wang, H., Diao, Y., Gao, Z., Smith, K.J., Guo, X., Ma, D., Shi, C., 2022. H2 Production from Methane Reforming over Molybdenum Carbide Catalysts: From Surface Properties and Reaction Mechanism to Catalyst Development. ACS Catal 12, 15501–15528. https://doi.org/https://doi.org/10.1021/acscatal.2c04619