

Microwave-Heated Carbon-Coated Monolithic Reactor for Steam Reforming of Ethanol

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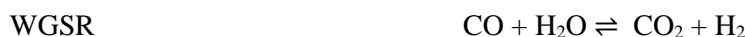
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Highlights

- Higher hydrogen yield and purity in the microwave-heated reactor than conventionally-heated one.
- Nickel-loaded carbon-coated monolith showed highly stable performance in ethanol reforming (SRE).
- Formation of instantaneous micro-plasmas helps decrease methane and coke formation in MW reactor.
- Volumetric heating of monolith by MW causes higher catalytic performance in SRE.

1. Introduction

There is an increasing need and demand for clean and environmentally friendly energy carriers due to the fast depletion of fossil fuels and the increase in the amount of environmentally harmful gases like carbon dioxide and methane. Hydrogen is an environmentally friendly and promising energy carrier and can be used as an alternative fuel for electricity generation in fuel cells. Bioethanol, which is a non-toxic alcohol, has a very high hydrogen content. Hence, ethanol steam reforming reaction (SRE) is considered a promising approach to producing high-purity hydrogen.



Microwave heating is brought to the fore due to the low energy consumption and improved catalyst performance [1]. Higher reaction rates and, thus, higher product selectivity and yield values are accomplished by using the microwave heating system by providing material-focused volumetric heating and by removing any potential cold spots in the reactor bed [2, 3]. Moreover, the formation of instantaneous micro-plasmas causes hot spots in the reactor, which help to obtain higher rates and product yields. Efficient heating by microwaves can be achieved with catalyst support materials having high microwave absorptivity such as a carbon-based material. Moreover, monolith-type catalysts can be used to minimize the mass transfer limitations of conventional fixed-bed systems.

2. Methods

Carbon-coated Cordierite monolith ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) was used as the catalyst support. Carbon coating was performed using sugar as the carbon source via a dip-coating method. The carbon-coated monolith was carbonized at 900°C and then, nickel (10%) was incorporated into the carbon layer of the monolith by an incipient wetness impregnation route. An image of the catalyst is shown in Fig.1a.

SRE catalytic activity tests were performed both in the microwave (MW) and conventionally (CONV) heated reactor systems at different temperatures (400°C - 600°C) at atmospheric pressure, with a feed composition of $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ being 1:1 by volume. Weight hourly space velocity of the reaction gas mixture was 4.8 h^{-1} in the activity tests. All these tests lasted 5 hours.

3. Results and discussion

In this study, nickel-impregnated carbon-coated monolithic catalysts were prepared, characterized, and tested in the SRE reaction in both MW-heated and CONV-heated reactors. The carbon-coated monolith is macroporous with an average pore diameter of $25.7 \mu\text{m}$. The surface area of the carbon layer of the monolith was $24.7 \text{ m}^2/\text{g}$, while the surface area of Ni incorporated material (Ni-CCM) was only $2.75 \text{ m}^2/\text{g}$, due to the blockage of the pores with nickel metal particles.

Almost complete conversion of ethanol and stable product distributions were obtained both in the CONV and MW-heated reactors. Activity test results proved the achievement of higher hydrogen concentration and yield in the MW-heated system than in the CONV-heated system. Hydrogen yield, which is defined as the number of moles of hydrogen produced per mole of reacted ethanol, showed an increase from 3.9 to 5.15 with an increase in temperature from 400°C to 600°C in the MW-heated reactor; while the corresponding value in the CONV-heated reactor was only 2.23 at 400°C (Fig.1b). Minimization of the radial temperature variations in the reactor by volumetric heating and formation of instantaneous hot spots (micro-plasmas) are the reasons of higher reaction rates and hence higher hydrogen yield in the MW system. The temperature of the instantaneous hot spots was reported as 100-200 K higher than the bulk temperature [4]. Another important advantage of the microwave-heated reactor is the minimization of methane concentration in the product stream (Fig.1c). While the methane mole fraction was 6 % at 600°C in the product stream of the CONV-heated reactor, this value was only 0.25 % in the MW-heated reactor. The presence of instantaneous hot spots may also be responsible for the decrease in the mole percentage of methane since higher temperatures favor the methane-reforming reaction. Another significant difference in the average product distributions of the MW and the CONV systems is related to the carbon monoxide and carbon dioxide concentrations. While the product stream contained 11.6 % CO in the CONV-heated system, this value increased to 21.3 % in the MW-heated reactor at 600°C. Moreover, while the product stream contained 10.3 % CO₂ in the CONV-heated system, this value decreased to 6.4 % in the MW-heated reactor at 600°C. The exothermic Boudouard reaction is the main coke formation reaction at lower temperatures. Compared to the CONV-heated reactor system, a greater mole percentage of carbon monoxide was obtained in the MW-heated system due to the suppression of the Boudouard reaction and also due to the contribution of reverse WGSR. These factors also caused coke minimization in the MW-heated reactor system.

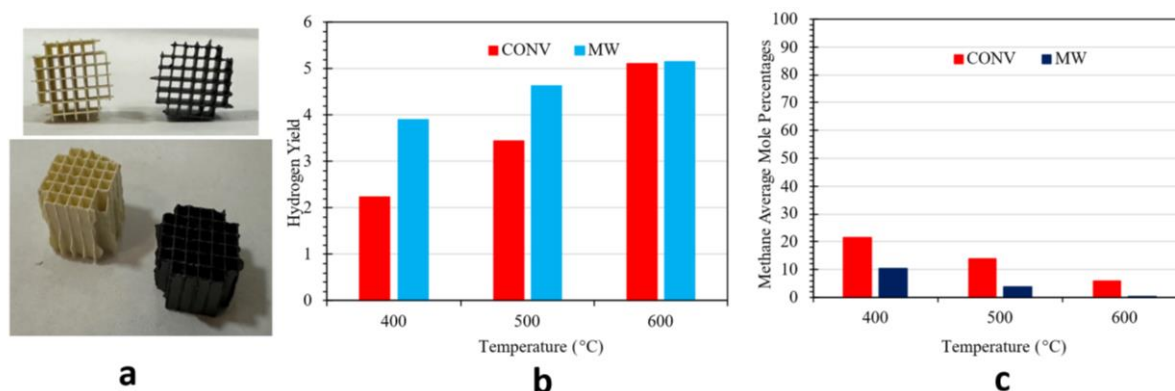


Figure 1. (a) Carbon-coated monolith; (b) Hydrogen yield in CONV and MW-heated reactors; (c) Comparison of the methane mole percent values in MW and CONV-heated reactors.

4. Conclusions

As compared to the CONV-heated reactor system, higher hydrogen purity and yield and also lower methane formation were achieved in the MW-heated system. Volumetric heating of the catalyst bed and the formation of instantaneous micro-plasmas in the MW-heated reactor cause instantaneous hot spots, which causes higher product yields and reaction rates. Results also proved that carbon-coated monolith was a promising support material to be used in the MW-heated reactor, by lowering the effects of transport resistances on the observed rate.

References

- [1] T. Dogu, G. Dogu, *Fundamentals of Chemical Reactor Engineering: A Multi-Scale Approach*, Wiley, 2022.
- [2] S. Gunduz, T. Dogu, *Appl. Catal. B: Env.*, 168 (2015) 497.
- [3] M. Sariyer, A.A. Bozdağ, N.A. Sezgi, T. Dogu. (2019). *Chem. Eng. J.* 377: 120138.
- [4] X. Zhang, D.O. Hayward, D.M.P Mingos, *Chem. Commun.* 9 (1999) 975-976

Keywords

Hydrogen; Microwave Heating; Monolith; Process Intensification.