ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Performances of Microwave and Conventionally Heated Reactors in Sorption Enhanced Reforming of Ethanol over Ni Impregnated SBA-15

Merve Sarıyer, Arzu Arslan Bozdag, Naime Aslı Sezgi*, Timur Dogu

Chemical Engineering Department, Middle East Technical University, Ankara, 06800
**Corresponding author: sezgi@metu.edu.tr*

Highlights

- Very high hydrogen yield obtained by sorption enhanced reforming of ethanol.
- Coke elimination was eliminated in the focused microwave heated reactor.
- Sorption enhanced reforming in the microwave reactor yielded high hydrogen purity.
- Ni impregnated SBA-15 gave excellent catalytic performance in ethanol steam reforming.

1. Introduction

Environmental concerns and fast depletion of fossil resources accelerated the research activities for the production of fuels and energy carriers from bio-resources. Advances in fuel-cell technology facilitated research activities for the production of hydrogen from renewables. Due to its high hydrogen content, non-toxicity and easy distribution possibilities, bio-ethanol is considered as a promising feedstock for hydrogen production at relatively low temperatures [1, 2]. However, thermodynamic limitations of ethanol steam reforming reaction (SRE) limit the achievement of high H_2 yields. Presence of CO in the product stream is also undesired for fuel-cell applications.

$$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2 \qquad \text{(SRE)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(WGSR)}$$

Sorption enhanced reforming of ethanol (SESRE) is a possible alternative to increase the yield of high purity hydrogen [3]. Coke formation is also an important undesired issue during SRE. Recent studies with microwave heated flow reactors indicated more stable reactor performance, higher yields and lower coke formation than the conventionally heated catalytic reaction systems [4-6]. Due to transfer of microwave energy directly to the catalyst particles and volumetric heating of the bed eliminates radial temperature gradients within the bed and more efficient utilization of energy. Formation of micro-plasmas within the catalyst bed was also reported to increase the activity of the catalyst, yielding higher hydrogen yields at lower temperatures, in the production of hydrogen from ammonia [5, 6]. In the present study, performances of microwave and conventionally heated flow reactors were compared for the production of high purity hydrogen, through steam reforming and sorption enhanced reforming of ethanol over a Ni impregnated SBA-15 type catalyst (Ni@SBA-15).

2. Methods

SBA-15 type silicate structured mesoporous catalyst support material having an ordered pore structure was synthesized by a hydrothermal route and 10% nickel was incorporated into SBA-15 following a wet-impregnation procedure. Catalytic activity tests for SRE and SESRE were performed both in a focused microwave (MWR) and conventionally heated tubular reactors (CHR). In the case of SESRE 0.15 g of catalyst was physically mixed with 1.5 g CaO, as a sorbent for in-situ removal of CO_2.

3. Results and discussion

Three well-resolved characteristic diffraction peaks for mesoporous SBA-15 were clearly observed in the low angle XRD patterns of the synthesized catalyst support. Moreover, both SBA-15 and Ni@SBA-15 showed type IV N_2 adsorption/desorption isotherms with H1 hysteresis loops. Surface area and mean pore diameter values of Ni@SBA-15 were 493 m^2/g and 6.6 nm, respectively.

Activity tests performed at 600°C gave complete conversion of ethanol. Comparison of the product distributions observed during the first hour of SRE and SESRE tests performed in both conventionally heated and microwave heated reactors clearly showed significant enhancement of hydrogen yield in SESRE tests (Fig.1a). In these tests, mole fraction of H_2 reached to 90% in the product stream, with negligible CO and CO_2. In-situ removal of CO_2 also facilitated WGSR, eliminating CO. In-situ removal CO_2 in the SESRE tests also decreased the occurrence of dry reforming of methane, causing some increase in CH_4 in the product stream. At reaction times higher than 120 min, decrease of H_2 and increase of CO, CO_2 mole fractions were observed, due to consumption of CaO as a result of its reaction with CO_2 (Fig.1b). It was also observed that the performance of the microwave reactor was more stable than the conventionally heated reactor, for both SRE and SESRE. Temperature uniformity in the radial direction and formation of micro-plasmas within the catalyst bed minimized coke formation in the microwave heated reactor (Fig.2). Experiments performed in the microwave reactor also showed higher activity of the catalyst in SRE at lower temperatures.

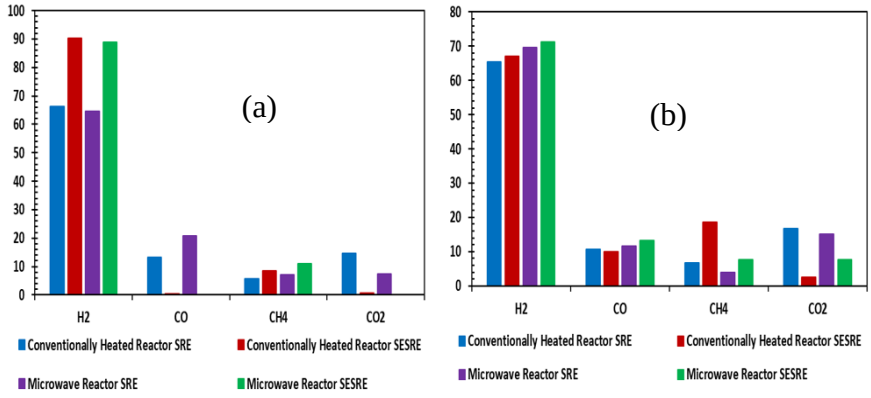

Figure 1. Comparison of product distributions for SRE ans SESRE in conventionally and microwave heated reactors at different reaction times at 600 °C: (a) 20 min; (b) 120 min

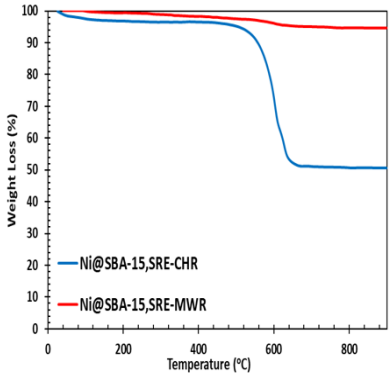

Figure 2. Amount of coke on spent catalysts evaluated by TGA.

4. Conclusions

In-situ removal of CO_2 in SESRE increased hydrogen purity and yield in both conventionally and microwave heated reactors. Highly stable reactor performance and minimization of coke formation was observed in the microwave heated reactor, in time-on stream tests. Results proved higher hydrogen purity in the microwave reactor compared to the conventional reactor. Volumetric heating of the bed instead of heating of the reaction feed stream increases the thermal efficiency of the microwave system. Elimination of radial temperature gradients and formation of micro hot spots (micro-plasmas) in the focused microwave system helped to increase activity of the catalyst and to eliminate coke formation.

Acknowledgement: TUBA and METU Research Funds.

References

[1] Arslan A., Gunduz S., Dogu T., Int. J. Hydrogen Energy, 39 (2014) 18264.
[2] Arslan A., Dogu T., Int. J. Hydrogen Energy, 41 (2016) 16752.
[3] Gunduz S., Dogu T., Ind. Eng. Chem. Res, 51 (2012) 8796.
[4] Gunduz S., Dogu T., Appl. Catal. B: Env., 168 (2015) 497.
[5] Varisli D., Korkusuz C., Dogu T. Appl. Catal B:Env., 201 (2017) 370.
[6] Guler M., Dogu T., Varisli D., Appl. Catal B:Env., 219 (2017) 173.

Keywords
Microwave–Assisted Reactions, Hydrogen, Ethanol Steam Reforming, Sorption Enhanced Reforming, Nickel, SBA-15