Chemical Engineering Journal 280 (2015) 468–474

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A microreactor with metallic catalyst support for hydrogen production by partial oxidation of dimethyl ether

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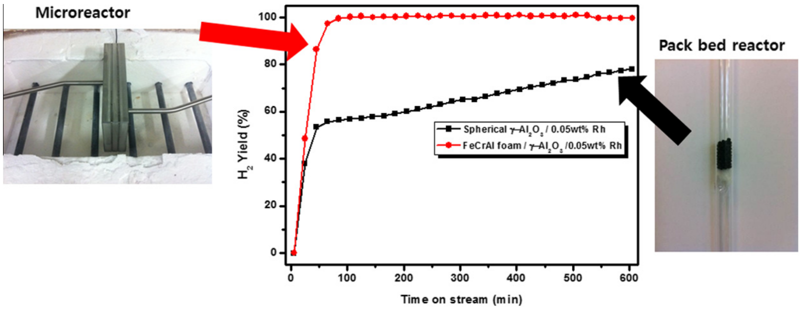
HIGHLIGHTS

- Microreactors with porous metallic catalyst support presented for hydrogen production.
- Its catalytic efficiency was compared with that of a conventional pack bed reactor.
- For similar catalytic activity, the microreactor used much less precious metal.
- Hydrogen production was stable up to 1200 h with the microreactor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 March 2015
Received in revised form 1 June 2015
Accepted 8 June 2015
Available online 15 June 2015

Keywords:
Microreactor
Metallic support
Hydrogen production
Dimethyl ether
Partial oxidation

ABSTRACT

A microreactor system with porous metallic catalyst support was prepared and its catalytic efficiency and long term stability were compared with those of a conventional pack bed reactor using partial oxidation of DME for production of hydrogen. The microreactor system had a thin layer of γ-Al_2O_3 on FeCrAl metal foam as catalyst support. The pack bed reactor had γ-Al_2O_3 balls densely packed in a quartz tube. With enough catalyst materials (0.5 wt% Rh), both of the reactors showed good hydrogen yield higher than 90% at reaction temperature up to 750 °C. However, with decreasing Rh content, the pack bed reactor showed deteriorating reaction efficiency while the microreactor maintained the efficiency. In the end, in order to maintain similar reaction efficiency for long term hydrogen production, 10 times more Rh content was necessary for the pack bed reactor than that needed for the microreactor. The pack bed reactor maintained hydrogen production only up to about 120 h, while the microreactor maintained hydrogen production up to 1200 h, 10 times longer than that of pack bed reactors. This comparison shows superior reaction efficiency and stability of metallic support loaded microreactors over conventional ceramic support loaded pack bed reactors for exothermic and high temperature reactions.

1. Introduction

Fuel cells are one of promising candidates for generating clean energy. Fuel cells utilize hydrogen or hydrogen rich gas as fuel. In order to make the fuel cell technology more available and widespread, it is essential to develop reliable technologies which ensure a steady supply of hydrogen as fuel. Therefore, there have been intensive research activities aiming for producing hydrogen through the processing of hydrogen rich fuels. For example, hydrocarbons [1–6], alcohols [7–9], and biomass have been studied as hydrogen source. Dimethyl ether (DME) has been also recognized as a potential hydrogen source for power generation. DME has many advantages as a hydrogen source such as high hydrogen to carbon ratio, non-toxic and non-corrosive nature, high energy density, no carbon–carbon bond, low reforming temperature (200–400 °C), and similar physical properties to LPG that possibly enable adoption of LPG infrastructure to process DME.

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http://dx.doi.org/10.1016/j.cej.2015.06.038
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Furthermore, DME can be easily synthesized from natural gas, coal, crude oil, and biomass [10–16].

For hydrogen generation using DME, steam reforming [15–20], and partial oxidation [12–14,21,22] have been investigated extensively using conventional pack bed type reactors. For these reactions, catalyst particles are dispersed on metal oxide carriers, typically on alumina powder. In practice, these metal oxide catalyst carriers are press formed in a ball shape and those balls are packed into pack bed reactors. Catalyst particles, usually precious metals, are impregnated on those metal oxide balls. During the impregnation, excessive amount of catalyst materials are impregnated deep into the metal oxide balls and not all of the impregnated catalyst particles may participate in the reaction, wasting expensive precious metals. Also, as PO of DME is exothermic, and the reaction could form hot spots in the reactor, leading to deactivation of the conventional pack bed catalyst. Metallic catalyst supports with thin layers of metal oxide carriers could be a solution for those problems by reducing excessive impregnation as metallic supports will not be impregnated and dissipating reaction heat through metallic support.

However, it is not easy to have a good adhesion between metallic catalytic support and metal oxide carriers coated onto it due to the big difference between their thermal expansion coefficients. In order to overcome this problem, for example, anodization of aluminum plate was tried and successfully demonstrated. This one-body metal (aluminum)–metal oxide (alumina) structure could be successfully implemented as plates for microreactors [23–25]. However, reaction temperature of this structure is limited up to 600 °C because the alumina structure cannot be maintained at higher temperature. Recently, we have demonstrated that the adhesion between metallic support and metal oxide carriers could be adequately strong to endure repeated thermal shock up to 700 °C by using FeCrAl foam as metallic support and making the support surface rough [26].

As metallic support can be planar, it is ideal to be used in a microreactor. Microreactor technology is attracting more and more interest for hydrogen production reactions for their small volume, excellent mass and heat transfer properties, controllable short residence times, uniform flow patterns, and safe operation in explosive regimes [27]. Most importantly, high mass and heat transfer rates in microreactors lead to development of more efficient and compact fuel processing systems compared to conventional pack-bed systems [24,25].

The objective of this study is to demonstrate a microreactor system with a metallic catalyst support as an efficient and sustained source of hydrogen fuel using Rh catalyst materials for PO of DME at reaction temperature up to 750 °C. We investigated the efficiency and the amount of the catalyst needed for the reaction in our microreactor and compared them with those of a conventional pack-bed reactor. By coating a thin layer of alumina on metal foam with good adhesion strength, we aimed to reduce the amount of precious metal impregnated on the alumina in the microreactor, while keeping the reactor efficiency as good as or better than conventional pack-bed reactors. Long term stability of the reactor was also compared to that of pack-bed reactor.

2. Experimental

2.1. Catalyst support preparation

We used FeCrAl alloy foams as metallic catalyst support (Alantum). Their composition was 20 wt% Cr, 6 wt% Al and Fe balance. Average pore size of the foam was 800 μm with 90% porosity [26]. The foam was cut 2 cm × 4 cm in size (Fig. 1). It has specific surface area (SSA) of 8.7 m^2/L. Macroscopically porous metal foams are ideal for maximizing exposed surface area to the reactant gases. The sample pieces were cleaned in acetone bath under ultrasonic vibration for 10 min and in distilled water for 10 min. γ-Al_2O_3 powder was from AEROXIDE (AluC) and had SSA of 107 m^2/g. Washcoat suspension was prepared with a standard composition of 70 g of γ-Al_2O_3, 90 g of distilled water, and 1 ml of nitric acid. γ-Al_2O_3 slurry was prepared by vigorous stirring of the suspension for 90 min in an attrition mill. Desired solid content in the slurry was controlled by regulating the ratio of the amount of γ-Al_2O_3 to that of distilled water. Acidity (pH value) of the slurry was adjusted using nitric acid (HNO_3). FeCrAl alloy foams were coated with the prepared washcoat by dipping the foams into the washcoat solution for 10 s. As our previous research [26], the amount of γ-Al_2O_3 incorporated to FeCrAl foam was approximately 20 wt% of FeCrAl foam. In a typical case, the weight of FeCrAl foam (2 cm × 4 cm) used for microreactor was about 1.6 g and loading of γ-Al_2O_3 was about 0.32 g. After washcoat, they were dried by air blowing (20 psi) to remove residual slurry. The washcoated FeCrAl foams were then dried thoroughly in an oven at 120 °C for 1 h, and subsequently calcined at 750 °C for 3 h. Heating and cooling rates of calcination were 3 °C/min and 5 °C/min, respectively [26]. Detailed analysis on the adhesion strength of γ-Al_2O_3 layer on FeCrAl foam under thermal and mechanical stresses was reported elsewhere [26]. In short, γ-Al_2O_3 layer on FeCrAl foam showed excellent adhesion under repeated thermal shock between room temperature and 700 °C. When the temperature was held at 700 °C for 1000 h, there was no noticeable damage to the coated γ-Al_2O_3 layer. Under mechanical stress of ultrasonic vibration in petroleum ether, weight loss of γ-Al_2O_3 layer coated FeCrAl foam was negligible compared to other previous similar studies. It was thought to be due to minimal interfacial force built up by thermal and mechanical stress at the interface surface with thin ligaments in the metal foam in the order of 10 μm [26].

2.2. Catalyst preparation

$RhCl_3 \cdot xH_2O$ (45.5% Rh content, Alfa aesar) was used as precursors for catalyst. Our previous study showed that metal concentration of 0.5 wt% Rh had a good efficiency for PO of DME [24]. Considering this result, γ-Al_2O_3 washcoated FeCrAl foams were impregnated with Rh catalyst with 0.5 (1.8 mg Rh), 0.1 (0.36 mg Rh), and 0.05 wt% (0.18 mg Rh) of Rh loading (to the weight of γ-Al_2O_3 washcoat) as follows. Rh precursor was dissolved with stirring in required amount of water. γ-Al_2O_3 washcoated FeCrAl foams were dipped in the solution for 1 min and dried at room temperature for 24 h. In order to remove water and chloride, impregnated samples were further dried at 120 °C for 1 h and calcined at 750 °C for 3 h. For comparison, Rh catalyst were impregnated in spherical γ-Al_2O_3 balls (1.7–2.0 mm, SSA 300 m^2/g) by the same method mentioned above with the same loading ratios. Rh-impregnated γ-Al_2O_3 balls were used in conventional pack bed reactor. The amount of γ-Al_2O_3 in the microreactor was the same with that in the pack bed reactor. For this reason, actual amount of Rh added to γ-Al_2O_3 washcoated FeCrAl foam was the same as that in γ-Al_2O_3 balls in the pack bed reactor for the same Rh loading wt%.

2.3. Surface area and pore size of prepared γ-Al_2O_3 supports

The BET method was used to measure specific surface area (SSA) and the BJH method was used to measure average pore size of prepared γ-Al_2O_3 supports (γ-Al_2O_3 washcoat on metal foams and γ-Al_2O_3 balls before and after Rh impregnation) by nitrogen sorption (ASAP 2000, Micromerities). Specific surface area (SSA) of γ-Al_2O_3 balls we used in a fixed bed system was 315.5 m^2/g. After Rh impregnation, the value was reduced to 164.2 m^2/g. SSA