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Performance and cold spot effect of methanol steam reforming for hydrogen production in micro-reactor

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ABSTRACT

Catalytic hydrogen production by methanol steam reforming is considered to be an attractive hydrogen source option. However, performance of conventional packed beds for methanol steam reforming may be limited by heat transfer, which results in a low effective factor of the catalyst. In this work, $CuO/ZnO/Al_2O_3$ catalyst particles with diameter of 0.5 mm were filled in the micro-reactor for hydrogen production by methanol steam reforming. At steam to methanol ratio of 1.3, effects of inlet temperature, space velocity on reactor performance were investigated. The temperature distribution in the catalyst bed has also been studied. Results showed that methanol conversion decreased with space velocity and it increased with inlet temperature. Hydrogen production yield increased firstly and then decreased with space velocity. And it increased with the increasing of temperature. However, CO content in the product also increased with temperature, and it decreased with the increasing of inlet space velocity, especially at low temperature condition. Compared to conventional tubular fixed bed reactor, the micro-reactor presented a slightly better performance due to the fixed bed nature of catalyst, which is inefficiency in tubular reactor. Cold spot was observed at inlet of micro-reactor reaction chamber, and the highest temperature difference at cold spot area reached about 6 K. The maximum temperature difference throughout the catalyst bed reached 10 K in the micro-reactor.

Introduction

Proton exchange membrane fuel cell (PEMFC) is recognized as an efficient, energy saving, environmentally friendly method of power generation in 21st century [1,2]. However, before PEMFC commercialization, convenient hydrogen source needs to be found [3]. Hydrogen production through methanol steam reforming (MSR) is an effective way for PEMFC, since it has the advantages of low reaction temperature, high hydrogen content and low carbon monoxide concentration at reactor outlet [4,5]. But MSR is an endothermic reaction, traditional fixed bed reactors are reported to be limited by heat and mass transfer and show a low reaction rate, slow dynamic response. That

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results in a temperature decline at reactor inlet which is usually called cold spot effect in its catalyst bed, leading to a lower catalyst efficiency and reactor efficiency [6,7]. Compared with conventional reactor, micro-reactor has the advantages of small, rapid startup and high safety performance, which is very suitable for mobile hydrogen production [8–11]. Therefore, lots of research has been carried out on MSR using micro-reactors.

In general, two aspects are focused on hydrogen production through MSR in micro-reactors. One is the catalyst preparation. MSR process is enhanced through the adoption of precious metal catalyst material, coating catalyst prepared by new methods [12–14]. However, precious metal catalysts predominantly are not selective for the methanol reforming reaction, and it accounts for a high portion of the reactor operating cost [14–16]. The other one is heat and mass intensification by reactor structure optimization, flow distribution, catalyst distribution et al. [17–20]. Micro-reactors can offer a higher heat transfer rate than the traditional Tubular reactors because of its high surface-to-volume ratio and short conduction paths. A shorter radial diffusion time is ensured when the smaller diameters of the reactor channels are adopted. This leads to a higher heat transfer coefficient, which is advantageous because the heat transfer coefficient is known to influence catalyzed reaction process [21–24]. Micro-reactors are increasingly a hot topic as a novel tool in process intensification for hydrogen production [25–30].

In this study, a plate-type stainless steel micro-reactor is designed and fabricated. It aims to compare the performance of the Micro-reactor with the Tubular reactor for MSR. Also, the effect of space velocity and temperature on the methanol conversion the hydrogen production rate is investigated. Temperature distributions in the reaction chamber are especially measured by thermocouples in order to study the cold spot effect in catalyst bed, since temperature gradient may lead to catalyst low efficiency and deactivation.

Experimental

Reactor and catalyst

The plate-type stainless steel micro-reactor consists two chambers. One chamber is used for reactant vaporization and superheating. The other is used for methanol steam reforming reaction. The mixture of reactants was superheated before entering reaction chamber with sizes of 50 mm × 60 mm × 3.5 mm. Holes of 1.5 mm in diameter were arranged at the cover plate to measure inside temperature of reaction chamber. T-type thermocouples were adopted for temperature monitoring. Heat was supplied to the vaporization/superheating and reaction sections of the reactor respectively by electrical heating, as shown in Fig. 1. The catalyst used is type CB-7 commercial $CuO/ZnO/Al_2O_3$ catalyst, with a diameter of 0.5 mm and weight of 5.6 g. The weight percentages of the catalyst are shown in Table 2. Quartz powders of the same diameter are used as inert material. Methanol conversion X_{MeOH}, hydrogen production rate Y_{H2} and weight hourly space velocity ($WHSV$) were calculated by the following equations.

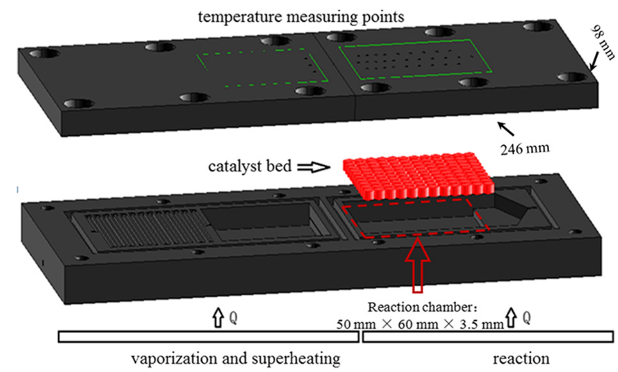

Fig. 1 – Schematic diagram of micro-reactor structure and catalyst distribution.

$$X_{MeOH} = \frac{F(y_{co} + y_{co2})}{22.4 \times \upsilon_{MeOH,in}} \times 100\% \quad (1)$$

$$Y_{H2} = F \times y_{H2} \quad (2)$$

$$WHSV = \frac{32 \times \upsilon_{MeOH,in}}{M} \quad (3)$$

where, $\upsilon_{MEOH,in}$ is the molar flow rate, F is effluent gas flow rate. y_{CO} and y_{CO2} are the volumetric fraction of CO and CO_2 respectively, which are measured by the gas chromatograph, and M is the weight of catalyst. For both plate-type and packed-bed tubular reactor, data processing procedure is the same.

In order to obtain the temperature distribution in the catalyst bed, thermocouples are used on the reactor reaction section. The layout of the thermocouples is shown in Fig. 1. According to Refs. [6,7], at reactor inlet, MSR reaction is stronger which may resulted in large variation of temperature, so the distribution of temperature measuring points is inhomogeneous along the reactant flow direction. Temperature

Table 1 – Uncertainty of the instruments.

Instrument	Model	Measurement range	Absolute error
Balance	FA1104	0.1–110 g	±0.1 mg
Soap foam flow meter	EL-102B	1-1000 mL/min	±0.1 ml/min
Data acquisition instrument	Agilent 34970A		±0.1 K
Injection pump	DSP-2	0.1–50 ml/min	±0.05 ml/min
Voltage regulator	TSGC	5-250 V	±0.5 V
High-precision stopwatch	ZSD-6005		±1 ms

Table 2 – Weight percentages of the catalyst.

Composition	Wt.%
CuO	≥65.0
ZnO	≥8.0
Al_2O_3	≥8.0
Other	≥2.0