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Experimental investigation of axially non-uniform catalysis for methanol steam reforming

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HIGHLIGHTS

- The performance of coating bed of uniform distribution is superior to packed bed.
- The catalyst activity distribution of coating-bed I turns out to be the optimal.
- The minimal temperature of 3 K has been detected in the case of coating bed I.
- The highest conversion of coating-bed I is 9.84% higher than the uniform case.

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ABSTRACT

To enhance the hydrogen production, we designed a plate-type reactor to investigate the effect of the catalyst activity distribution on methanol steam reforming. The methanol steam reforming performance on a commercial $CuO/ZnO/Al_2O_3$ catalyst in a packed bed and a coating bed were compared experimentally. We found that higher conversion was achieved for the coating bed of uniform axial catalyst distribution compared to the packed bed. The cold spot temperature difference is restricted by using a higher fraction of inert particles at the inlet of the reactor and using a lower fraction of inert particles near the outlet of the reactor. Alleviating the cold spot difference can contribute to the improvement of the reactor performance. The minimum temperature of 3 K was determined in the case of coating bed I. This improvement results from the use of the appropriate non-uniform catalyst distribution to induce a favorable interaction among the mass and heat transfers. The highest conversion of 96.26% was achieved at the inlet weight hourly space velocity of 0.97 h^{-1} when the temperature was 543 K.

1. Introduction

Methanol can be converted to hydrogen at lower temperature than most other fuels because it contains no carbon–carbon bonds that must be broken. Methanol can be produced from a variety of sources, such as natural gas, coal, and biomass [1]. In industry, methanol is primarily formed from natural gas. The energy balance moving from syn-gas to methanol and then back to hydrogen is negative [2]. However, methanol is an excellent hydrogen carrier and a reasonable energy carrier, and it does not suffer from storage and transportation issues [3]. Compared with hydrogen, methanol provides easier and safer transportation [1]. This conversion of methanol to hydrogen is justified because the reformation of liquid fuels may become an important process for hydrogen production for on-site stationary fuel cell or on-board mobile fuel cell applications [4]. From a health viewpoint, methanol is worse than some fuels but better than others. For example, methanol is safer than gasoline but is less safe than diesel. Methanol ingestion is the primary health concern because it produces formic acid in the human body when metabolized [5]. The overall absorption rate of methanol was found to be much less than its metabolism rate, even in a worst-case exposure situation [6]. Fuels for hydrogen production are numerous, and decisions on the choice of fuel are made based on which parameter is deemed most important for the system. Because methanol is inherently a synthetic fuel, it does not suffer from sulfur contamination [7,8]. Because a system does not require a front-end desulphurization operation or sulfur-tolerant catalysts to operate on methanol, methanol is very favorable for hydrocarbon reforming [9]. The methanol steam reforming approach could obtain lower CO production in the products compared to other methanol conversion methods. As a result, methanol steam reforming (MSR) is generally the most economic approach to

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producing H_2 [2]. The catalytic production of hydrogen by methanol steam reforming is an attractive option for on-site stationary fuel cell or onboard mobile fuel cell applications [3]. The conventional packed bed MSR method, which is widely used in industry, suffers from axial temperature gradients and the problems such as the occurrence of cold spots [8]. These disadvantages result from the severe limitations of mass and heat transfer [10]. These axial temperature gradients lead to thermal stresses in the channels [11]. Catalyst performance characteristics, such as stability and durability, are significantly affected by the thermal stresses [12]. Furthermore, because of the severe transfer resistance, conventional steam reformers are limited to an effectiveness factor of the catalyst that is typically less than 5% [13].

The $CuO/ZnO/Al_2O_3$ catalyst has been extensively used in methanol reforming [14]. It is generally agreed that the active component in the $CuO/ZnO/Al_2O_3$ catalyst is copper [15]. The role of ZnO is regarded as relatively minimal, but it is required as a textural support in segregating the Cu, which is highly susceptible to sintering [16]. The use of alumina creates a high surface area support that serves to increase copper dispersion and decrease the susceptibility to sintering [17]. Maintaining an optimum oxidization state is an important feature of the commercial $CuO/ZnO/Al_2O_3$ catalyst [14]. Research groups have sought to develop a novel catalyst to achieve improved performance in methanol reforming. Takahashi reported that an amorphous CuZrPd alloy catalyst was formed by adding palladium to a CuZr catalyst. Although the CuZrPd alloy accelerated methanol conversion, it produced more CO than CuZr alone because this alloy facilitated methanol decomposition [18,19]. Karim and Dagle reported that Pd was eventually alloyed with Zn and PdZn crystallites, resulting in the production of more CO [20,21]. Velu et al. studied methanol steam reforming over CuZnAl(Zr)-oxide catalysts. The surface area and dispersion of Cu were found to be improved by adding Zr to the CuZnAl catalyst. However, CO_2 and CO were both found to be primary products [22,23]. Precious metals and other group VIII metals exhibit more active performance for methanol conversion [24]. However, they predominantly catalyze methanol decomposition and are not selective for the methanol reforming reaction [25]. Although noble metal catalysts dealt with the problem of the sintering and deactivation of Cu-based catalysts at high temperature, the high cost and the production of more CO remain problematic because it is acknowledged that CO is a poison for the anode electro catalyst of proton exchange membrane fuel cell [18]. In addition, the catalyst accounts for a high portion of the reactor operating cost. As a result, we used the commercial $CuO/ZnO/Al_2O_3$ catalyst for our study.

Micro-reactors are also used because their high surface-to-volume ratio and short conduction paths are able to offer a higher heat transfer rate than the traditional chemical reactors [26]. The small diameters of the reactor channels ensure a short radial diffusion time, leading to a high heat transfer coefficient, which is advantageous because the heat transfer coefficient is known to influence the homogeneously catalyzed reaction [27]. Thus, micro-reactors are increasingly recognized in recent years as a novel tool for chemistry and chemical process. Deqing Mei and Wei Zhou enhanced the performance of hydrogen production through the use of a micro-reactor [28,29]. B. H Howard achieved a 90% conversion efficiency by integrating a micro-channel heat exchanger [30]. However, several difficulties and challenges persist. Ayman Karim investigated the effect of reactor diameter on the cold spot temperature difference, and he found that the MSR in a packed bed reactor only 1 mm in diameter suffered from a cold spot temperature difference of up to 22 K due to the heat transfer limitation [31,32]. Moreover, the temperature difference or cold spot could be removed only when the equivalent diameter was as small as 300 μm [31]. Unfortunately, such micro-scale reactors are impractical for real industrial applications. One problem is that the characteristics of such micro-scale reactors lead to a large amount of heat losses from the reactor to the ambient because micro-reactors exhibit high specific surfaces [26]. Another problem is the difficulty in introducing the catalytic active phase into the micro-channel when using micro-reactors in heterogeneously catalyzed gas-phase reactions [33]. In addition, each channel must be packed identically to avoid misdistribution because random packing would result in a high-pressure drop [33].

The reforming reactions are a complex catalytic process consisting of multicomponent flow and diffusion. A reforming reaction is controlled not only by the kinetics of the reaction but also by the catalyst activity and thermal effects load at local position [1]. Dalla Betta described a method to avert the hot spot problem, which is a factor for coking and unsatisfactory reactor yield, by using a graded catalyst distribution in a highly exothermic methanol combustion reaction [34,35]. Tronci demonstrated that non-uniform distributions could shift the light-off position towards the inlet of the monolith [12]. Quina and Berger applied catalyst dilution to produce a higher yield without increasing the peak temperature [36]. Sung-won Hwang used side-streams and inert pellets to control the temperature profiles; the feed-stream distribution could not reduce temperature peak as effectively as catalyst dilution [29,37]. This behavior is attributed to the superior thermal management in local areas.

This study aims to investigate the effect of the catalyst activity distribution on methanol steam reforming and to compare the performance of a packed bed to a coating bed. The use of catalyst dilution was explored to reduce the reaction rate and heat consumption at critical points inside the plate-type reactor. While the total catalyst amount was kept constant, the dilution ratios in the three different coat-beds were used to control the temperature profile at the maximization of yield. Because the degree of stream bypass depends on the degree of segregation of the catalyst and the diluents, the catalyst is sufficiently well mixed with the inert particles to prevent the conversion decrease.

2. Experimental apparatus

2.1. Plate-type reactor design

Two chambers were integrated into a plate-type stainless steel micro-reactor. The steam of water and methanol was superheated before entering the 6 mm × 6 mm × 125 mm reaction chamber. Holes 1.5 mm in diameter, for measuring the temperature, were arranged axially in the cover plate of the reaction chamber. The axial temperatures of the reaction chamber were monitored using T-type thermocouples, as shown in Fig. 1.

2.2. Packed bed design and preparation

The commercial $CuO/ZnO/Al_2O_3$ catalyst (CB-7) from Chuanhua Co. Ltd. was used in all the experiments. For the packed bed, the catalyst was crushed and sieved to a particle size of approximately 0.5 mm. Next, 3.5 g of the catalyst was homogeneously mixed with 1.6 g of quartz particles (0.5 mm in diameter), which exhibited no catalysis for this reaction, and then, the mixture was uniformly packed into the reaction chamber.

2.3. Coating bed design and preparation

Slabs of commercial aluminum were used as supports. The dimensions of the support samples were 20 mm × 6 mm and 1 mm in height. The supports were pre-treated before wash coating. The