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Measurement of concentration profiles over $ZnO–Cr_2O_3/CeO_2–ZrO_2$ monolithic catalyst in oxidative steam reforming of methanol

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Abstract

Oxidative steam reforming of methanol (OSRM) reaction was investigated over a novel monolithic $ZnO–Cr_2O_3/CeO_2–ZrO_2$ catalyst developed in our laboratory. A novel flat-bed reactor was designed to measure the concentration profiles of the monolithic catalyst beds under different operation conditions: water-to-methanol mole ratio (W/M) between 1 and 1.5; oxygen-to-methanol mole ratio (O/M) in the range of 0.1–0.3; space velocity ranging from 1840 to 2890 h^{-1}; and reaction temperature in the scale of 400–440 °C. On the basis of these results, reaction pathways for the OSRM were discussed. It is indicated that only three independent reactions dominate in our reaction system, namely, the partial oxidation of methanol, the steam reforming of methanol and the methanol decomposition reaction, whereas the water–gas shift and the reverse water–gas shift reactions should be ignored. In addition, the steam reforming of methanol proceeds along all the catalyst bed, whereas methanol decomposition and oxidation reactions occur mainly at the entrance of the catalyst bed.

Keywords: Concentration profile; Methanol; Oxidative steam reforming; Monolithic catalysts

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1. Introduction

Today hydrogen is expected as an attractive candidate for alternative power sources in the future. Therefore many efforts have been made to develop fuel processing technology for producing hydrogen [1,2]. Among the various processes that have been proposed for hydrogen generation, oxidative steam reforming of methanol (OSRM) is regarded as one of the leading candidates [3–11].

With respect to the detailed thermodynamic analysis of the oxidative steam reforming, most researchers regarded the OSRM reaction as a combination of partial oxidation (POX, Eq. (1)) and steam reforming of methanol (SRM, Eq. (2)) reactions at such a certain ratio that the overall reaction is thermally neutral [3–8].

$$\begin{aligned}&CH_3OH(g) + 1/2O_2 = CO_2 + 2H_2\\&\Delta H^0 = -192.3\ \mathrm{kJ/mol}\end{aligned} \tag{1}$$

$$\begin{aligned}&CH_3OH(g) + H_2O(g) = CO_2 + 3H_2\\&\Delta H^0 = 49.5\ \mathrm{kJ/mol}\end{aligned} \tag{2}$$

On the other hand, Lyubovsky and Agrell et al. [9–11] have proposed that OSRM is the coupling of the exothermic total oxidation (Eq. (3)) reaction with the endothermic steam reforming (Eq. (2)) reaction.

$$\begin{aligned}&CH_3OH(g) + 3/2O_2 = CO_2 + 2H_2O(g)\\&\Delta H^0 = -675\ \mathrm{kJ/mol}\end{aligned} \tag{3}$$

In the OSRM process, the oxidation and reforming reactions can thermally balance each other. This allows the system to be more compact and efficient, as well as showing a fast response to load changes. Therefore, studies concerning oxidative steam reforming of methanol for hydrogen production have received considerable attention. These studies were mostly concerned with the effects of catalyst composition, reaction temperature, water-to-methanol molar ratio (W/M) and oxygen-to-methanol molar ratio (O/M), as well as space velocity of methanol, on the performances of the catalysts [3–7,11]. Furthermore, due to the complexity of reaction network of OSRM process, besides SRM and POX, other reactions such as combustion of methanol, decomposition of methanol and water–gas shift reaction can also occur [9,11–14]. As a

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result, reaction mechanisms and the pathway of CO formation are widely debated [4,12–15].

The configuration of the catalyst in OSRM has also been regarded as a focus. Traditionally, methanol reforming has been performed over pellet catalyst, which may be unsuitable for mobile applications due to their attrition. Comparatively, ceramic monoliths are uniform flow-through structures, characterized by a good mechanical strength and a low pressure drop [16]. For exothermic reactions, such as partial oxidation or combined reforming (operating under exothermic conditions), the use of monoliths can be of advantage, since heat can be transferred axially through each channel thus obtaining a uniform temperature distribution [17].

To our knowledge, differing from other reaction systems producing hydrogen [18,19], few investigations on the OSRM reaction over monolithic catalysts have been conducted [17], especially concerning measurement of concentration profiles over the catalyst bed length [9,20]. This is mainly due to the difficulties in sampling from narrow channels.

In this work the OSRM reaction was studied experimentally over a novel $ZnO–Cr_2O_3/CeO_2–ZrO_2$ monolithic catalyst which had been proved to be highly active in our previous tests [21]. A flat-bed reactor was designed to measure the concentration profiles of the monolithic catalyst bed under different operating conditions. On the basis of these results, reaction pathways for the OSRM were discussed.

2. Experimental

2.1. Monolithic catalyst preparation

Cordierite ($2MgO·2Al_2O_3·5SiO_2$) monolithic substrates with 400 cpsi (cells per square inch) supplied by Corning Corporation, were firstly pretreated with diluted acid, then coated with a $CeO_2–ZrO_2$ wash-coat via the sol–gel method to increase the surface area and to enable a good dispersion of the catalytic materials. Afterwards, they were calcined at 800 °C for 2 h. The procedure was repeated until 20–60 wt.% $CeO_2–ZrO_2$ had been deposited on the monolith. Subsequently, the active materials Zn and Cr, all in the form of nitrates, were dissolved in water and mixed in fixed weight ratios. Then the monolith coated with $CeO_2–ZrO_2$ was dipped into the metal nitrate solutions by a unique hot-impregnation method, followed by drying, and finally calcined at 800 °C for 2 h. The procedure was repeated until the metal loading in each monolith was 20–60 wt.% of the wash-coat. This catalyst had been proved to have a high activity and stability. It did not require an activation process before use, and could maintain 100% conversion even after 1000 h time on stream [21].

2.2. Experimental setup

2.2.1. Flow scheme

The experiments were carried out under atmospheric pressure in a flat-bed quartz-glass reactor. Fig. 1 shows the flow scheme. First, the methanol–water mixture with a specific proportion was introduced to an evaporator by a HPLC pump (supplied by Lab Alliance), then mixed with a pre-heated O_2/N_2 gas mixture (O_2 20.37%, N_2 79.63%) controlled by a mass flow controller. Subsequently all the gas mixtures entered the flat-bed reactor. The reactor was thermostated by two electric heating bandages, controlled by two temperature controllers respectively to maintain the isothermal condition along the reactor. The temperature was measured by two chromel–alumel thermocouples close to the inlet and the outlet of the monolith inside the quartz tube, as shown in Fig. 1. The temperature deviation along catalyst length was only several centigrades. After the reaction, the product gases passed through a condenser which was followed by a desiccator to dry the gases. The dry-base gases were then analyzed by two sets of on-line GC. A HP6890 equipped with an active carbon column and TCD was used to analyze the primary components of H_2, CO, CH_4 and CO_2, whilst another GC960 equipped with a molecular sieve 5A column and TCD was used to analyze the primary components of O_2 and N_2. The flux of the reformate gas was measured by a bubble flow meter at the end. Prior to and after each experiment N_2 was injected for half an hour to the reaction system to flush the remnant reactants and products.

2.2.2. Reactor

To achieve the measurement of concentration profiles along the monolith catalyst, a rectangular flat-bed reactor and a sliced catalyst were specially designed, as shown in Fig. 2. The reactor was made of quartz, which showed negligible catalytic activity under our operating conditions. To eliminate the

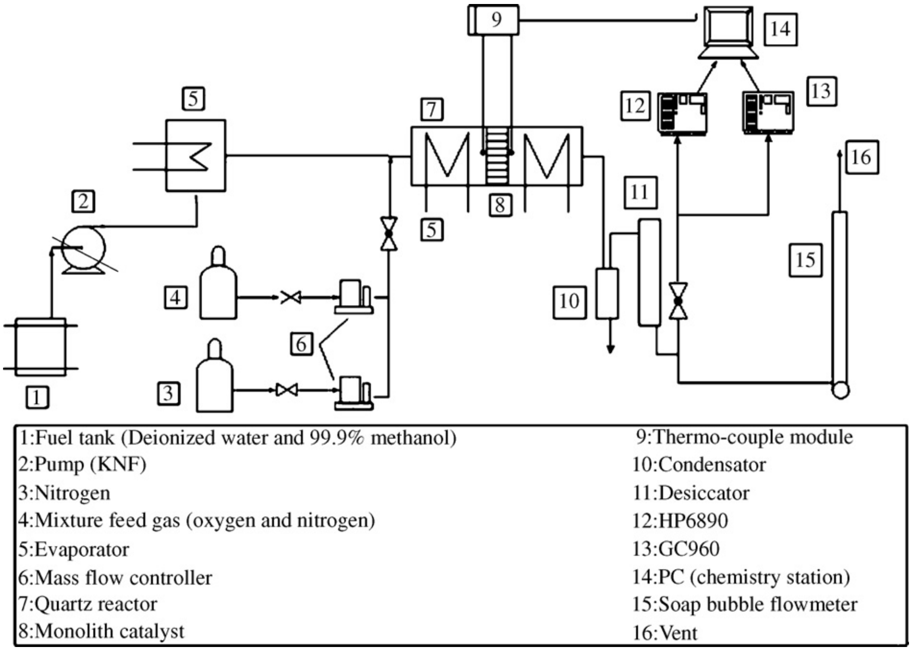

Fig. 1. Scheme of an OSMR system.