Intensification of hydrogen production by methanol steam reforming

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ABSTRACT

This paper studies the methanol steam reforming intensification to enhance the hydrogen production in a multi-channel block type micro-reformer. The effects of operating parameters such as reforming temperature, space velocity and catalyst layer thickness on reforming performance are investigated. For optimized design and operating conditions, the 8 cm^3 reformer unit produced 170 LH$_2$/h containing on dry basis 75.0% H$_2$, 23.5% CO$_2$, 0.06% CH$_3$OH and 1.44% CO at 648 K allowing the production of 218−255 W in a commercial PEMFC with 80% hydrogen utilization. This study shows that high methanol conversion can be achieved with high Pd/ZnO catalyst loading at 648 K with very low CO content (<1.5%) in the outlet stream.

Introduction

Owing to the high-energy efficiency, along with low pollution emissions and low operating temperature, the proton exchange membrane fuel cell (PEMFC) is considered one of the most promising portable power sources [1,2]. They transform the energy resulting from the reaction between hydrogen and oxygen into electrical power, with water vapor being the only waste product. However, utilization of improved reactors and reaction systems for hydrogen production and delivery to the fuel cell is of high importance for the optimized operation of the cell, due to the difficult hydrogen storage and transport.

Reforming of alcohols and hydrocarbons allows hydrogen production *in situ*. Methanol is often considered the best liquid fuel to generate hydrogen due to its high energy density, low cost and easy transportation [3]. Besides all this, it is known that methanol steam reforming (MSR) yields a product gas containing up to 75% H$_2$ at relatively low reforming temperatures (523−623 K) because no C−C bond cleavage is necessary in methanol reforming [3].

In the conventional reactor design, the reformer consists of a packed-bed filled with catalyst particles, but this type of reactors presents certain limitations. The main disadvantages of this type of reformer are the large pumping power required to drive the reactants and products flowing through the reactor and the poor heat transfer characteristics that is important in the reforming reaction due to its high endothermic character [4,5]. To solve these problems, the use of structured catalysts like monoliths and foams has been proposed [6,7]. The catalyst forms a thin film that coats the walls of the channels or pores of a structure, which allows for higher fluid flow with low

pressure drop. However, in the case of fuel processors for the production of hydrogen there is a further limitation, which is the need of compact and lightweight systems for small-scale applications and transportation that are becoming increasingly frequent. To meet this need, micro-channel reactors have been recently developed, allowing a remarkable integration of catalytic processes with the heat transfer needed for fuel processing systems for hydrogen production [8]. Wild et al. [9] observed that micro-channel showed better performance in MSR as compared to foam and packed beds. This was attributed to the god heat transfer characteristics of the micro-channel reactor. The temperature difference between gas outlet and gas inlet was less than 2 °C for micro-channel reformer and 80—90 °C for packed bed reactors.

In recent years, many experimental and simulation studies have been carried out focusing on designing the micro-channel reactor. Precision machining (micro-milling, micro-electro discharge machining, embossing, laser micro-machining, etc.) enables high pattern density and resolution for constructing microfluidic systems capable of realizing complex two- and three-dimensional reactor architectures for greater portability, thermal management, and process intensification [8,10,11]. According to Stankiewcz and Moulijn any chemical engineering development that leads a substantially smaller, cleaner, safer and more energy efficient technology is process intensification [12]. The process intensification by micro-devices occurs because miniaturization significantly reduces the resistances to heat and mass transfer.

Process intensification in fuel reforming can be benchmarked by the hydrogen productivity per reactor volume. But obtaining high hydrogen productivity requires also the use of a very active catalyst. Copper-based catalysts are the most commonly used to coat microreactors for methanol steam reforming due to their high activity and selectivity at low reforming temperature (503—573 K) [9,13—19]. It has been reported that high hydrogen production, 12—240 LH_2/h g_{cat} and $X_{CH3OH} = 80$—99%, with washcoated Cu type catalyst [9,13—22]. The microchannel reactor designed by Shon et al. [21] produce the highest hydrogen production, 240 LH_2/h g_{cat}, with low CO production (1.24%) at 573 K, but with methanol conversion no greater than 80%. Analyzing the productivity per reactor volume with these catalysts, it has been reported hydrogen productivity in the range of 0.02—9.4 L_{H2}/h cm^3 [9,13—22]. Nevertheless, sintering of the metal at temperatures >553 K and other deactivation issues remain problematic with copper catalysts [3,23,24]. This makes difficult to increase productivity by increasing reformer temperature. In addition, CO formation, the undesired product, is promoted by increasing the reforming temperature because Cu based catalyst forms CO by reverse water gas shift reaction [3,25].

The increasing research on MSR catalysts is resulting in the production of new and efficient catalysts with promising results. Thus, group 8—10 catalyst have been proposed in the literature as highly stable catalyst with similar selectivity to Cu-based catalysts, being Pd/ZnO the most studied due to its high performance [26]. Although comparing the activity of both groups, copper-based catalysts emerge as the most active ones, group 8—10 catalysts are more stable. Penner et al. [27] reported that the PdZn alloy phase, that is responsible for a high performance in this group, is thermally stable in a broad

temperature range: 473—873 K. However, the structuration of this catalyst on microreactors has been less studied. Echave et al. [28,29] and Pfeifer et al. [19,30] prepared Pd/ZnO coated on micromonoliths and micro-channel plates, respectively. Pfeifer et al. [19] obtained high hydrogen production with aluminum micro-channels reactors coated with and PdZnO catalyst at 583 K, 16 LH_2/h g_{cat} and 11.2 L_{H2}/h cm^3. However, methanol conversion was low (60%) and production of dimethyl ether was observed during MSR. Alumina, that is present in the aluminum micro-channel plate, promotes the methanol dehydration responsible of dimethyl ether production, which is an undesired product during methanol steam reforming [28,31].

As a continuation of our previous work on structured catalysts [28,29], the main objective of the present article is to study process intensification in a compact cross flow methanol steam reformer based on Pd/ZnO catalyst. Process intensification was studied measuring hydrogen productivity per unit volume varying feeding flow, reforming temperature and catalyst load.

Experimental part

Micro-channel reactor

The metallic micro-channel reactor was manufactured using FeCrAl alloy containing 22% Cr, 4.8% Al, 0.3% Si, 0.3% Y and balance Fe (Fecralloy®, Goodfellow). Two types of micro-channels were engraved on 1 mm thick metallic plates: by micro-milling (Fig. 1A) and by microetching (Fig. 1C). The engraved plates (20 × 20 × 1 mm) were joined together placing 25 μm metallic glass sheets (Fe79/B16/2 Goodfellow) between the edges and further were diffusion bonding welded using the transient liquid phase (TLP) bonding process [32]. Final blocks designed to combine combustion and MSR were composed of 10 plates for MSR welded intercalated by 10 additional plates for combustion, resulting in 100 micro-channels in each direction for blocks obtained with micro-milling plates (μMB, Fig. 1B) and in 80 micro-channels in each direction for blocks obtained with microetching plates (μEB, Fig. 1D). The geometric characteristics of the investigated blocks are compiled in Table 1.

In order to improve the interaction between the washcoat layer and the metallic substrate, Fecralloy® micro-channel blocks were pretreated in air for 22 h at 1173 K to generate a 5—6 μm thick and rough oxide layer, which consisted mainly of α-Al_2O_3 (Fig. 2) [33].

Catalyst coating

The 2.5%-Pd/Zn catalyst was selected to deposit micro-channel blocks. 2.5% Pd is in the range usual in the literature for catalysts Pd/ZnO [3,28,29]. Preliminary studies in our laboratory showed that increasing Pd content produced no improvements in the catalyst to offset the cost increase.

The washcoating method was used to deposit the catalyst on micro-channel blocks. The washcoating procedure developed in previous work for micromonoliths of the same alloy and channel size [29] included the following preparation steps: