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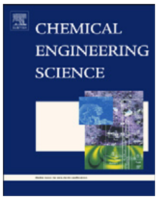

Steam reforming of methanol over a CuO/ZnO/Al_2O_3 catalyst part II: A carbon membrane reactor

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ABSTRACT

The reaction of methanol steam reforming was studied in a carbon membrane reactor over a commercial CuO/ZnO/Al_2O_3 catalyst (Süd-Chemie, G66 MR). Carbon molecular sieve membranes supplied by Carbon Membranes Ltd. were tested at 150 °C and 200 °C. The carbon membrane reactor was operated at atmospheric pressure and with vacuum at the permeate side, at 200 °C. High methanol conversion and hydrogen recovery were obtained with low carbon monoxide permeate concentrations. A sweep gas configuration was simulated with a one-dimensional model. The experimental mixed-gas permeance values at 200 °C were used in a mathematical model that showed a good agreement with the experimental data. The advantages of using water as sweep gas were investigated in what concerns methanol conversion and hydrogen recovery. The concentration of carbon monoxide at the permeate side was under 20 ppm in all simulation runs. These results indicate that the permeate stream can be used to feed a polymer electrolyte membrane fuel cell.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are an attractive power source for small scale applications. Electricity is generated using hydrogen as fuel in an electrochemical reaction where only water is produced. The lack of an easy and efficient way to transport and store hydrogen is leading to the development of *in situ* hydrogen production systems. The reforming of alcohols and hydrocarbons (Ahmed and Krumpelt, 2001; Damle, 2008; Löffler et al., 2003; Men et al., 2008; Telotte et al., 2008) are a good example of that. In comparison to other fuels, methanol presents several advantages as a hydrogen carrier. Although it is known for its high toxicity, it has the advantages of being biodegradable, liquid at atmospheric conditions and having a high hydrogen to carbon ratio. Moreover, the temperature range for the methanol steam reforming (MSR) is low (200–300 °C), unlike the one for methane (above 500 °C (Chen et al., 2008)), or ethanol (around 400 °C (Tosti et al., 2008)). As methanol is a reliable source of hydrogen for fuel cell applications, several studies of MSR reaction, Eq. (1) have been reported in the literature (Agarwal et al., 2005; Basile et al., 2008; Gao et al., 2008a; Palo et al., 2007; Peppley et al., 1999a, b; Purnama et al., 2004).

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2 \quad (1)$$

The resulting gas mixture is composed by hydrogen and carbon dioxide. However, another reaction between these products place, the so-called reverse water gas shift reaction (rWGS):

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad (2)$$

As a consequence, the resulting gas mixture contains a certain amount of carbon monoxide, thus a purification step is needed before feeding the produced stream to the PEMFC. This is particularly important in what concerns the carbon monoxide concentration. CO poisons the anodic catalyst of PEM fuel cells, thus its concentration must be lower than 10 ppm (Dhar et al., 1987).

This separation step can be integrated in the reaction unit using a membrane reactor. Several authors have reported significant improvements in the reactor's performance when using a hydrogen selective membrane (Basile et al., 2005; Basile et al., 2008; Israni and Harold, 2011; Sá et al., 2009). Although palladium membranes are the most common ones for this application, promising results with carbon molecular sieve (CMS) membrane reactors have also been reported (Harale et al., 2007; Sá et al., 2009; Zhang et al., 2006). In fact, CMS membranes can be particularly advantageous for low temperature membrane reactors. With the increasing development of catalysts for this reaction, several studies have been published with significant catalytic activities at increasingly lower temperatures (150–200 °C) (Agrell et al., 2003; Águila et al., 2009; Gao et al., 2008b; Lindström et al., 2002; Yao et al., 2006). For this temperature range, CMS membranes present high permeabilities and high selectivities. Palladium membranes, on the other hand,

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present very low permeabilities under 200 °C and thus are not suitable for this application.

In this work, a membrane module of carbon molecular sieve hollow fibres from Carbon Membranes Ltd. was assembled. Permeance measurements were performed at 150 and 200 °C for single gas and gas mixtures. A carbon membrane reactor (CMR) with a $CuO/ZnO/Al_2O_3$ catalyst from Süd-Chemie was assembled to produce PEMFC grade hydrogen from methanol steam reforming. The effects of the total feed flow rate in methanol conversion, hydrogen yield and hydrogen recovery were studied. Model simulations were carried out to evaluate how the water permeation affects the reactor's performance. In general, this work aims to show that a carbon membrane reactor can produce a hydrogen rich permeate stream to feed a PEMFC.

2. Membrane reactor model

The mathematical model used in this work comprises steady-state mass balance equations for the reaction and permeation sides, as well as the respective boundary conditions. Isothermal conditions and ideal gas behaviour were considered. The retentate, filled with a methanol steam reforming catalyst, was assumed to have an uniform cross-sectional void fraction and follow an axially dispersed plug flow pattern with pressure drop described by the *Ergun* equation (Ergun, 1952). The permeate side was assumed to be plug flow with no axial dispersion and with no pressure drop. The model equations as well as the numerical solution strategy are described elsewhere (Sá et al., 2009). Due to the lack of a complete kinetic study for this specific catalyst, several reaction rate expressions were tested and compared in Part I of this work (Sá et al., submitted for publication), in order to find the one that best fits to the experimental data. The MSR kinetic model proposed by Peppley et al. (1999a) was the one with better results. A kinetic expression for the rWGS reaction was proposed by the authors based in the same assumptions of Peppley et al. (1999a).

3. Experimental

A scheme of the experimental set-up used in both permeation and reaction experiments is presented in Fig. 1. The membrane module for permeation experiments and the carbon membrane reactor were placed inside a temperature-controlled oven. The temperature of the reactor and the membrane module were measured with type K thermocouples. Mass flow controllers from Bronkhorst (model F-201C, ±0.1% FS) were used to control the gas feed flow rate. A CEM-System (Controlled Evaporation and Mixing) from Bronkhorst promoted controlled evaporation of the required methanol aqueous solution before entering the oven. Both feed and permeate pressures were monitored with Druck pressure transducers (PMP 4010, ±0.08% FS) and the respective flow rates were measured with Bronkhorst mass flow meters (models F-111B and F-110C, ±0.1% FS). The un-reacted water and methanol were separated from the gas mixture in a condenser at ca. −10 °C placed outside the oven. The composition of this mixture was analysed in a Karl Fisher titrator from Metrohm. The retentate and permeate gas streams were analysed in a quadrupole mass spectrometer, Pfeiffer Vacuum OmniStar GSD 320 (detection limit < 1 ppm).

4. Results and discussion

4.1. Carbon membranes permeance

The membranes used in this work are carbon molecular sieve hollow fibres from Carbon Membranes Ltd.—Fig. 2. These membranes were produced by pyrolysis of dense cellulose cupra-amonia hollow fibres in an inert atmosphere, following a strict temperature history. Afterwards, they were subjected to several carbon chemical vapour deposition/activation steps, this last performed at elevated temperature using air. This post-treatment assigns to the membranes a precise pore size distribution that allows very high permeabilities and selectivities. A more detailed description of the membrane's production and characteristics can be found elsewhere (Lagorsse et al., 2004).

Gas permeation experiments were performed in a permeation module according to the scheme in Fig. 3. As summarised in Table 1, the prepared module contained 15 fibres of 6.5 cm long, housed in a ¼ in stainless steel tube. Preliminary tests were performed to choose the sealant for the membrane module. Several epoxy glues and silicon adhesives were tested for gas permeability, resistance to water, temperature and pressure. The best performance was obtained with a high temperature silicon glue from Shin-Etsu Chemical. The feed was applied to the shell side of the module, while vacuum was applied to the permeate

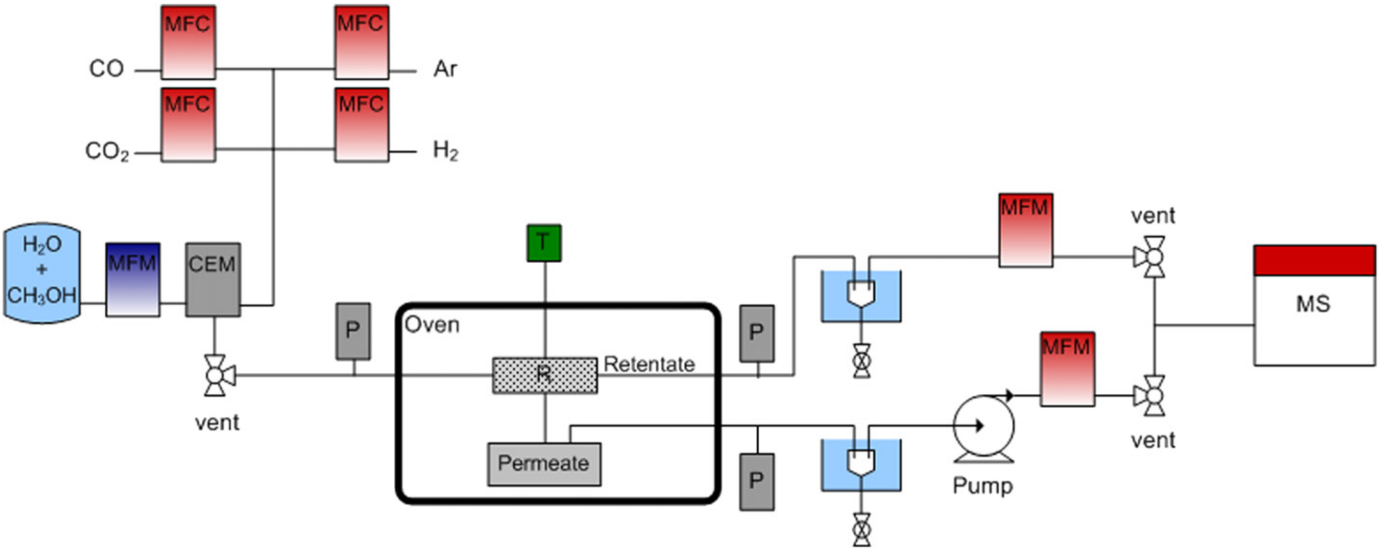

Fig. 1. Scheme of the experimental unit. CEM—controlled evaporation and mixing system; MFC—mass flow controller; MFM—mass flow meter; MS—mass spectrometer; P—pressure transducer; T—thermocouple.