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Full Length Article

Experimental study of 2-methoxyethanol steam reforming in a membrane reactor for pure hydrogen production

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HIGHLIGHTS

- 2-Methoxyethanol steam reforming experiments were performed in a membrane reactor.
- Pure hydrogen yield and recovery in a Pd-Ag membrane reactor were evaluated.
- Hydrogen recovery of 90% and pure hydrogen yield of 0.5 were reached at 10 bar.
- A mechanism for 2-methoxyethanol steam reforming was suggested.
- The results were compared to steam reforming of ethylene glycol and methanol.

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ABSTRACT

For the first time, 2-methoxyethanol ($C_3H_8O_2$) was used for producing pure hydrogen in a catalytic membrane reactor (CMR) via steam reforming (SR). The SR experiments were performed at 923 K and 1–10 bar using a mixture of 2-methoxyethanol (MEX) and water at S/C ratio of 3. Moreover, SR experiments were performed under the same operating conditions using ethylene glycol (EG), methanol (MET), and a mixture of EG + MET, keeping a constant carbon molar flow rate into the CMR to study the reaction pathway through which 2-methoxyethanol is converted to SR products (CH_4, CO, CO_2, and H_2). Hydrogen recovery values of up to 90% and pure hydrogen yields of 0.5 and 0.63 at 10 bar were reached in the case of the steam reforming of MEX and EG + MET, respectively. An outstanding value of 4 mol of pure hydrogen per mol of MEX was obtained at 10 bar. The presence of methanol promoted the SR of EG. The experimental results showed that 2-methoxyethanol is a promising source for producing hydrogen, especially in a CMR where a better efficiency (complete fuel conversion and high hydrogen yield) is reached.

1. Introduction

As an alternative to fossil fuels, hydrogen is considered as a clean energy carrier that can be combusted similar to the conventional carbonaceous fuels or be converted efficiently to electricity by fuel cells [1]. In this regard, production of a hydrogen rich stream by steam reforming (SR) of hydrocarbons or oxygen containing organic compounds has been investigated vastly [2,3]. Methane, methanol (MET), ethanol, acetic acid, and ethylene glycol (EG) are among the fuels most used as the source of hydrogen in steam reforming processes [2–10]. Apart from the prevalent fuels, the use of larger molecules such as dimethoxymethane (DMM) and trimethoxymethane (TMM) have attracted attention recently for production of hydrogen-rich gas via SR [11–13] or direct oxidation in low temperature fuel cells [13–15]. High hydrogen yield (steam-reformed easily), high H/C ratio, and absence of C—C bond are mentioned as the advantages of such molecules regarding the SR process [11,12].

Similarly, the experimental results for hydrogen production via SR of 2-methoxyethanol (methyl cellosolve, $C_3H_8O_2$) have been reported in a few works [13,16]. 2-Methoxyethanol (MEX) has a lower H/C ratio compared to ethanol (H/C = 3) but equal to EG or DMM (H/C = 2.6). The preliminary results of methoxyethanol steam reforming (MEX SR) experiments show high hydrogen yield (higher than methanol and ethanol steam reforming) and low carbon deposition at high temperature and high steam to carbon (S/C) ratio, i.e. in presence of excess water [13,16]. MEX does not occur as a natural product, but it can be manufactured easily from methanol and ethylene oxide [17]. Methanol can be obtained by fermentation of biomass (bio-methanol) and ethylene oxide is

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synthesized via direct oxidation of ethylene. Renewable pathways for producing ethylene via conversion of biomass [18], bio-ethanol [19], and biological methods [20,21] have been studied recently. Therefore, there is a promising perspective of renewable production of MEX via conversion of biomass and natural resources.

Regarding pure hydrogen production, catalytic membrane reactors (CMRs), where the generation and separation of hydrogen take place simultaneously, are beneficial in terms of producing pure hydrogen (in the case of dense metallic membranes) and higher process efficiency [22,23]. The shift effect that occurs in CMRs results in even higher hydrogen yields because the presence of a membrane selective to the hydrogen permits attaining very high conversion values in comparison with the traditional reactors operating under the same conditions [24]. In fact, CMRs represent a modern configuration in which an integrated reaction/separation unit has many potential advantages: reduced capital costs, improved yields and selectivity towards hydrogen and drastically reduced downstream separation costs [25,26]. Among CMRs, palladium-based membrane reactors fulfill the requirements to obtain an ultra-pure hydrogen stream (full hydrogen perm-selectivity) suitable for low-temperature fuel cell feeding [9,10,27]. Palladium membranes are among the oldest membranes studied for gas permeation and separation applications and are still the membranes with the highest hydrogen permeability and selectivity [28].

In this work, MEX was used for hydrogen production via catalytic steam reforming over RhPd/CeO_2 catalyst in a membrane reactor equipped with Pd-Ag dense metallic membranes, aiming to produce fuel cell-grade hydrogen. We investigated the catalytic reactivity and the performance of the CMR in terms of selectivity towards hydrogen and the production rate of pure hydrogen. Further, the reaction mechanism was studied and a reaction pathway for MEX SR was suggested. RhPd/CeO_2 was the catalyst selected due to its activity towards breakage of C—C bond, robustness, low coke formation, and high selectivity towards hydrogen [29]. To the best of our knowledge, this is the first time that MEX SR, EG SR, and the related reaction mechanisms are studied for pure hydrogen production in a membrane reactor.

2. Material and methods

2.1. Experimental setup

The RhPd/CeO_2 catalyst (0.5% Rh–0.5% Pd) was deposited over cordierite pellets of about 1–3 mm following the procedure described by López et al. [30]. The laboratory setup used for the SR experiments (fuel reformer) consisted essentially of a fuel tank, a liquid pump, a catalytic membrane reactor (CMR), a pressure transducer and a condenser. The scheme of the experimental setup and the CMR is presented in Fig. 1.

A heating tape was wrapped around the reactor wall and was controlled by a PID electronic controller (Fuji PXR4) connected to K-type thermocouples. A HPLC pump (Knauer) was used to pump the mixture of distilled water and MEX/MET/EG and to keep the pressure. A backpressure regulator (Swagelok) adjusted the retentate pressure. No pressure regulation was implemented on the permeate side, so the permeate side pressure was kept at ambient pressure. No sweep gas was used so pure hydrogen was obtained at ambient pressure.

The reactor was 10 in. tall and 1 in. in diameter. There were four Pd-Ag membrane tubes highly selective to hydrogen inside the reactor; each one 3 in. tall and 1/8 in. diameter in order to separate hydrogen. The membrane tubes consisted of Pd-Ag (30 μm layer) supported on porous stainless steel (PSS) provided by REB Research & Consulting, MI, USA, accounting for 30.4 cm^2 total active membrane area. The reactor was filled with 26 g of the RhPd/CeO_2 catalyst so that the metallic membranes were fully covered. The composition of the non-condensable portion of the outlet gas (retentate) was analyzed using an online Gas Chromatograph (Agilent 3000A MicroGC equipped with MS 5 Å, PlotU and Stabilwax columns). The condensable portion of the outlet gas was collected from the condenser and analyzed by gas chromatography (Shimadzu GC-2100 Plus) for the presence of any unconverted carbon-containing species. The flowrate of pure hydrogen (permeate side) was measured with a dedicated mass flow meter (Bronkhorst F-111B) and the flow rate of the retentate gas was measured with a conventional bubble meter.

MEX SR experiments were performed using a mixture of 2-methoxyethanol (Acros Organics, 99+%) and water at S/C (steam to carbon) ratio of 3. The experimental conditions are given in Table 1. The SR experiments were performed firstly without membrane (outlet valve of the permeate side of the CMR closed, no hydrogen permeation) and then with hydrogen permeation through the membrane (outlet valve of the permeate side of the CMR open). The experiments with the open valve (hydrogen permeation) were run at 6, 8, and 10 bar because of very low hydrogen permeation rate at lower pressures. The gas hourly space velocity (GHSV) was calculated as the ratio between the volumetric gas flowrate of the reactants (MEX/EG/MET + H_2O) with respect to the reactor volume.

2.2. Data analysis

Apart from the pure hydrogen production rate, hydrogen yield (Y_{H_2}) and hydrogen recovery (R_{H_2}) were calculated based on the experimental results to evaluate the performance of the CMR.

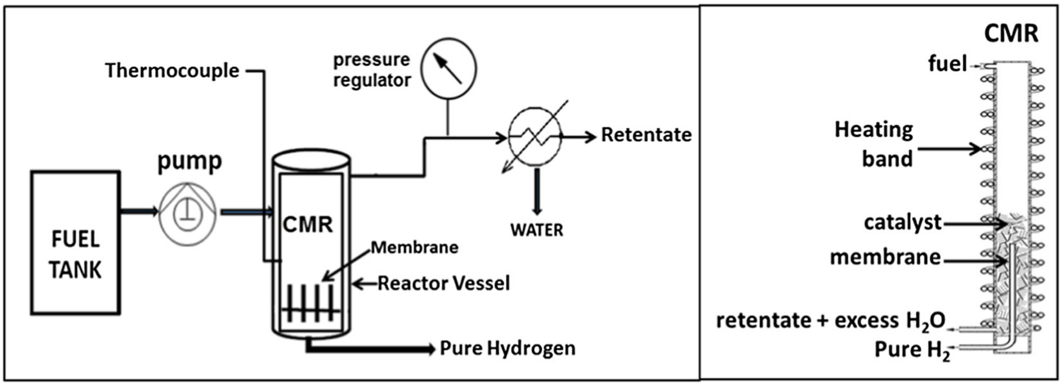

Fig. 1. Scheme of the catalytic membrane reactor (CMR).