Directing selectivity of ethanol steam reforming in membrane reactors

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ABSTRACT

In a system of parallel reversible reactions, separating the corresponding product can enhance a desired reaction. If the same product is produced in several reactions, its concurrent separation enhances the reaction with the higher stoichiometry. Here we demonstrate this effect by separating hydrogen from ethanol during steam reforming in a Pd membrane reactor packed with a $Pt/Ni–CeO_2$ catalyst. Interest in ethanol SR stems from the need to produce ultra-pure H_2 from renewables (the energy will be supplied by solar-heated molten salt).

For the conditions tested full conversion (of reaction (1) below) has been achieved with H_2, CO_2, CH_4 and CO as products. These products can be represented by three reactions (W = H_2O): 1. EtOH $\leftrightarrow$ CH_4 + CO + H_2 (ethanol decomposition), 2. CH_4 + 2W $\leftrightarrow$ CO_2 + $4H_2$ (methane steam reforming, MSR) and 3. CO + W $\leftrightarrow$ CO_2 + H_2 (water gas shift, WGS). Separating H_2 directs the selectivity towards CO and CO_2, resulting also in increased ratio between CO and CH_4 mole fraction.

In general, increasing temperature (613–753 K), pressure (6–10 bar) and introducing sweep flow (0.5 NL/min N_2 for a similar feed rate) led to better separation, to an increase in selectivity towards CO and CO_2 and in hydrogen yield. Increasing pressure and introducing sweep flow also increased hydrogen recovery. A further increase of sweep gas flow rate (to 1 NL/min) did not result in an appreciable improvement.

The results of this work show that the combination of the Ni/Pt catalyst and the Pd membrane for hydrogen removal produce very high values of hydrogen yield, despite the low steam to ethanol ratio and the moderate pressure levels. In particular about 4.5 mol H^2/mol EtOH were produced at 753 K, feed and sweep flow rates of 0.5 NL/min each in the entire pressure range examined. A one-dimensional model based on the kinetics of a limited but realistic set of reactions has been developed to simulate the behavior of the reactor. With a literature kinetics model and only two adjustable parameters, the permeance and heat transfer coefficient, a very good agreement with experimental data has been obtained. The results indicate strong permeance inhibition compared to pure hydrogen measurements.

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Introduction

The worldwide hydrogen demand is increasing, and its use in Fuel Cells (FCs) is expected to make hydrogen one of the widely-used fuels in a future energy system, mainly thanks to its low environmental impact when used in FC systems. On the other hand, the extensive introduction of hydrogen as energy vector is limited by the actual lack (and costs) of a reliable hydrogen distribution infrastructure. This barrier can be surmounted by the development of systems for decentralized hydrogen production (i.e. close to the end-user). Fuel-flexibility and the possibility to power the process with renewables (solar and biomass) are two additional preconditions for sustainable hydrogen production. The above considerations are at the basis of the CoMETHy project (Compact Multifuel-Energy to Hydrogen converter). CoMET-Hy's general objective is to support the intensification of hydrogen production processes, by developing a membrane reformer that can operate with various fuels and that eventually will be heated by solar-heated molten salt [1]. An electrically-heated lab membrane reformer was tested in the Technion with methane SR [2], and this work extends that study to ethanol SR using the same catalyst, membrane and system.

Hydrogen production from biomass derived oxygenates has attracted interest for its potential application in fuel cells. Bio-fuels for the production of hydrogen could bring significant environmental benefits, as the carbon dioxide produced is consumed in biomass production giving a CO_2 neutral energy supply. Steam reforming of bioethanol has been widely investigated over supported transition and noble metal catalysts [3,4].

Hydrogen production by SR of ethanol often encounters several problems, which are addressed in the CoMETHy project:

- High-purity hydrogen is required for its application in fuel cells: the most promising FCs, based on PEM, require low levels of CO; hydrogen separation by a Pd membrane should satisfy this condition.
- Steam reforming is highly endothermic and requires heat supply; in this project the reformer is heated by solar energy.
- The reaction is accompanied by the formation of various by-products, which greatly affect the selective production of hydrogen; as we show in this article, hydrogen separation will shift the product distribution in the desired direction, i.e., toward the reaction that produces most hydrogen.
- The reaction is limited by equilibrium; hydrogen separation will shift the equilibrium conversion.
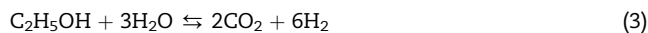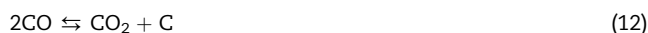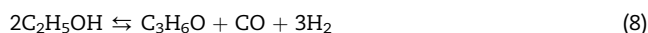
The ethanol steam reforming (ESR) reaction is:

$$C_2H_5OH + H_2O \leftrightarrows 2CO + 4H_2 \tag{1}$$

The conversion of CO to CO_2 is considered through the water–gas shift (WGS) reaction:

$$CO + H_2O \leftrightarrows CO_2 + H_2 \tag{2}$$

The overall ESR reaction, which refers to complete conversion of CO to CO_2, is therefore:

$$C_2H_5OH + 3H_2O \leftrightarrows 2CO_2 + 6H_2 \tag{3}$$

Aside from these desired reactions, several others may take place [5].

$$C_2H_5OH \leftrightarrows C_2H_4O + H_2 \tag{4}$$

$$C_2H_4O \leftrightarrows CH_4 + CO \tag{5}$$

$$C_2H_4O + H_2O \leftrightarrows 2CO + 3H_2 \tag{6}$$

$$C_2H_5OH \leftrightarrows C_2H_4 + H_2O \tag{7}$$

$$2C_2H_5OH \leftrightarrows C_3H_6O + CO + 3H_2 \tag{8}$$

$$C_2H_5OH + 2H_2 \leftrightarrows 2CH_4 + H_2O \tag{9}$$

$$C_2H_5OH \leftrightarrows 0.5CO_2 + 1.5CH_4 \tag{10}$$

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \tag{11}$$

$$2CO \leftrightarrows CO_2 + C \tag{12}$$

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O \tag{13}$$

Achieving the desired product is usually obtained by a proper choice of catalyst and support (see below) and operating conditions. Selectivity may be further directed through the use of membrane reactors, which shift the equilibrium in the direction of the selectively permeating component (hydrogen in this case).

Recently, catalysts containing more than one active species have also been investigated because of their significantly different catalytic properties with respect to either of the parent metals [6,7]. A synergic effect of Pt addition to Ni-based catalysts was shown to improve the activity of the non-noble metal towards hydrogenation reactions, resulting in decreased coke formation rates with respect to the ones observed over monometallic Ni-catalysts [8]. When Pt and Ni are supported on CeO_2, by depositing the non-noble metal on the support surface earlier than the noble one, as Pt is directly available at the gas–solid interface, ethanol adsorption is favored and a better agreement with thermodynamic data in a regular fixed bed was observed [9].