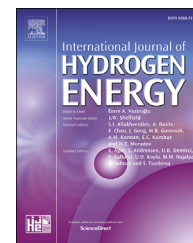


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Performance assessment and evaluation of catalytic membrane reactor for pure hydrogen production via steam reforming of methanol

Majid Saidi

Faculty of Engineering, Shahrekord University, Shahrekord, Iran

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ABSTRACT

The steam reforming of methanol was investigated in a catalytic Pd–Ag membrane reactor at different operating conditions on a commercial Cu/ZnO/Al₂O₃ catalyst. A comprehensive two-dimensional non-isothermal stationary mathematical model has been developed. The present model takes into account the main chemical reactions, heat and mass transfer phenomena in the membrane reactor with hydrogen permeation across the PdAg membrane in radial direction. Model validation revealed that the predicted results satisfy the experimental data reasonably well under the different operating conditions. Also the impact of different operating parameters including temperature, pressure, sweep ratio and steam ratio on the performance of reactor has been examined in terms of methanol conversion and hydrogen recovery. The modeling results have indicated the high performance of the membrane reactor which is related to continuous removal of hydrogen from retentate side through the membrane to shift the reaction equilibrium towards formation of hydrogen. The obtained results have confirmed that increasing the temperature improves the kinetic properties of the catalyst and increase in the membrane's H₂ permeance, which results in higher methanol conversion and hydrogen production. Also it is inferred that the hydrogen recovery is favored at higher temperature, pressure, sweep ratio and steam ratio. The model prediction revealed that at 573 K, 2 bar and sweep ratio of 1, the maximum hydrogen recovery improves from 64% to 100% with increasing the steam ratio from 1 to 4.

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Introduction

Nowadays, due to growth of population and increasing energy demand, which lead to progressive depletion of conventional fossil fuels, renewable energy carriers have represented an essential role at present global energy system. Hydrogen as a promising and clean alternative fuel to generate energy is a topic of increasing attention as world's energy resources

diminish [1]. Presently, H₂ production via steam reforming of methane is the technology most commonly used in industrial scale. Recently, there is a progressive interest for hydrogen production from renewable alcohol sources such as methanol, ethanol or butanol [2–7]. Among the liquid fuel alternatives, methanol indicates an emerging and alternative source. In particular, methanol constitutes an important and very attractive source due to its liquid state at ambient conditions, high H:C ratio of 4:1, low cost, easy to handle, non-toxicity and

E-mail address: m.saidi@eng.sku.ac.ir.

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safety [7–9]. Since there is no C–C bond that has to be cleaved, reducing the risk of the elevated temperature needed to produce hydrogen and prevent coke formation during the process [7,8]. Also from the thermodynamic point of view, steam reforming of methanol (SRM) is favored at high temperature and low pressure, since it is an endothermic reaction [10–12]. The steam reforming of methanol can be described by reaction (R-1). Additionally, side reactions such as water gas shift (WGS) reaction (R-2) can occur affecting to this equilibrium and producing non-desirable byproducts. Also it is well known that hydrogen can be obtained through thermal decomposition of methanol (DEC), (R-3) [13–16]. In comparison with other hydrocarbons and alcohols, methanol steam reforming needs a relatively low reaction temperature and also only minor amount of CO produces through WGS or DEC reactions.

Methanol Steam Reforming: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2$ (R-1)

Water–Gas Shift Reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ (R-2)

Methanol Decomposition: $\text{CH}_3\text{OH} \leftrightarrow \text{CO} + 2\text{H}_2$ (R-3)

Conventional steam reforming process is equilibrium limited and requires elevated temperatures to achieve a high enough conversion of methanol to be economically viable. In addition, it has such disadvantages as the deactivation of the catalyst by sintering or coke formation, and the consequent need for continuous or periodic catalyst regeneration at frequent intervals throughout the process. The use of catalytic membrane reactor (CMR) as a novel technology can significantly improve the efficiency of this process [17–19]. Hiramatsu et al. [20] applied the stacked etched aluminum flow-through membranes for SRM and concluded that this novel catalytic membrane support reacted more effectively than the regular one. Also techno-economic assessments of energy systems represent that the use of CMR can be beneficial under specific market and regulatory conditions. The application of CMR is beneficial where the production and separation process of H_2 from the mixture of produced gases simultaneously occur in the same reactor vessel. In this technology, the methanol undergoes the steam reforming reaction over the catalyst in the tube side and produced hydrogen permeates through the membrane to the shell side. Selective hydrogen removal through the membrane allows one to shift the reaction equilibrium towards the desired products. It is well documented that among different CMR, Cu-based catalyst membranes, especially Cu/ZnO and Cu/ZnO/ Al_2O_3 produce high H_2 fluxes at theoretically infinite H_2 selectivities due to their high activity and selectivity. Different types of Cu and Cu-alloy membranes have been investigated under experimental or pilot conditions, representing an excellent performance suitable for their application in large-scale industrial settings. In the Pd-alloy CMR technology, process intensification by the constant removal of H_2 from the reaction zone leads to higher conversions. Some reported data in literature shows that the coexistence of Cu and ZnO facilitated the SRM reaction [21–25]. In order to keep the chemical and thermal

stability of Cu-based catalysts in industrial application, ZnO is often added as spacer and stabilizer to avoid direct contact of the Cu particles and prevent them from sintering [26]. In a related study, Günter et al. [27] observed that the interaction between Cu and ZnO had a significant influence on the activity of catalyst. Also they reported that the bulk structure and the active surface were considerably modified by the intimate Cu–ZnO interface. In another work, Chang et al. [21] observed that Cu-based catalysts are so active in adsorbing and converting methanol into methoxy, while coexistence of ZnO promotes dehydrogenation of methoxy to formate, which was in turn converted into carbonate and subsequently decomposed to H_2 and CO_2 . Peppley et al. [28] developed surface mechanisms for all possible overall reactions of SRM on Cu/ZnO/ Al_2O_3 catalysts. Also the presence of Al_2O_3 inhibits the thermal sintering, but high amount of Al_2O_3 has a negative effect on the catalyst activity [21,22,29]. Phongboonchoo et al. [30] studied the catalytic activities of Ce–Mg promoted Cu/ Al_2O_3 catalysts with different Cu content during the SRM process. They observed that the Ce–Mg bi-promoter catalysts have better performance with respect to other catalyst types due to Mg penetration into the cerium structure. Their optimization results revealed that the optimal Cu content and Mg/(Ce + Mg) are 46–50 wt% and 16.2–18.0%, respectively. In another related study, He et al. [31] used Cu supported on ZnAl–LDHs precursor for the SRM process. Their experimental investigations indicated that the Cu surface areas and the interactions between Cu and support had a significant effect on the catalytic activity in H_2 production by SRM. Ribeirinha et al. [32] applied an integrated unit, including a methanol steam-reforming cell with commercial reforming catalyst CuO/ZnO/ Al_2O_3 , and a high temperature polymer electrolyte membrane fuel cell. They reported that by using this new configuration, higher hydrogen flow rate produces and consequently the fuel cell can operate at higher current densities. Liu et al. [33] studied the hydrogen production from SRM over Al_2O_3 - and ZrO_2 -modified $\text{CuOZnOGa}_2\text{O}_3$ catalysts. They inferred that this new catalyst type has high resistance to carbon formation and also the performance of $\text{CuOZnOGa}_2\text{O}_3$ -based catalysts for SRM is increased by the presence of ZrO_2 promoter.

In the current study, the steam reforming of methanol over a commercial Cu/ZnO/ Al_2O_3 catalyst in a membrane reactor at wide range of operating condition, including 473–623 K, 2–16 bar, sweep ratio of 1–3 and steam ratio of 1–4 is studied. The main objective is to develop a clear understanding of the effects of various design and operating parameters on the methanol conversion and H_2 recovery. A two-dimensional non-isothermal stationary mathematical model is established to investigate the behavior of a catalytic membrane reactor by taking into account the main chemical reactions, heat and mass transfer phenomena, where they play crucial role in the performance of process. In comparison with previous related studies, the development of CMR model taking into account the hydrogen flux through the membrane, diffusion and thermal conductivity in the radial direction for tube side, ceramic support and shell side is considered as quite actual. Also, thermal analysis is carried out and temperature distributions are predicted. In sum, the ability of the proposed model to predict the trends in the data should help to advance more generally membrane reactor modeling for

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