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A simulation study on methanol steam reforming in the silica membrane reactor for hydrogen production☆

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ABSTRACT

The main aim of this study is the presentation of a quantitative operating analysis of silica membrane reactor for carrying out the methanol steam reforming reaction to produce hydrogen. For this, a 1-dimensional isothermal model is developed and the simulation study is carried out for evaluating the catalyst loading, sweep gas flow rate and silica membrane hydrogen selectivity effects on silica MR performance in terms of methanol conversion and hydrogen recovery. These parameters effects are investigated at different reaction temperatures and pressures. The model validation results show good agreement with literature experimental data. As a main consequence, simulation results indicate that the catalyst loading and sweep gas flow rate have positive effects on silica MR performance. However, this result is devoted to lower catalyst contents (<3 g) and sweep factor values (SF < 6). Moreover, the increase of silica membrane hydrogen selectivity increases the hydrogen recovery and methanol conversion. However, the improvement of membrane hydrogen selectivity in lower hydrogen permeance ranges cannot be more useful on silica MR performance in MSR reaction. According to the reaction pressure effect on silica MR performance, methanol conversion trends are various at different orders of hydrogen permeance.

Introduction

With increasing concerns over gradual depletion of non-renewable fossil fuels and global warming, considerable attention has been paid to hydrogen for fuel cells in various applications owing to their zero emission and high efficiency [1]. One of the major challenges associated with the potential implementation of H_2 economy is the issue of hydrogen production. It has been produced mainly via the steam reforming of methane, methanol and ethanol where the conversion of feed is limited due to the thermodynamic equilibrium. Unlike hydrocarbon fuels, methanol is a sulphur free fuel and this avoids additional sulphur removal steps in the fuel

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processing. In addition, methanol can be reformed at relatively lower temperatures around 573 K, and this makes the fuel processing relatively simple. The traditional methanol steam reforming (MSR) process consists of different process steps such as feed gas preheating, pretreatment (for example hydrodesulphurisation), primary and secondary reformers (often multi-tubular fixed-bed reactors), high and low temperature shift converters, CO_2 removal and methanation units [2,3].

In recent years, membrane reactors (MRs) as a new approach combine reaction and separation and have attracted attention because of their compactness and possible cost-savings over traditional reactors (TRs). To avoid higher process costs, Pd-based MRs for pure hydrogen production have been proposed in literature for different reaction systems such as MSR reaction [4–16]. Nevertheless, there are not many studies about other kinds of membrane performances in MRs for MSR reaction. Regarding the membrane kinds to be housed in an MR, both MR cost and performance should be considered. Owing to the high cost of Pd-based MRs, a cheaper solution is strongly needed. Although these membranes are only permeable to hydrogen, their applications have limited due to lower permeability compared to porous inorganic membranes [17,18]. As a possible alternative, silica membranes can be considered because of their lower cost and higher permeabilities with respect to Pd-based membranes. On the other hand, as a drawback, they present lower hydrogen selectivities with respect to all the other gases.

Indeed, according to our best knowledge, Lee et al. [19,20] have presented several experimental studies comparing a TR with silica MR. They concluded that higher methanol conversion can be realized in MR with respect to TR. Nevertheless, a low hydrogen recovery was achieved. Therefore, in order to enhance the hydrogen recovery, the authors have carried out the water gas shift (WGS) reaction in the permeate side simultaneously with MSR reaction in the retentate side, improving the silica MR performance in terms of both methanol conversion and hydrogen recovery. These promising results have justified the need for a detailed study of potential advantages achievable using the silica MR. To evaluate the silica MR performance as an alternative in MSR reaction, a comprehensive analysis seems necessary.

In order to avoid high experimental costs and to develop a better understanding of the effects of several parameters for the study of MR, the numerical simulation can be useful. Nevertheless, few works have been presented from modelling point of view for silica MR performance or other inorganic MR. Sa et al. [21,22] have compared the performances of palladium MR with a carbon molecular sieve (CMS) MR. They developed a 1-dimensional model and validated it with literature experimental data. Ghasemzadeh et al. [23] evaluated silica and palladium MR performances for hydrogen production via MSR reaction by 1-dimensional model. In this case, a 1-dimensional isothermal numerical model was developed and its validation was realized by comparing the theoretical results with experimental data. Also, the effect of some of the important operating parameters (reaction temperature, pressure and GHSV) on the performance of both MRs was studied in terms of methanol conversion and hydrogen recovery. Furthermore, Ghasemzadeh et al. [24] was investigated hydrogen production in silica MR via MSR reaction using HAZOP study and modelling analysis. In fact, the main aim of the mentioned work was the presentation of both qualitative safety and quantitative operating analyses of silica MR for carrying out the MSR reaction to produce hydrogen.

In the present study, regarding the leakage of numerical studies about silica MR performance in MSR reaction, a 1-dimensional isothermal model was developed for evaluating sweep gas flow rate and catalyst loading effects. Moreover, as a first approach, a simulation study is carried out for investigating silica membranes hydrogen selectivity effect on silica MR performance during the MSR reaction. A set of simulation results shows some key points about the silica MR performance in terms of methanol conversion and hydrogen recovery.

Model development

The following assumptions were made to develop a model for silica MR.

1. Steady state, isothermal operation.
2. Uniform flow in shell and tube sides, so no radial distribution of components exists.
3. Permeation through the membrane is proportional to the partial pressure difference in shell and tube sides.
4. The catalysts and packing materials that are used to dilute the catalyst bed have the same size and shape.
5. Ideal gas behaviour.
6. Steam effect on silica membrane is negligible.
7. Flux equations of permeating components for silica membrane were derived from single gas permeation test at different temperatures.
8. Pseudo-homogeneous model is assumed in the catalyst bed.

The model takes into account all the reactions (Eqs. (1)–(3)) for silica MR, along with the methanol steam reforming reaction [25,26],

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2 \quad \Delta H = +49.4\ \text{kJ mol}^{-1} \tag{1}$$

the methanol decomposition reaction

$$CH_3OH \leftrightarrow 2H_2 + CO \quad \Delta H = +90.5\ \text{kJ mol}^{-1} \tag{2}$$

and the water gas shift reaction

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H = -41.1\ \text{kJ mol}^{-1} \tag{3}$$

take place in the MR.

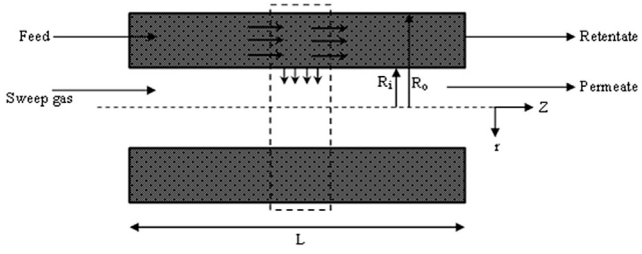

Fig. 1 – Schematic of the silica MR model.