



Theoretical and experimental study of methane partial oxidation to syngas in catalytic membrane reactor with asymmetric oxygen-permeable membrane

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ABSTRACT

This paper presents results of theoretical and experimental research concerning synthesis of multi-layer asymmetric oxygen-permeable membrane and its application for partial oxidation of methane. The membrane is based on macroporous Ni–Al foam substrate with three layers of perovskite-fluorite nanocomposites with graded (meso–micro) porosity, thin dense $\text{MnFe}_2\text{O}_4\text{–Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ layer and porous layer of $\text{LaNi}_{0.9}\text{Pt}_{0.1}\text{O}_3/\text{Pr}_{0.3}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_{2-x}$ catalyst. Testing of membrane in methane partial oxidation process demonstrates a good and stable performance.

The mathematical modeling of the methane partial oxidation process in the catalytic membrane reactor has been provided. The developed model was applied to find the process (temperature, gas flow rates, etc.) and membrane (pore diameter of porous layer, thickness of porous layer) parameters corresponding to highest methane conversion and syngas selectivity.

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1. Introduction

Such processes as coal gasification, partial oxidation of hydrocarbons, methane steam and dry reforming are well known to be used for syngas production. From these processes catalytic partial oxidation of methane (CPOM) is considered as an advantageous route from both economic and technical points of view [1–4]. Slight exothermic nature of the process makes it less energy- and capital cost-intensive. Additionally, the lower H_2/CO ratio of 2 is more favorable with respect to downstream processes such as methanol synthesis and Fischer–Tropsch synthesis of higher hydrocarbons.

Catalytic partial oxidation of methane as well as higher hydrocarbons into syngas at short contact times has been carried out using a lot of structured catalysts [5–25] based on ceramic and metal foil honeycombs [5–14], gauzes [6,8], foams [16] and microchannel plates [6,8,15,20–25]. For structured catalysts, both

axial and radial-type flow modes in reactors were used [6,8]. For the latter design of reactor additionally equipped with the heat exchanger a high productivity and stable performance with syngas yield close to equilibrium value were demonstrated in the partial oxidation of the natural gas when the feed (feed rate up to $15\text{ m}^3/\text{h}$) was supplied at room temperature into the central part of reactor equipped with multiple catalyst beds of a cylindrical architecture corresponding to a total volume of about 580 cm^3 (a stack of catalytic microchannel washers 106 cm^3 , gauze catalyst bed 134 cm^3 , microspherical catalyst bed 340 cm^3). However, despite all these achievements, for partial oxidation of methane into concentrated syngas suitable for synfuels generation, pure oxygen must be added to the feed, which requires additional expenses for its separation from air. This problem stimulated research aimed at development of catalytic membrane reactors for partial oxidation/autothermal reforming of hydrocarbons into syngas by oxygen separated from air using oxygen-permeable membranes [27–30]. Additional advantage of catalytic membrane reactors is that they are potentially able to provide more uniform temperature profile distribution [27,30], thus solving the problem of the overheating

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List of symbols

A_m	Area of membrane (m^2)
$C_i^{r.s.,a.s.,p.l.}$	Concentrations ($kmol\ m^{-3}$)
$D_{e_i}^{p.l.}$	Effective coefficient of diffusion of component i ($m^2\ s^{-1}$)
D_{ij}	Molecular diffusivity for component i in a binary mixture of i and j ($m^2\ s^{-1}$)
D_m	Coefficient of molecular diffusion ($m^2\ s^{-1}$)
D_{kn}	Knudsen diffusion coefficient ($m^2\ s^{-1}$)
d_m	Membrane diameter (m)
d_p	Membrane pore diameter (porous layer) (nm)
$G^{r.s.,a.s.}$	Gas flow rate ($ml\ min^{-1}$)
M_i	Molecular weight of i th compound ($g\ mol^{-1}$)
N_R	Number of reactions within the reaction side of reactor
perm	Permeability
P_0	Pressure at normal conditions (atm)
$P_i^{r.s.,p.l.}$	Partial pressure of components (atm)
Q_{O_2}	Oxygen permeation rate through the dense membrane ($kmol\ s^{-1}$)
r_{cap}	Capillary radius (m)
R	Universal gas constant ($J\ mol^{-1}\ K^{-1}$)
S	Selectivity (%)
T_0	Temperature at normal conditions (K)
T	Temperature (K)
u_i	Average thermal velocity of molecule ($cm\ s^{-1}$)
w_j	Rate of reaction ($kmol\ kg^{-1}\ s^{-1}$)
X	Conversion (%)
y_i	Mole fraction of i th component

Greek letters

δ_m	Membrane thickness (dense layer) (m)
$\delta^{p.l.}$	Thickness of porous layer (m)
ε	Porosity of catalyst layer
γ_{ij}	Stoichiometric coefficient for i -component into j -reaction
ρ_{cat}	Density of catalyst ($kg\ m^{-3}$)

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in	Inlet
m	Membrane
r.s.	Reaction (fuel) side
a.s.	Air side
p.l.	Porous layer

of the inlet part of monolithic catalysts where the gas phase oxygen is consumed in total oxidation of methane [5–7,11–15] leading to sintering of active component, corrosion of metal substrates, spallation of supported layers and cracking of ceramic substrates [15,25,26].

The *single phase perovskite materials* are known to have the number of disadvantages such as instability in reducing atmosphere, low oxygen diffusivity, high coefficient of thermal expansion and low thermal stability. On the other hand, *composite materials* are characterized by high mixed conductivity, activation of oxygen, chemical stability and compatibility with other materials.

As concerning the membrane structure the *dense bulk membranes* are characterized by relatively large thickness and low oxygen flux. Contrariwise, the *asymmetric membranes* contain thin gas-tight and porous layers, and the last one provides oxygen activation thus increasing the oxygen flux. A number of studies clearly showed the great potential of using the asymmetric supported membranes for a high oxygen permeability [31–33].

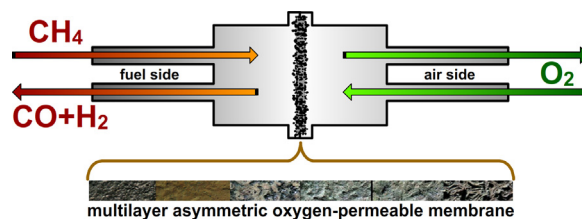


Fig. 1. The scheme of the membrane reactor.

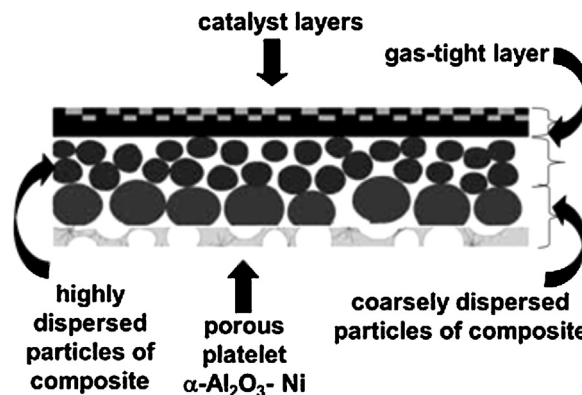


Fig. 2. The scheme of the asymmetric multilayer membrane.

The promising approach to asymmetric membrane synthesis is the consecutive deposition of MIEC nanocomposite layers characterized by a graded porosity and chemical composition on a macroporous substrate [32]. Recently, the nanocomposites based on $Ce_{0.9}Gd_{0.1}O_{1.95}$ fluorite and $La_{0.8}Sr_{0.2}Fe_{0.6}Ni_{0.3}O_3$ perovskite (LSFN-GDC) were shown to have good oxygen permeability along with stable performance [34].

The paper presents the results of theoretical and experimental research aimed at design of asymmetric multilayer membrane, its lab-scale testing in the CPOM process and theoretical study of both process and membrane parameters. The effect of certain relevant parameters of the model on methane conversion and syngas selectivity has been investigated with the developed mathematical model.

2. Model development

The mathematical model of the CPOM process in catalytic membrane reactor (CMR) was developed in accordance with reactor configuration represented in Fig. 1. The reactor consists of air and fuel sides separated from each other by the oxygen-permeable membrane with diameter of 3 cm. The membrane is oriented by the catalytic layer to the fuel side.

To describe the membrane for modeling three layers were considered as shown in Fig. 2: supports layer, working porous layer and gas-tight layer. No diffusion limitation in macro- and mesoporous layers (porous platelet $\alpha-Al_2O_3-Ni$ and coarsely dispersed particles of composite, Fig. 2) was taken into account during the modeling procedure.

The several simplifying assumptions were used:

1. Steady-state conditions.
2. Well-mixed continuous flow reactor (batch flow reactor).
3. Isothermal conditions.

It should be noted, that in some cases the assumption about well-mixed continuous flow reactor could not be good for modeling of present reactor system at higher flow rates. In our case the

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