Numerical investigation of porous surface parameters on the performance of micro-channel reactor for hydrogen production by methanol steam reforming

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Abstract. To enhance the energy conversion of a micro-channel reactor with a porous surface for hydrogen production, the effects of structural parameters of the porous surface (surface area ratio, ratio of depth-diameter and distribution of pores) on the comprehensive performance of the reactor are numerically investigated. The CFD model is established to simulate the process of hydrogen production in the micro-channel reactor with a porous surface. Then, a series of numerical simulations with different structural parameters of porous surface are carried out. The distribution fields of flow rate, temperature, pressure and gas concentration can be obtained through the numerical analysis. Results indicate that with the increase of surface area ratio, the methanol conversion and hydrogen production rate is greatly improved, while the ratio of depth-diameter and distribution of pores have little effect on the performance. When the reaction temperature is 290 ℃, the methanol conversion rate of the micro-channel reactor with a porous surface can reach above 90%.

1. Introduction
In recent years, great progress has been made in the field of hydrogen fuel cell, and in-situ hydrogen production via a micro-channel reactor is an effective method for its hydrogen supply[1]. A micro-channel reactor features quantities of channels with size of under 1-2 mm, and has the advantage of large specific surface area, high heat and mass transfer rate [2-3]. The structure of the micro-channel reactor has great impact on its performance of hydrogen production. There are two types of traditional micro-channel reactor: parallel micro-channel and porous material. The parallel micro-channel structure has the advantages of low pressure drop and high thermal conductivity[4], while the porous material has the advantages of high specific surface area and uniform catalyst coating ability[5-6]. By combining the advantages of the above two structures, a novel micro-channel reactor with a porous surface was proposed in our previous study[7-9]. However, it’s essential to analyse the effect of structural parameters of the porous surface and realize their optimization.

In this study, the effects of structural parameters of the porous surface on the comprehensive performance of the micro-channel reactor are numerically investigated. Based on fluid dynamics software Fluent, the CFD model is established to simulate the process of hydrogen production in the reactor, and the effects of surface area ratio, ratio of depth-diameter and distribution of pores are studied. Then, a series of numerical simulations with different structural parameters of porous surface are carried out. The distribution fields of flow rate, temperature, pressure and gas concentration are obtained through the numerical analysis.
2. Numerical modelling of the hydrogen production in the micro-channel reactor

2.1. Description of structural design

One of the key components in the micro-channel reactor is the catalyst support, which affects the fluid flow, reaction rate and thermal conduction. The designed micro-channel catalyst support with a porous surface is shown in figure 1. The width and depth of the micro-channel are respectively 1000 μm and 500 μm, and pores with diameter at 60-150 μm are evenly distributed in the bottom of micro-channel. The reactor mainly includes the upper cover plate, evaporation plate, reforming plate, catalyst support and lower cover plate, etc. Flexible graphite pads are used between the layers to seal the micro-reactor, and bolts are used to assemble the structure of each layer. The liquid fuel used in this paper is methanol, which has many advantages such as low reaction temperature, high hydrogen-carbon ratio, low cost and renewable. A commercial copper-based catalyst is utilized and is coated evenly on the porous surface of micro-channel catalyst support by wash-coating method[9]. Under the action of copper-based catalyst, reaction of methanol steam reforming is carried out to finally generate gas products rich in hydrogen. The primary reaction process is endothermic methanol steam reforming:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2, \Delta H_{298} = 49 \text{ kJ/mol} \]  

(1)

![Figure 1. The structure of micro-channel reactor with a porous surface.](image)

2.2. CFD modelling of the hydrogen production process

In order to analyse the hydrogen production performance of the micro-channel reactor with a porous surface, a numerical model of its fluid dynamics needs to be established. Using computational fluid mechanics by Fluent, the numerical method is used to solve the nonlinear differential equations of mass, momentum, energy and components, and the results can be used to predict the fluid flow, heat and mass transfer. The porous surface structure was modelled by particle method, and the geometric model of the hydrogen production process is shown in figure 2, which contains micro-channel catalyst support with a porous surface, catalytic layer and mixed reaction gas. After passing through the evaporation plate, the mixed liquid of methanol and water has been transformed into a mixed reaction gas, which enters the reaction area from the inlet and continuously produces hydrogen via the catalytic reforming reaction. The catalytic layer has a thickness of around 30 μm and is evenly distributed on the porous surface of catalyst support. In order to obtain the hydrodynamic results of hydrogen production by methanol steam reforming, the boundary conditions of the model must be established. According to the characteristics of the designed structure, five boundary conditions are set as shown in figure 2, which are velocity inlet boundary, pressure outlet boundary, micro-channel heating wall, porous catalytic layer and contact surface of reaction gas layer.
To establish a dynamic model of fluid flow, heat transfer and reaction in porous micro-channels, the flow equation of the reaction fluid must be analyzed. Since the process of hydrogen production involves heat transfer such as reaction of heat absorption and surface heating, it is necessary to establish the energy equation considering heat transfer. In the process of hydrogen production by methanol steam reforming, convective heat transfer dominates, so the energy conservation equation in the process is:

\[
\rho \left( \frac{\partial T}{\partial t} + \frac{u}{\rho} \frac{\partial T}{\partial x} + \frac{v}{\rho} \frac{\partial T}{\partial y} + \frac{w}{\rho} \frac{\partial T}{\partial z} \right) = k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + R_e + \varphi \tag{2}
\]

where \( \rho \) is the density of mixed gas; \( x, y \) and \( z \) represents the Cartesian coordinate system; and \( u, v, \) and \( w \) represents the velocity components of the mixed gas flow along the three directions respectively. In the reaction process, material transfer and diffusion are involved, so the material transfer equation should be considered:

\[
\rho \left( \frac{u}{\rho} \frac{\partial Y_s}{\partial x} + \frac{v}{\rho} \frac{\partial Y_s}{\partial y} + \frac{w}{\rho} \frac{\partial Y_s}{\partial z} \right) = D_{off} \rho \left( \frac{\partial^2 Y_s}{\partial x^2} + \frac{\partial^2 Y_s}{\partial y^2} + \frac{\partial^2 Y_s}{\partial z^2} \right) + R_e \tag{3}
\]

where \( Y_s \) is mass fraction of certain species (\( \text{CH}_3\text{OH}, \text{H}_2\text{O}, \text{H}_2, \text{CO} \) and \( \text{CO}_2 \)); \( D_{off} \) is mass diffusion coefficient.

Based on the structural characteristics and manufacturing process of the porous micro-channel catalyst support[8, 10], the parameter range of porous surface structure is set as specific surface area (1, 1.5, 2, 2.5 and 3), ratio of depth-diameter (0.6, 1.5 and 4) and pores distribution state (aligned and staggered), and some of the different porous surface structures are shown in figure 3. The circles represent the surface micro-pores.

Figure 3. Different porous surface structures: surface area ratio of (a) 1, (b) 2, and (c) 3; pores of (d) aligned, (e) staggered distribution.

3. Results and Discussion
The mole fraction distribution of the methanol and hydrogen in the micro-channel with a porous surface (surface area ratio is 2) is shown in figure 4. The initial mole fraction of methanol was 0.45. Figure 4 (a) shows that under the effect of catalyst, methanol concentration gradually reduces, reaching around 0.07 near the outlet, which indicates the methanol reaction is sufficient in the porous micro-channel. Figure 4 (b) shows the mole fraction distribution of hydrogen. It can be found that the hydrogen concentration increases continuously along the channel, reaching up to the level of 0.576 near the outlet. The gas mole fraction in the micro-channel without porous surface (surface area ratio
is 1) is shown in the figure 4 (c) and (d). The mole fraction of methanol near the outlet is 0.166, and mole fraction of hydrogen maximum is only 0.432, which implies that hydrogen production by methanol steam reforming reaction is not yet fully conducted.

When reaction temperature is 250 ℃ and inlet velocity is 0.1 m/s, effects of different specific surface area of the porous micro-channel on the hydrogen production performance is shown in figure 5. It can be found that increasing specific surface area of catalyst support can effectively improve the methanol conversion. This is because when the specific surface area increases, the catalytic reaction area and rate of heat and mass transfer are both improved. In addition, the porous surface structure will lead to the increase of the reaction pressure drop, and the pressure drop will slowly increase with the increase of the specific surface area, for two reasons: First, the flow of the fluid inside the micro-pores has an adverse pressure gradient, which can enhance the disturbance and mass transfer velocity of the reaction gas in the micro-channel; Second, due to the large specific surface area and the increase of methanol conversion, the gas quantity of flow in the micro-channel is larger.
When the reaction temperature is 250 °C, and the inlet flow velocity is 0.1 m/s, the methanol conversion rate and pressure drop levels of the porous micro-channels with different ratios of depth-diameter and micro-pore distribution are shown in figure 6. Results show that when the specific surface area of the catalyst support is fixed, the different distribution of pores has little influence, because the catalytic reaction area stays the same. The depth-diameter ratio of micro-pores has a certain effect on the methanol conversion rate, and the results show that the methanol conversion rate decreases slowly with the increase of the depth-diameter ratio, and the pressure drop changes little at the same time. This is because porous surface layer has a certain thickness, it will take time for the reaction gas diffusion. But overall, the depth-diameter ratio of surface pores still has little effects on the methanol conversion.

Figure 6. Effects of depth-diameter ratio and micro-pores distribution on the performance.

Under different temperature conditions, the methanol conversion rate of porous micro-channel catalyst support with various specific surface areas and depth-diameter ratios is shown in figure 7. It can be found that the influence of temperature on the methanol conversion is very obvious. With the increase of temperature, methanol conversion rate increases significantly, and the methanol conversion rate can be increased to nearly 100 % at 290 °C. This is due to the hydrogen production from methanol steam reforming reaction is endothermic, the increasing of temperature is helpful for the process. Under normal operating temperature (230-270 °C) of the copper-based catalyst, the hydrogen production performance of the porous micro-channel catalyst support with specific surface area at 2 is significantly better. Besides, for the porous micro-channel catalyst support with a depth-diameter ratio at 0.6, the methanol conversion rate is slightly higher than that of the catalyst support with a depth-diameter ratio at 4. This is because the smaller depth-diameter ratio can ensure the rapid diffusion of the reaction fluid to the catalytic layer at the bottom of the micro-pores.

Figure 7. Methanol conversion at different reaction temperatures.
4. Conclusions
To enhance the energy conversion of the micro-channel reactor with a porous surface for hydrogen production, the effects of structural parameters of the porous surface on the comprehensive performance of the reactor are numerically investigated, and the parameter range of porous surface structure is set as specific surface area (1, 1.5, 2, 2.5 and 3), ratio of depth-diameter (0.6, 1.5 and 4) and pores distribution state (aligned and staggered). Based on the fluid dynamics software Fluent, the CFD model is first established to simulate the process of hydrogen production in the micro-channel reactor with a porous surface. Then, a series of numerical simulations with different structural parameters of porous surface are carried out. It can be found that increasing specific surface area of catalyst support can effectively improve the methanol conversion, while the ratio of depth-diameter and distribution of micro-pores have little effect on the performance. This is because when the specific surface area increases, the catalytic reaction area and rate of heat and mass transfer are both improved. With the increase of temperature, methanol conversion rate increases significantly, and the methanol conversion rate can be increased to above 90% at 290°C.

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