Peculiarities of hydrogen production using methane steam reforming in a microstructured reactor-heat exchanger

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Abstract. This paper presents the description of the rhodium catalyst synthesis and the results of numerical study of the methane-steam reforming in a microstructured reactor-heat exchanger. The kinetics of the reforming reactions on a synthesized catalyst was determined using the numerical simulations and experimental data on activation energy of the methane reactions. It allows finding the characteristics of methane steam reforming that can be used for optimization of the microstructured reactor implementing the microchannel technology.

1. Introduction

Hydrogen is related to clean energy source and it is the important component of low carbon economy. In connection with the program of using hydrogen fuel in energy and transport, adopted in many countries, the development of technologies for producing hydrogen in compact fuel processors is of great importance because it allows integrating a hydrogen production system with fuel cells to increase the total system efficiency. For compact catalytic systems, the most effective method for producing synthesis gas and hydrogen during methane steam reforming is application of a microreactor-heat exchanger with enhanced heat and mass transfer. The use of microchannel technologies for manufacturing the reactors for syngas and hydrogen production allows as elimination of eliminate diffusion and thermal restrictions on the reaction rate, so intensification of the conversion process, which, in turn, can significantly reduce the size of the reactors and carry out the catalytic conversion at short residence time [1, 2]. This can be implemented both in metallic and ceramic microreactors [3]. The advantages of microchannel reactors are most fully manifested in the case of strongly exothermic or endothermic reactions where the catalyst temperature control is required to support high conversion efficiency [4]. The aim of the current study is the description of the rhodium catalyst synthesis that can be applied to the microchannel walls and the numerical study of methane steam reforming in a microchannel reactor which operates with this catalyst. The kinetics of the reforming reactions on a synthesized catalyst was determined using the numerical simulations and experimental data on activation energy of the methane reactions.

2. Catalyst preparation and characterizing

The use of microstructured reactors for hydrogen production necessitates the development of catalyst deposited on the inner surface of microchannels and provided necessary conversion of methane to synthesis gas. In these reactors the catalyst based on metal support has high thermal conductivity and can be used for catalytic combustion and steam conversion of methane in conjugated channels of a fuel processor. To prepare stable catalyst, a thin layer of titanium oxide was deposited firstly on the
inner wall of an annular microchannel. The washcoat of γ-Al₂O₃ with specific surface area of 150–170 m²/g was used as a support. The micro grains of aluminum oxide were impregnated with an aqueous solution of salts La(NO₃)₃·6H₂O and Ba(NO₃)₂ so that the weight content of oxides La₂O₃ and BaO were 2 and 3%, respectively. The resulting suspension was dried and calcined at high temperature to decompose the nitrates. The doped support was impregnated with an aqueous solution of Rh(NO₃)₃ so that the weight content of oxides La₂O₃ and BaO were 2 and 3%, respectively. After preparing the catalyst has been sprayed onto the channel surface and dried.

Before starting the experiments, rhodium oxide was reduced in 5% mixture of hydrogen with nitrogen during 3 h at the reactor temperature of 650°C.

The kinetic of the catalytic reactions was determined using experimental data on methane steam conversion obtained in the annular microchannel reactor with a gap of 950 μm and length of 40 mm. The description of the reactor and experimental procedure are given in [5]. The inner cartridge-cylinder of the annular channel was covered by a thin layer of catalyst. The experiments were performed in the through flow mode. Experimental data were obtained for residence time of 127 ms in the range of walls temperature from 680°C to 870°C. The ratio of the mole fractions of water and methane in initial composition and pressure at the reactor inlet equalled 2.4 and 1.24 bar, respectively.

To measure the species composition in dry gas at the microchannel outlet, the gas chromatograph of Perkin Elmer was used.

To determine activation energy, the first order reaction kinetics with respect to methane was assumed. According to [6], the rate of heterogeneous reaction is determined by the Arrhenius law and within the framework of one-dimensional model the reaction rate constant is determined as follows

\[
\frac{1}{k_e + k_D/k_D} = \frac{u'_z \ln \left( \frac{C_{CH_4}L}{C_{CH_4}^0} \right)}{S_v \ln \left( \frac{u_0}{u_0'} \right)}
\]

Here \( S_v \) is the surface-to-volume ratio for the reactor, \( u'_z \) is the mixture velocity gradient, \( C_{CH_4} \) is the methane concentration at reactor inlet \( 0 \) and outlet \( L \), \( k_D \) is the mass transfer coefficient. The dependence of the \( k_e \) logarithm on the catalyst temperature is shown in figure 1. As it is seen, the points corresponding to the reaction rate constant at high and low temperatures do not lie on the straight line. This shows that two reactions with participation of methane occur simultaneously during methane steam reforming and have different activation energies. A similar kinetic scheme for steam reforming on nickel catalyst was proposed in [7]. It includes three elementary reactions as follows

\[
1. \quad CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{(1)}
\]
\[
2. \quad CH_4 + 0.5CO_2 \rightarrow 2H_2 + 2CO \quad \text{(2)}
\]
\[
3. \quad CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(3)}
\]

**Figure 1.** Dependence of reaction rate constant on catalyst temperature, points are experimental data and calculation results.
\[ CH_4 + H_2O \leftrightarrow 3H_2 + CO, \quad \Delta H_{298}^\circ = 206 \text{ kJ/mol} \]  
\[ CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298}^\circ = -41 \text{ kJ/mol} \]  
\[ CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2, \quad \Delta H_{298}^\circ = +165 \text{ kJ/mol} \]  

where methane is used in reactions (2), (4), and carbon monoxide is obtained in reaction (2) for reaction (3). To determine the activation energies of reactions (2) and (4), let us set the rate constant of the overall reaction in the form of \( k_\text{e} = a_1 \exp(-E_1/RT) + a_2 \exp(-E_2/RT) \). The comparison of calculations of total reaction rate constant with experimental data shows their good agreement for designed catalyst if \( a_1 = 2 \times 10^6 \text{ m/s}; a_2 = 80 \text{ m/s}; E_1 = 160 \text{ kJ/mol}; E_3 = 80 \text{ kJ/mol} \).

3. Numerical simulation of steam reforming in micro-structured reactor  
To determine the kinetic parameters of reactions on synthesized rhodium catalyst in an annular microchannel and substantiate the operating mode of the microstructured reactor-heat exchanger, the numerical simulations of the methane steam reforming were carried out according to [8]. The mathematical model of steam methane reforming in a slotted microchannel consists of the Navier-Stokes equations for the laminar flow of a multicomponent compressible gas, supplemented by the kinetics of reactions in a catalytic layer located on the channel walls. The viscosity and thermal conductivity of the mixture depend on the temperature and concentration of the components and are calculated using semi-empirical equations [9,10]. For all components of the mixture, one diffusion coefficient of methane in water vapor is used, which depends on pressure and temperature according to [11].

The following boundary conditions for dimensionless variables are set on the wall in the reaction region:

\[
-\rho D_i \frac{\partial Y_i'}{\partial y} = D_{ai}s_i'
\]  

Here dimensionless variables are scaled by the channel gap size \( d \), initial velocity of mixture \( u_0 \), density \( \rho_0 \), viscosity \( \mu_0 \), and diffusion coefficient \( D_0 \); \( Y_i \) is the molar fractions of the component \( i \), \( s_i = \sum_j v_{i,j} \cdot r_j \) is the resulting molar flux of component \( i \) from all reactions scaled by \( s_{1,0} = k_\text{e}C_{CH_4,0}\rho_{\text{cat}} \); \( v_{i,j} \) is the stoichiometric coefficients of the \( j \)-th species in the \( j \)-th reaction with a plus sign if the species is produced, or with a minus sign if the species disappears, \( D_{ai} = ds_{1,0}M_i/\rho_{l,0}D_0 \) is the second Damköhler number, which characterized the ratio of molar flux of methane to the rate of mass transfer, \( n_i \) is the reaction rate of the \( j \)-th reaction, \( k_\text{e} \) is the rate constant of reaction (2), and \( \rho_{\text{cat}} \) is the catalyst density.

To determine the reaction rates of the reactions (2) - (4) for synthesized rhodium catalyst, a method of selection of the pre-exponential factors \( A_i \) for kinetic scheme [7] was used based on a comparison of the numerical results with experimental data. For this case, the rates of chemical reactions (2) - (4) proposed in [7] by using the Langmuir–Hinshelwood–Hougen–Watson approach and Freundlich adsorption concept depend on the partial pressures of components and temperature as follows:

\[
r_1 = A_1e^{-\frac{E_1}{RT}} \left( \frac{p_{CH_4}^{0.5}p_{H_2O}^{0.5}}{p_{H_2}^{1.5}} \right) \left( \frac{1 - p_{CO}p_{H_2}^3}{k_{p_1}p_{CH_4}^p p_{H_2O}^q} \right) \left( 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2}^{0.5} + K_{H_2O}p_{H_2O}p_{H_2} \right)^2
\]

\[
r_2 = A_2e^{-\frac{E_2}{RT}} \left( \frac{p_{CO}^{0.5}p_{H_2O}^{0.5}}{p_{H_2}^{1.5}} \right) \left( \frac{1 - p_{CO}p_{H_2}^3}{k_{p_2}p_{CO}^p p_{H_2O}^q} \right) \left( 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2}^{0.5} + K_{H_2O}p_{H_2O}p_{H_2} \right)^2
\]

\[
r_3 = A_3e^{-\frac{E_3}{RT}} \left( \frac{p_{CH_4}p_{H_2O}}{p_{H_2}^{1.5}} \right) \left( \frac{1 - p_{CO}p_{H_2}^3}{k_{p_3}p_{CH_4}^p p_{H_2O}^q} \right) \left( 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2}^{0.5} + K_{H_2O}p_{H_2O}p_{H_2} \right)^2
\]
In the calculations, the activation energies of reactions (2) and (4) were set equal to 160 and 80 kJ/mol, respectively. The activation energy of the shift reaction (3) was set as $E_2 = 15.4$ kJ/mol, the equilibrium constants of the reactions and the absorption constants were selected as in [7]. The definition of the pre-exponential factors $A_i$ for the reactions (2) through (4) is obtained during minimizing the function $\sigma = \sum_{i=1}^{N} (Y^i_c - Y^i_m)^2$ where $Y^i_c$ and $Y^i_m$ are the values of the molar fractions of the reaction products obtained in the calculation and measured at the highest and lowest temperatures. As a result of minimization, the following values of the pre-exponential factors $A_i$ were obtained: $A_1 = 1.72 \cdot 10^4$ kmol/(kgcat·s·(kPa)$^{0.25}$); $A_2 = 6.03 \cdot 10^{-3}$ kmol/(kgcat·s·kPa); $A_3 = 36.07$ kmol/(kgcat·s·(kPa)$^{0.25}$).

The results of numerical calculations performed for activation energies $E_1 = E_3 = 130$ kJ/mol, $E_2 = 15.4$ kJ/mol (dashed lines), as well as for $E_1 = 160$, $E_3 = 80$ kJ/mol (solid lines) at residence time of 127 ms are shown in figure 2. As it is seen, numerical results obtained under the assumption of the same activation energy $E_1 = E_3$ are less consistent with experimental data than the calculations with different activation energies. It indicates that the proposed approach for determination of the kinetic parameters using complex kinetic scheme allows for the reliable prediction of the conversion products at the reactor outlet.

![Figure 2](image)

**Figure 2.** Dependence of molar species concentration on temperature, solid lines are calculation at $E_1 = 160$, $E_3 = 80$ kJ/mol; dashed lines are calculation at $E_1 = E_3 = 130$ kJ/mol, points are experimental data.

4. Conclusions

An experimental study of steam methane conversion in an annular microchannel reactor has shown its high efficiency for hydrogen production. The developed method for the synthesis of rhodium-based catalyst with high phase composition homogeneity allows production of the efficient compact processor for hydrogen production. Analysis of the dependence of the logarithm of reaction rate constant on inverse temperature of the catalyst showed that two reactions with different activation energies occur simultaneously in the microchannel with the participation of methane. For the kinetic scheme based on the Langmuir-Hinshelwood model, the kinetic parameters of the reactions on synthesized rhodium catalyst were determined taking into account the difference in activation energies. Using these kinetic parameters, the numerical study of steam methane reforming in a slotted microchannel shows good agreement of calculation results with experimental data.
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