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A comparative study between modeling and experimental results over rhodium supported catalyst in dry reforming reaction

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HIGHLIGHTS

- A comparative study between modeling and experimental data over Rh catalyst.
- The overall good agreement between modeling results and experimental data.
- Modeling of pseudo-homogeneous catalytic reactor for syngas production.

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ABSTRACT

Production of synthesis gas (syngas) in order to use as a feed of different important industrial reactions such as Fischer–Tropsch, methanol synthesis and other chemicals has been attended. Dry reforming of methane is one of the main ways to produce syngas. In this work an appropriate kinetic model was developed and employed for modeling of dry reforming reaction over Rh supported catalyst. In order to compare the experimental results with modeling data, a rhodium catalyst supported on alumina-stabilized magnesia was prepared and employed in dry reforming reaction. The overall good agreement between modeling results and experimental data indicate that the present model correctly predicts the catalytic results.

1. Introduction

Catalytic dry reforming of methane, which converts two gases, CH_4 and CO_2, with high global warming potential to valuable synthesis gas, a mixture of hydrogen and carbon monoxide, has received considerable attention in recent years [1–3]. The H_2/CO ratio obtained by this reaction is about one that is quite appropriate for the synthesis of hydrocarbons through Fischer–Tropsch synthesis. Development of active and stable catalysts for dry reforming of methane attracted significant attention of researchers in recent years [4–7]. Research on the nickel catalysts used for this reaction has mainly focused on the intrinsic activity of the metal phase, stability towards carbon formation, the type of the support most suitable for improving the efficiency of the catalyst, and the reaction mechanism. Although the extensively developed nickel catalysts have shown very high activity from the industrial point of view, they are completely deactivated within a few hours of reaction due to the formation of stable and inactive carbon on the surface [8–10]. Recently, several studies on the dry reforming of methane focused on the noble metal catalysts, which exhibit better activity and very high stability due to the less sensitivity to carbon deposition [11,12]. Modeling of process is a technique that normally applied to analyze and optimize process parameters. Moreover, it can also be used to optimize the operating parameters in the scale-up process prior to experimental testing. Many researchers have implemented mathematical models for analyzing reactors [13]. In this work, mathematical modeling of catalytic reactor for dry reforming of methane over rhodium noble metal catalyst was investigated and the obtained results were compared with experimental data.

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Nomenclature

F	gas flow in the reactor, m^3/s
k_0	preexponential coefficient for the rate constant of reaction, (unit is given in Table 1)
k	rate constant of reaction, (unit is given in Table 2)
E	activation energy of chemical reaction, (unit is given in Table 2)
K_i	equilibrium constant for the reaction i, (unit is given in Table 3)
K_{0j}	preexponential coefficient for the adsorption rate constant of component j, (unit is given in Table 3)
K_j	adsorption coefficient for the component j, (unit is given in Table 3)
P	pressure, Pa
T	temperature, K
T_f	temperature of furnace, K
C_p	heat capacity, J/m^3 K
rj	reaction rate of component j
Ri	rate of reaction i
R	universal gas constant, J/mol K
k_q	thermal conductivity of quartz, W/m K
X	reactant conversion, dimensionless
Y	yield of product, dimensionless

Greek letters

v_{ji}	stoichiometric constant of component j in reaction i
ΔH_i	Enthalpy of reaction i, J/mol K
ΔG_{0i}	heat of adsorption of component j, (unit is given in Table 2)

Subscripts

i	number of reactions
j	components

Abbreviations

EXP	experimental results
MOD	modeling results

2. Methodology of modeling

2.1. Simulation of packed bed reactor

The reactor used for this work was a quartz tube with an inner diameter of 7 mm and a length of about 30 cm. The catalyst was placed in the middle of reactor. Usually in a packed bed catalytic reactor, uniformly sized catalytic particles with a limit range of particle size distribution (0.25–0.5 mm) held in position within a tube.

To simulate a packed bed reactor, we make the following assumptions:

1. Plug flow in the bed, no radial profiles. Described by the pseudo-homogeneous plug flow model.
2. Uniform catalyst pellet exterior.
3. Particles are small compared to the length of the reactor.
4. Neglect axial diffusion in the bed.
5. Conditions are considered steady state.

The reactions network in this case is complex (Table 1) [14], but the main reactions, which may occur in CO_2 reforming of methane are considered as below:

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad (1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (2)$$

2.2. Mathematical relationship

2.2.1. Material and energy balance

A schematic view of microreactor is shown in Fig. 1. In a plug flow reactor the composition of the fluid varies from point to point along a flow path; consequently, mass balance for each five species ($j = CH_4$, CO_2, H_2, CO and H_2O) involved in these reactions presents by Eq. (3).

$$\frac{dF_j}{dz} = \sum_i v_{ji} r_j A_t \quad (3)$$

When the heat absorbed or released by reaction can markedly change the temperature of the reacting fluid, this factor must be accounted for this design. Thus we need to use both the material and energy balance expressions. Energy balance for this packed bed reactor exposure reactions was expressed in Eq. (4).

$$\frac{dT}{dz} = \frac{[U - R_1 A_t \Delta H_1 - R_2 A_t \Delta H_2 - T\sum_i (C_{p_j} \frac{dF_j}{dz})]}{\sum_j C_{p_j} F_j} \quad (4)$$

Quantity of U calculated from Eq. (5)

$$U = \frac{2\pi \times k_q (T_f - T)}{\ln\left(\frac{R_{out}}{R_{in}}\right)} + 2\pi \times R_{out} \sigma (T_f^4 - T^4) \quad (5)$$

The Enthalpy for these reactions is calculated from the Gibbs–Helmholtz relation:

$$\Delta H = \Delta H^{298} + \int_{T_{298}}^{T} \nabla C_P dT \quad (6)$$

MATLAB software was applied to solve the system of ordinary differential equations with considering boundary conditions ($z = 0$, $F_i = F_{i0}$, $T = T_0$).

Table 1
The reaction network in dry reforming reaction.

Reaction number	Reaction	$\Delta H_{298\ K}$ (kJ/mol)
1	$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$	261
2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
3	$CH_4 \leftrightarrow C + 2H_2$	74.9
4	$2CO \leftrightarrow C + CO_2$	−172.4
5	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	−90
6	$H_2 + CO \leftrightarrow H_2O + C$	−131.3
7	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	−165
8	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	−206.2

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