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Kinetics for hydrogen production by methanol steam reforming in fluidized bed reactor

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Abstract Hydrogen is one of the best energy carriers. Fluidized bed reactor provides a promising approach for hydrogen production. To describe the hydrogen generating rate with methanol steam reforming in fluidized bed reactor quantitatively, dual-rate kinetic models of the reactions with exponent form were developed, including that of steam reforming reaction (SR) and decomposition reaction (DE). The reaction rate per unit mass of catalyst was related to partial pressures of components. The exponentials in kinetic equations were obtained by linear least-squares method based on the experimental data. The variance homogeneity test (F test) shows that the dynamic models are feasible with high accuracy, which can be used to predict the generating rate of hydrogen under different reaction temperatures and feed flow rates in fluidized bed reactor. The SR and DE activation energy obtained indicates that $E_{SR} < E_{DE}$, which can explain the previous observation that the CO_2 selectivity decreased with the temperature increase.

Keywords Kinetics model · Methanol steam reforming · Hydrogen production · Fluidized bed reactor

1 Introduction

Hydrogen is one of the best clean energy carriers and has been widely used in various fields of industry, including that of aerospace, food processing, organic synthesis, biofuel and fuel cells [1–4]. Methanol steam reforming (MSR) for hydrogen production is widely used, because of its low reaction temperature and low energy consumption, high content and high quality of hydrogen in the product, simple process control, etc. [5, 6]. Compared to fixed bed reactor, the fluidized bed reactor (FBR) has the advantages of more uniform temperature distribution, higher heat-transfer rate, larger surface volume ratio and longer contacting time. Hence, a fluidized bed reactor can achieve much higher conversion efficiency than that of fixed bed reactors [7–9]. However, at present, the studies mainly focus on the selection of catalysts, operating conditions and reactors. There are few studies about kinetics of the reaction of methanol steam reforming in FBR. In present paper, based on the previous experimental study [10], the kinetic equations are to be established for further design for hydrogen production in FBR.

2 Kinetic model and governing equations

It has been revealed that the methanol steam reforming can be described on the basis mainly of the following reactions, including that of steam reforming reaction (SR), decomposition reaction (DE) and water gas shift reaction (WGS) [11, 12],

$$\text{SR: } CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \ (\Delta H_R = 49.0\,\text{kJ/mol}), \quad (1)$$

$$\text{DE: } CH_3OH \rightarrow CO + 2H_2 \ (\Delta H_R = 90.0\,\text{kJ/mol}), \quad (2)$$

$$\text{WGS: } CO + H_2O \Leftrightarrow CO_2 + H_2 \ (\Delta H_R = -41.0\,\text{kJ/mol}). \quad (3)$$

Based on the chemical reaction equations, the model can be divided into single-rate, dual-rate and three-rate kinetic

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model [13]. Three-rate model is complex and difficult to solve dynamics equations. At present, dual-rate model is widely used, especially for parallel reaction mechanism of SR and DE.

There are totally five components in the reaction system, namely, CH_3OH, H_2O, CO_2, CO and H_2. According to Refs. [14–16], methanol steam reforming reaction rate, r_{SR}, in mol/(s kg) is related to partial pressures of CH_3OH, H_2O, CO_2 and H_2. Methanol decomposition reaction rate, r_{DE}, in mol/(s kg) is related to partial pressures of CH_3OH, CO and H_2. Therefore, kinetic equation with the exponential model can be expressed as follows,

$$r_{SR} = k_{11} e^{-\frac{E_{a1}}{RT}} P_{CH_3OH}^{k_{21}} P_{H_2O}^{k_{31}} P_{CO_2}^{k_{41}} P_{H_2}^{k_{51}}, \quad (4)$$

$$r_{DE} = k_{12} e^{-\frac{E_{a2}}{RT}} P_{CH_3OH}^{k_{22}} P_{CO}^{k_{32}} P_{H_2}^{k_{42}}, \quad (5)$$

where k_{11} and k_{12} are the pre-exponential factors and positive, determined by the experiment; E_{a1} and E_{a2} are the activation energies, J/mol; R is the molar gas constant, 8.314 J/(mol K); T is the thermodynamic temperature, K; $P_{CH_3OH}, P_{H_2O}, P_{CO_2}, P_{CO}$ and P_{H_2} in Pa are the partial pressures of CH_3OH, H_2O, CO_2, CO and H_2, respectively; $k_{21}, k_{31}, k_{41}, k_{51}, k_{22}, k_{32}$ and k_{42} are the exponential of reaction rate changing with the pressure of each corresponding component.

Exponential kinetic equations can be transformed into a linear equation. Taking Eqs. (6) and (7) as the objective functions, the parameters can be determined by the linear least-square parameter estimation method.

$$f_{SR} = \sum_I (\ln r_{SR} - \ln \widehat{r_{SR}})^2, \quad (6)$$

$$f_{DE} = \sum_I (\ln r_{DE} - \ln \widehat{r_{DE}})^2, \quad (7)$$

where $\widehat{r_{SR}}$ and $\widehat{r_{DE}}$ are the calculated values of SR and DE reaction rate, respectively, the subscript I represents the collection of data sets, and in this study I takes from 1 to 18.

3 Experimental setup

The experimental system has been established to reveal the transport characteristic on methanol steam reforming in FBR [10], of which the flowchart is shown in Fig. 1.

During the experiments, the pure methanol and high-purity distilled water were mixed at a certain H_2O-to-CH_3OH ratio, and then fed by a peristaltic pump at a certain flow rate to flow through the heat exchanger and preheater successively. The reactants were heated to the determined temperature and evaporated, and then flowed into the fluidized bed reactor under the atmospheric pressure conditions. The methanol steam reforming reaction took place under $Cu/Zn/Al_2O_3$ catalysts. The producing gases, including that of CO, CO_2, N_2 and H_2, as well as liquids, mainly methanol and water, which did not participate in the reaction, were cooled by the condenser, were separated and collected with sample bags and sample bottles, respectively.

In the present experiments, the parameters measured are the inlet flow rate of reactants, the pre-heating and reaction temperature, and the products composition.

The peristaltic pump (BT100-2J), with the flow rate range of (0.007–380) mL/min, was employed to send the reactants to the reactor, and the feed flow rate was

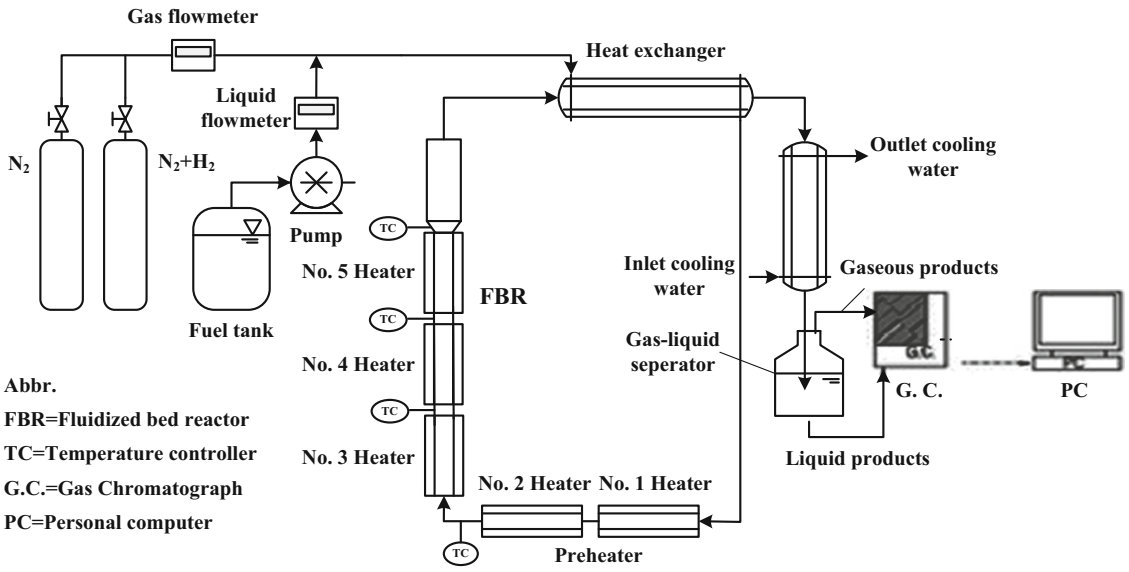

Fig. 1 The flowchart of the experimental setup