



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

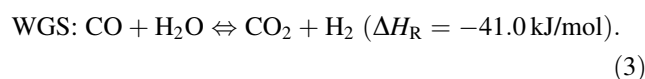
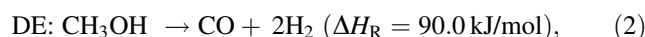
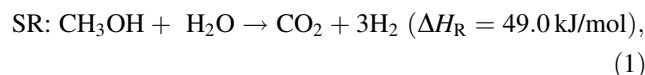
1 Introduction

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],



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, CH₃OH, H₂O, CO₂, CO and H₂. According to Refs. [14–16], methanol steam reforming reaction rate, r_{SR} , in mol/(s kg) is related to partial pressures of CH₃OH, H₂O, CO₂ and H₂. Methanol decomposition reaction rate, r_{DE} , in mol/(s kg) is related to partial pressures of CH₃OH, CO and H₂. Therefore, kinetic equation with the exponential model can be expressed as follows,

$$r_{\text{SR}} = k_{11} e^{-\frac{E_{a1}}{RT}} P_{\text{CH}_3\text{OH}}^{k_{21}} P_{\text{H}_2\text{O}}^{k_{31}} P_{\text{CO}_2}^{k_{41}} P_{\text{H}_2}^{k_{51}}, \quad (4)$$

$$r_{\text{DE}} = k_{12} e^{-\frac{E_{a2}}{RT}} P_{\text{CH}_3\text{OH}}^{k_{22}} P_{\text{CO}}^{k_{32}} P_{\text{H}_2}^{k_{42}}, \quad (5)$$

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; $P_{\text{CH}_3\text{OH}}$, $P_{\text{H}_2\text{O}}$, P_{CO_2} , P_{CO} and P_{H_2} in Pa are the partial pressures of CH₃OH, H₂O, CO₂, CO and H₂, 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.

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

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

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 H₂O-to-CH₃OH ratio, and then fed by a peristaltic pump at a certain flow rate to flow through the heat exchanger and pre-heater 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/Al₂O₃ catalysts. The producing gases, including that of CO, CO₂, N₂ and H₂, 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

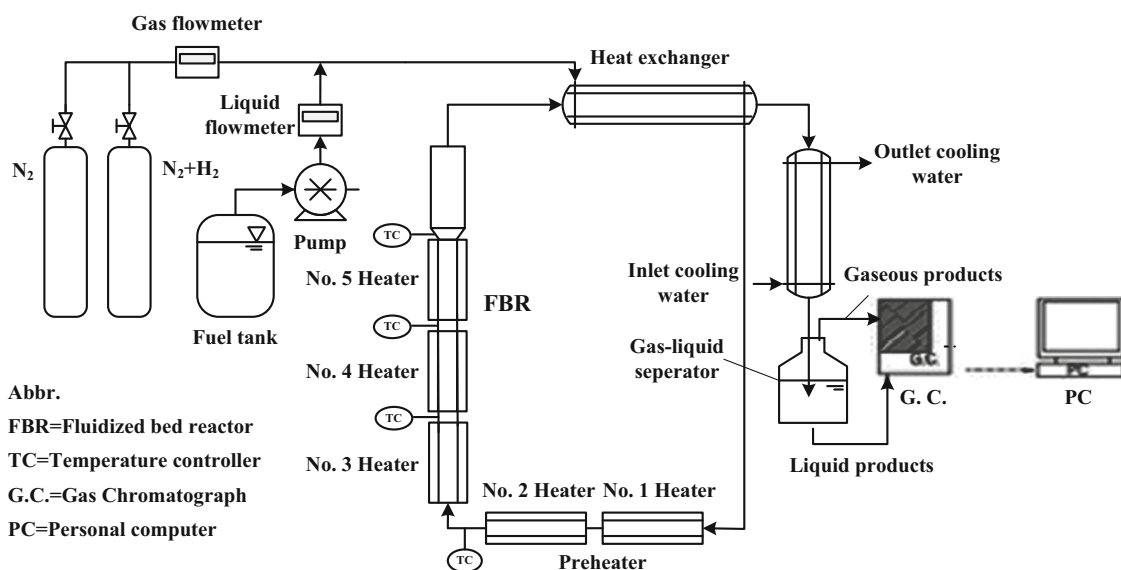


Fig. 1 The flowchart of the experimental setup

measured by the flow meter (Alicat 40, error $\pm 2\%$) with the range of (0–100) mL/min. Four K-type thermocouples (error $\pm 0.5\%$) were inserted to the axis of the tube. One thermocouple was used to measure temperature of the reactants heated by the pre-heater, and the others were arranged along the reactor length at each 150 mm. The out surface of the heaters, heat exchanger and tubes was wrapped by asbestos. The temperatures were controlled by adjusting the PID temperature controllers (XMT7-C11*K-00), with measurement range of (0–1,300) K, grad of accuracy, 0.5, proportional constant, $KP = 0$, hysteresis limit set value, $Sd = 400$, integration constant, $KI = 21$, and derivative constant, $Kd = 5$.

The producing gases and liquids were analyzed through gas chromatograph (Thermo Scientific ISQ GC/MS, error $\pm 0.1\%$), with different columns. Liquids were analyzed through columns I (TDX-01, length 2 m, mesh range 60–80, OD 1/8). The gases were analyzed through columns II (Porapak T, length 2 m, mesh range 80–10, OD 3 mm). The producing gases collected in a certain time were measured by volume. The yield rate of hydrogen could be then acquired under certain operating conditions.

More details of the experiments and data process can also refer to Ref. [10].

4 Results and discussions

The ranges of experimental parameters are as follows: reaction temperature, T , (553–603) K; H_2O -to- CH_3OH molar ratio, S/C , 1–4; feed flow rate, V , (435–800) mL/h; catalyst mass, 40 g.

In order to eliminate the interference of internal diffusion on kinetics, the influence of catalyst size on the methanol conversion was investigated firstly in the same reactor, under the operating conditions of $T = 593$ K, $V = 540$ mL/h and $S/C = 1.3$. It can be shown in Fig. 2 that methanol conversion rate increases with the catalyst particle size decrease. However, it is also shown that the

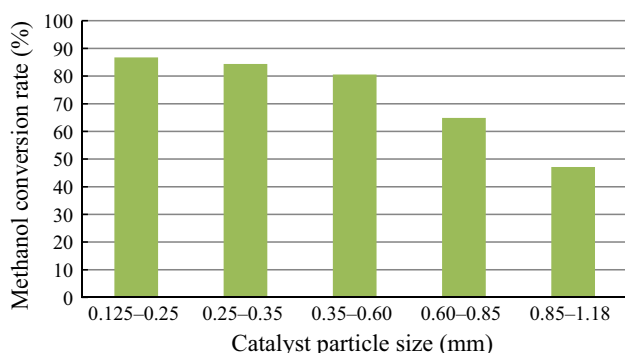


Fig. 2 (Color online) The influence of catalyst size on the methanol conversion

methanol conversion rate is not changed obviously, while the particle size is less than (0.25–0.35) mm. Under this condition, the internal diffusion is considered to have been eliminated. Based on the results, the range of catalyst size in the present experiments is set to be (0.125–0.25) mm.

Methanol steam reforming and decomposition reaction rate can be calculated by component content, X , exhaust dry gas flow rate, F_{dry} , in mol/s, and the amount of catalyst, W , in g [14],

$$r_{SR} = X_{CO_2} \times F_{dry} / W, \quad (8)$$

$$r_{DE} = X_{CO} \times F_{dry} / W, \quad (9)$$

in which, the reaction rates are defined as the generating rate of the products per unit mass of catalyst.

The measured component content is dry basis during experiments, while kinetic data in the model need to be wet basis. So based on material balance principle and combining Eqs. (8) and (9), the experimental data were translated and sorted, as listed in Table 1.

The static tests were run in the present study. During each experiment, data acquisition began when the reaction temperature had been stable for 1 h. And the experiments were carried out for at least three times.

Exponential kinetic equations can be transformed into a linear equation. Applying the linear least-square method for the experimental data in Table 1, the parameters of reaction rate expressions can be obtained with the best fitting. Following the format of Eqs. (4) and (5), the reaction rate expressions can be then obtained as follows,

$$r_{SR} = 84.185e^{-\frac{57178}{RT}} P_{CH_3OH}^{0.321} P_{H_2O}^{-0.00685} P_{CO_2}^{0.858} P_{H_2}^{-0.634}, \quad (10)$$

$$r_{DE} = 65.595e^{-\frac{63374}{RT}} P_{CH_3OH}^{0.310} P_{CO}^{0.738} P_{H_2}^{-0.475}. \quad (11)$$

Neglecting the interference of internal diffusion, the above dual-rate kinetic models can be employed to predict the reaction rate of methanol steam reforming in fluidized bed reactor over the catalyst of $CuO/ZnO/Al_2O_3$.

The kinetic model can be proved by the variance homogeneity test (F test), which is used to identify whether the model best fits the data that were sampled. The results are listed in Table 2. ρ^2 is correlation coefficient of linear fit to parity plots. The regression equation is considered reliable when $\rho^2 > 0.9$.

Figures 3 and 4 show the comparisons between experimental data and predicted values by kinetic equations. It is shown that the experimental and predicted values fit quite well. f represents the sampling distribution in probability statistics, and $f_a(P, MP - 1)$ is upper the fractile of the f distribution, which means the degree of linear correlation. While $f > 10f_a(P, M - P - 1)$, it means that the resulting kinetic equations are highly significant, as shown in Table 2, indicating that the reaction rate over $CuO/ZnO/Al_2O_3$ in FBR can be calculated by Eqs. (10) and (11).

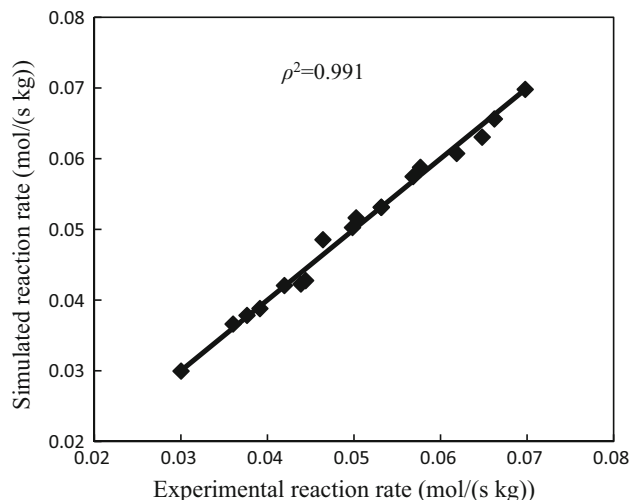
Table 1 The experimental results of methanol steam reforming in fluidized bed reactor

No.	Gas composition (Pa)					$-1/(RT)$	r_{SR} (mol/(s kg))	r_{DE} (mol/(s kg))
	P_{CH_3OH}	P_{H_2O}	P_{H_2}	P_{CO_2}	P_{CO}			
1	8,983	17,445	56,173	18,574	151	-0.000218	0.0300	0.000254
2	1,549	46,409	40,025	13,155	187	-0.000203	0.0360	0.000512
3	925	45,263	41,353	13,574	210	-0.000199	0.0376	0.000582
4	9,908	16,216	57,909	19,144	159	-0.000214	0.0391	0.000345
5	2,169	37,537	46,214	15,185	220	-0.000203	0.0420	0.000606
6	6,534	14,705	60,064	19,817	204	-0.000210	0.39	0.000452
7	1,225	35,982	48,089	15,782	248	-0.000199	0.0444	0.000697
8	5,205	13,234	62,164	20,471	251	-0.000206	0.0464	0.000568
9	3,396	25,229	54,525	17,914	261	-0.000203	0.0498	0.000727
10	3,320	11,146	65,144	21,400	315	-0.000203	0.0502	0.000739
11	1,964	9,655	67,279	22,053	373	-0.000199	0.0531	0.000900
12	1,964	9,652	67,282	22,057	370	-0.000199	0.0531	0.000891
13	5,109	13,169	62,285	20,463	299	-0.000203	0.0568	0.000829
14	2,527	10,280	66,389	21,773	356	-0.000199	0.0577	0.000944
15	3,020	10,832	65,604	21,523	345	-0.000199	0.0619	0.000996
16	6,501	14,741	60,062	19,738	283	-0.000203	0.0648	0.000930
17	3,784	4,235	69,980	22,876	450	-0.000199	0.0662	0.00130
18	4,785	12,823	62,788	20,606	324	-0.000199	0.0698	0.00110

Table 2 Statistical examination for the parameters of kinetic models

Item	Expression	SR	DE
No. of experiments	M	18	18
No. of variables	P	6	5
S_t	$S_t = \sum_{i=1}^M (\hat{r}_i - \bar{r})^2$	0.907	2.934
S_r	$S_r = \sum_{i=1}^M (r_i - \hat{r}_i)^2$	0.00834	0.0169
S_e	$S_e = \sum_{i=1}^M (r_i - \bar{r})^2$	0.915	2.951
ρ^2	$1 - S_r/S_e$	0.991	0.994
f	$\frac{S_t/P}{S_e/(M-P-1)}$	260.917	565.104
$f_a(P, M - P - 1)$	$a = 0.05$	3.09	3.11
$f_a(P, M - P - 1)$	$a = 0.01$	5.07	5.06

It can be also obtained from the equations that the SR activation energy, 57.178 kJ/mol, is less than the DE activation energy, 63.375 kJ/mol. Hence, the methanol decomposition reaction (DE) will be more susceptible to the reacting temperature variation. In addition, as shown in Eq. (2), the methanol decomposition is an endothermic reaction with $\Delta H_R = 90.0$ kJ/mol. Therefore, increasing temperature has greater influence on methanol decomposition reaction [17]. This is consistent with and can explain

**Fig. 3** Comparison between experimental reaction rate and calculated reaction rate in SR

the previous observation that the CO_2 selectivity decreased with the temperature increase.

5 Concluding remarks

Based on the experimental data of methanol steam reforming in fluidized bed reactor, dual-rate kinetic models

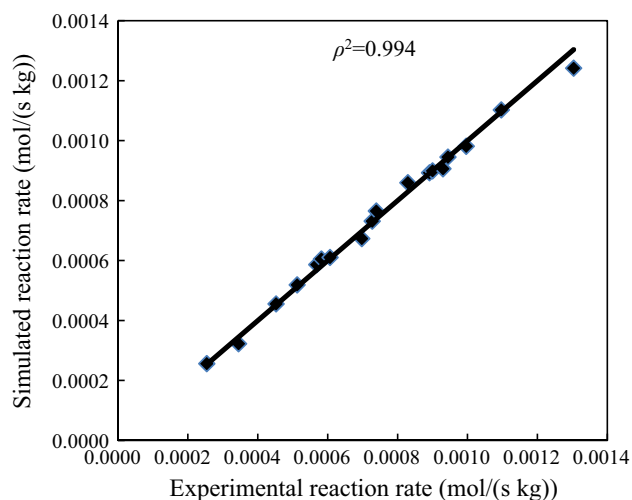


Fig. 4 Comparison between experimental reaction rate and calculated reaction rate in DE

with exponent form of the reactions were employed and established by linear least-squares method. The generating rate of hydrogen per unit catalyst can be then predicted under different reaction temperatures, feed flow rates and compositions of products. *F* test showed that the dynamic model was feasible with high accuracy. The SR and DE activation energy obtained indicates that $E_{SR} < E_{DE}$, which can be an explanation of the previous observation that the CO_2 selectivity decreased with the temperature increase.

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Conflict of interest The authors declare that they have no conflict.

References

1. Kolb G (2013) Review: microstructured reactors for distributed and renewable production of fuels and electrical energy. *Chem Eng Process* 65:1–44

2. Abbas HF, Daud W (2010) Hydrogen production by methane decomposition: a review. *Int J Hydrogen Energy* 35:1160–1190
3. An L, Zhao TS, Yan XH et al (2015) The dual role of hydrogen peroxide in fuel cells. *Sci Bull* 60:55–64
4. Zhao J (2015) Development of China's biofuel industry and policy making in comparison with international practices. *Sci Bull* 60:1049–1054
5. Agarwal V, Patel S, Pant KK (2005) H_2 production by steam reforming of methanol over Cu/ZnO/ Al_2O_3 catalysts: transient deactivation kinetics modeling. *Appl Catal A Gen* 279:155–164
6. Pan M, Wu Q, Jiang L (2015) Effect of microchannel structure on the reaction performance of methanol steam reforming. *Appl Energy* 154:416–427
7. Ortiz M, Luis F, Abad A et al (2010) Hydrogen production by auto-thermal chemical-looping reforming in a pressurized fluidized bed reactor using Ni-based oxygen carriers. *Int J Hydrogen Energy* 35:151–160
8. Gallucci F, Sintannaland M, Kuipers J (2010) Theoretical comparison of packed bed and fluidized bed membrane reactors for methane reforming. *Int J Hydrogen Energy* 35:7142–7150
9. Chen ZX, Grace JR, Lim CJ et al (2007) Experimental studies of pure hydrogen production in a commercialized fluidized-bed membrane reactor with SMR and ATR catalysts. *Int J Hydrogen Energy* 32:2359–2366
10. Shi YS, Du XZ, Yang LJ et al (2013) Experiments on hydrogen production from methanol steam reforming in fluidized bed reactor. *Int J Hydrogen Energy* 38:13974–13981
11. Cao C, Xia G, Holladay J et al (2004) Kinetic studies of methanol steam reforming over Pd/ZnO catalyst using a microchannel reactor. *Appl Catal A Gen* 262:19–29
12. Maxim L, Subir R (2004) Novel catalytic reactor for oxidative reforming of methanol. *Appl Catal B Environ* 54:203–215
13. Agrell J, Birgersson H, Boutonnet M et al (2003) Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO_2 and Al_2O_3 . *J Catal* 219:389–403
14. Won JY, Jun HK (2006) Performance of microchannel reactor combined with combustor for methanol steam reforming. *Catal Today* 111:158–163
15. Jiang CJ, Trimm DL, Wainwright MS (1993) Kinetic study of steam reforming of methanol over copper-based catalysts. *Appl Catal A Gen* 93:245–255
16. Patel S, Pant KK (2007) Experimental study and mechanistic kinetic modeling for selective production of hydrogen via catalytic steam reforming of methanol. *Chem Eng Sci* 62:5425–5435
17. Zhao T, Guo ZY (2015) The duality of internal energy of ideal gas. *Sci Bull* 60:1355–1358