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Reduced rate method for discrimination of the kinetic models for the water–gas shift reaction

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Abstract

All the kinetic models of the water–gas shift reaction proposed in the past have been discriminated by a new approach, which is based on the effect of total pressure upon the reduced rate r_R. The reaction rate, from which the experimental values of reduced rate were obtained, has been measured experimentally on an internal circulating gradientless reactor at 670.8 K in the pressure range 0.1–1.4 MPa and with the same conversion gas. On the other hand, the experiments varying the content of the species CO, H_2O, CO_2 and H_2 in the conversion gas were performed on a micro-integral reactor so as to estimate the parameters in the rival models and to gain the calculated values of reduced rate. If the calculated values of the reduced rate of the rival model coincide with the experimental values of the reduced rate of the shift reaction, this model could be regarded as the most appropriate kinetic equation. The results of the discrimination manifested that the most appropriate intrinsic kinetic equation is the one suggested by Fott [P. Fott, Collection Czechoslov. Chem. Commun. 44 (1979), 652] © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The water–gas shift reaction is a reversible exothermic chemical reaction assisted by an iron oxide-based catalyst:

$$CO + H_2O(g) \leftrightarrow CO_2 + H_2$$
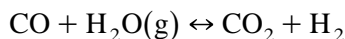
$$\Delta H_R = -40.6 \, kJ/mol$$

This reaction is widely used in the ammonia synthesis process and the preparation of hydrogen. The kinetics of this reaction is of theoretical and practical significance. Since the 30s of this century, the kinetics of this reaction was studied by many scholars [1]. A great variety of models and different mechanism hypotheses [2–6] have been proposed, but the style and parameters of these models are not the same, and some are quite different. So it is necessary further to discriminate among the alternative kinetic models. In this paper the existent kinetic models of the shift reaction have been discriminated by a new approach. The results of discrimination manifested that the most appropriate intrinsic kinetic equation of the water–gas shift reaction is the one proposed by Fott [5].

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2. Kinetic models and discrimination

The discrimination of the kinetic model is based on the effect of total pressure upon the reduced rate r_R. The reduced rate is defined as $r_R = r_P / r_0$, where r_P is the reaction rate at elevated total pressure P, and r_0 is the reaction rate at the datum pressure P_0, which is normal atmosphere or a certain selected pressure. The reaction rates at different pressures P are measured on a gradientless reactor at a constant temperature. The inlet gas of the reactor is the same, so y_i^0 (i: CO, H_2O, CO_2 and H_2) is constant respectively. The composition of the exit gas of the reactor at different pressure is maintained to be identical by means of adjusting the gas velocity, i.e., keeping y_i to be constant respectively. Thus the reduced rate r_R could be expressed as follows:

$$r_R = \frac{r_P}{r_0} = \frac{k_T f(p_i, P)}{k_T f(p_{0i}, P_0)} = \frac{f(y_i, P)}{f(y_i, P_0)} = F(P),$$
(1)

where $k_T = k_0 e^{E/RT}$; $p_i = P y_i$; $p_{0i} = P_0 y_i$;

At the same temperature the rate constant k_T is identical. Therefore, the reduced rate r_R is the function of total pressure P only. The five representative models are adopted as the rival models and are listed in Table 1. The calculating expressions of r_R of the rival models are

also shown in Table 1. The model that the calculated values of r_R coincide with the experimental values of r_R of the shift reaction could be regarded as the most appropriate kinetic equation.

3. Experimental

In order to get the experimental values of the reduced rate of the shift reaction, the reaction rates have been measured experimentally at 670.8 ± 0.3 K in the pressure range 0.10–1.40 MPa.

3.1. Set-up

A diagram of the experimental set-up is shown in Fig. 1. The gases were supplied through the steady pressure valve (2) and the purifying column (3) to the water saturator (6) where liquid water was introduced by means of a dosing micro-pump (17). When the total pressure was elevated, it was necessary to raise the temperature of the oil bath so as to keep the identical content of the water vapor in the conversion gas. The mixture of water vapor and gases entered the reactor (10). The exit gas of the reactor was passed through the throttle valve (13) and the condenser (14), which removed the water vapor among the exit gas. The flow rate was measured by a flow meter (15). When the

Table 1
Rival models and calculating expressions of r_R

| Number	Rival models	Reference	Calculating expressions of r_R
1	$r = k_T p_{H_2O} p_{CO}(1 - \beta)$	[2]	$r_R = (P/P_0)^2$
2	$r = k_T p_{CO}^a p_{H_2O}^b p_{CO_2}^c p_{H_2}^d (1 - \beta)$	[3]	$r_R = (P/P_0)^{0.65}$
3	$r = k_T \dfrac{p_{CO_2} p_{H_2}(1 - \beta)}{A p_{H_2O} + p_{CO_2}}$	[4]	$r_R = (1/P_0)P$
4	$r = k_T \dfrac{p_{CO} p_{H_2O}(1 - \beta)}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{H_2O} p_{H_2O}} + K_{CO_2} p_{CO_2}\right)^3}$	[5]	$r_R = \dfrac{p_0 \left(1/p_0 + K_{CO} y_{CO} + \sqrt{K_{H_2O} y_{H_2O}} + K_{CO_2} y_{CO_2}\right)^3}{p \left(1/p + K_{CO} y_{CO} + \sqrt{K_{H_2O} y_{H_2O}} + K_{CO_2} y_{CO_2}\right)^3}$
5	$r = k_T \dfrac{p_{CO} p_{H_2O}(1 - \beta)}{\left(1 + K_{CO} p_{CO} + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2}\right)^2}$	[5]	$r_R = \dfrac{\left(1/P_0 + K_{CO} y_{CO} + K_{H_2O} y_{H_2O} + K_{CO_2} y_{CO_2}\right)^2}{\left(1/P + K_{CO} y_{CO} + K_{H_2O} y_{H_2O} + K_{CO_2} y_{CO_2}\right)^2}$
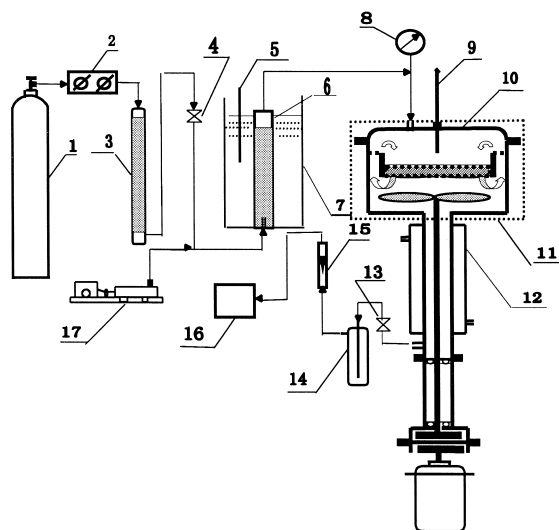
Fig. 1. Experimental set-up. (1) Cylinder. (2) Steady pressure valve. (3) Purifying column. (4) Throttle valve. (5) Thermometer. (6) Saturator. (7) Oil bath. (8) Pressure meter. (9) Thermocouple. (10) Reactor. (11) Electric Heater. (12) Water jacket. (13) Throttle valve. (14) Condenser. (15) Flow meter. (16) Chromatograph. (17) Dosing micro-pump.

total pressure was changed, the composition of the exit gas of the reactor was kept to be identical by means of adjusting the gas velocity. A chromatograph analyzed the exit gas for the composition.

3.2. Reactor

The reactor was an internal circulating gradientless one. It has been confirmed experimentally that this reactor showed good gradientless performance when the rotational speed was 2000–2500 rpm.

3.3. Catalyst

The catalyst used was a commercial iron oxide-based catalyst. The specific surface area was 45 m^2/g cat. The composition (by mass) before reduction was following: Fe_2O_3, 63–75%; Cr_2O_3, 12–14%; MgO, 3.5–4.5%. The particle size was 0.2–0.3 mm. The amount of the catalyst was 0.2000 g. The catalyst was reduced with the reaction gas in the flow regime

Table 2
Experimental values of reaction rate and reduced rate

P	0.10	0.30	0.50	0.70	1.00	1.40
r_P	0.0160	0.0350	0.0397	0.0417	0.0437	0.0493
r_R	1.00	2.20	2.49	2.61	2.74	3.09

with the recirculation. The space-velocity was 1000 h^{-1}. Raising temperature from 303 K to 473 K was for 3 h. The reduction of catalyst was run at 473–523 K for 2 h, at 523–723 K for 3 h. The final reduction of catalyst was run at 723 K for 5 h.

3.4. Gases

The conversion gas was taken from an ammonia plant, diluted by hydrogen and laid in a cylinder. The composition of the inlet gas of the reactor (by mole fraction) was y_{CO}, 0.0779; y_{H_2O}, 0.1557; y_{CO_2}, 0.0229; y_{N_2}, 0.1067; y_{H_2}, 0.6351; y_{CH_4}, 0.0017. The degree of conversion of carbon monoxide at different pressures was maintained to be 0.306 ± 0.006 by means of adjusting the gas velocity, i.e., the average composition of the exit gas of the reactor (by mole fraction) was y_{CO}, 0.0541; y_{H_2O}, 0.1319; y_{CO_2}, 0.0467; y_{N_2}, 0.1067; y_{H_2}, 0.6589; y_{CH_4}, 0.0017.

In order to get the calculated values of the reduced rates of the rival models, the experiments varying the mole fractions of the species CO, H_2O, CO_2 and H_2 in the reaction gas have been performed so as to estimate the parameters in the rival models. Except for the reactor, the

Table 3
Experimental kinetic data

Run number	y_{CO}^0	$y_{H_2O}^0$	$y_{CO_2}^0$	$y_{H_2}^0$	V_0	α
1	0.1786	0.3109	0.0877	0.2833	0.06921	0.383
2	0.1838	0.2850	0.1325	0.2339	0.06538	0.3333
3	0.1684	0.2646	0.1584	0.2011	0.06503	0.3047
4	0.1301	0.2295	0.0727	0.1835	0.05889	0.4208
5	0.1555	0.2647	0.1306	0.2026	0.06430	0.3590
6	0.1311	0.3107	0.1456	0.2301	0.06830	0.3393
7	0.0845	0.1504	0.0923	0.1116	0.05298	0.4174
8	0.0774	0.1903	0.1449	0.1748	0.05650	0.3138
9	0.0866	0.1992	0.1908	0.1356	0.05752	0.2481

set-up was much the same as the above mentioned one. The reactor was a micro-integral type with diameter of 5 mm and made of stainless steel. The catalyst used and the reducing conditions are the same as those of aforementioned. The amount of the catalyst was 0.3000 g. The gases with the different compositions were prepared from pure gas of the species CO, H_2O, CO_2, H_2, and were laid in the cylinders, respectively.

4. Results

For the measurement of the reaction rate, the catalyst used was stabilized by running for 30 days at working conditions before starting the measurements. Three series of runs have been made with the same batch of catalyst on the above stated conditions. The catalyst, with the uniform activity, was lasted all the way. A typical set of the data of the reaction rate at different pressures is listed in Table 2. Selecting 0.1 MPa to be datum pressure P_0, i.e., r_0 is 0.0160 mol/g h, the experimental values of the reduced rate are calculated from $r_R = r_P/r_0$ and also listed in Table 2.

For the experiment varying the mole fractions of the species CO, H_2O, CO_2 and H_2 in the reaction gas, the catalyst was stabilized by running for 42 days at working conditions before starting the measurements. Four series of runs have been made with the same batch of catalyst at 696.3 K and atmospheric pressure. A typical set of the data obtained is summarized in Table 3.

The procedure for the estimation of the parameters is as follows: using the integral reactor, the rate constant k_{Tj} can be expressed as follows:

$$k_{Tj} = \frac{V_0 y_0}{22.4W} \int_0^\alpha \frac{\bar{d}\alpha}{f(y_i, P_0)} \quad (2)$$

j being the number of run. Take an average over all of k_{Tj}.

$$k_{Tm} = \sum_1^9 \frac{k_{Tj}}{9}. \quad (3)$$

The parameters of the rival models could be computed by means of the regressive analysis procedure, the criterion of which is taking the minimum of the following residual sum of squares:

$$S = \sum_1^9 \left(\frac{k_{Tm} - k_{Tj}}{k_{Tm}} \right)^2. \quad (4)$$

The results are listed in Table 4.

Calculating the values of the reduced rate from the expressions of the rival models at different pressures, the results obtained together with the experimental values of the reduced rate of the shift reaction are shown in Fig. 2.

5. Conclusion

The effect of pressure P on the reduced rate of the water gas shift reaction is illustrated in Fig. 2. It is obvious that the calculated values of the reduced rate of model 5 agree with the experimental values, but not the other rival models. Therefore, model 5 could be regarded

Table 4
Parameters of rival model

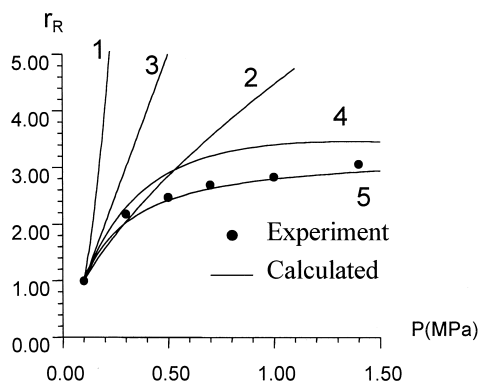| Model number	K_{CO}	K_{H_2O}	K_{CO_2}	A	a	b	c	d	S
2					0.93	0.33	−0.63	−0.02	0.0146
3				13.1					0.0667
4	13.2	84.1	46.6						0.0131
5	17.7	58.4	79.7						0.0152

Fig. 2. The effect of pressure P on the reduced rate.

as the most appropriate kinetic equation. The expression of model 5 differs significantly from model 1 proposed by Laupichler, the model 2 reported by Bohlbro and model 3 suggested by Temkin. Model 5 was suggested by Pavell Fott in 1979, and derived from the Langmuir–Hinshelwood concept for the case when the rate-determining step is a surface reaction.

From the result shown in Fig. 2, it will be seen that the reduced rate method for discrimination of the kinetic models has a good ability to differentiate.

6. Discussion

The reduced rate method is very convenient to make the discrimination of the power type of model, this is because the calculated expressions of their reduced rate have simple relations with pressure P (see Table 1). With the reduced rate method, 17 [1,6] existent power kinetic equations, which are not selected as the rival models, have been proved easily that these are not the most appropriate models.

The reduced rate method can very easily make the discrimination of the kinetic equations such as the model 3 . The calculated expressions of their reduced rate not only have simple relations with pressure P (see Table 1) but are independent of the kinetic parameter A. Thus it is unnecessary to estimate the parameter A for

the calculation of r_R. Three existent kinetic equations of a kind [1,6], which are not selected as the rival models, are not the most appropriate model, this is because the calculated expressions of their reduced rate are all the same with that of the 3.

It is worth noticing that the residual sums of squares of models 2, 4 and 5 shown in Table 4 are almost identical (0.0143 ± 0.0008). Three kinetic expressions, which have approximately the same accuracy, correspond with a set of the kinetic data listed in Table 3. Therefore, by taking the minimum of the residual sum of squares, the regressive analysis procedure could not determine which is the most appropriate kinetic model. But by the reduced rate method, the most appropriate kinetic equation determined is unique.

The experiment values of reduced rate shown in Fig. 2 increase with pressure according to a downward convex curve. The style of this curve is regular and smooth. It seems that the reaction mechanism or the rate-determining step may be not to change in going from one pressure to another.

The reduced rate method was successively used also for the discrimination of the kinetic models for the ammonia synthesis reaction, the detailed description of which will be published in another paper.

7. Notation

A	constant
a,b,c,d	exponents
E	apparent activation energy (kJ/mol)
i	species i, i: CO, H_2O, CO_2, H_2
k_0	preexponential factor
k_T	reaction rate constant
K_i	adsorption equilibrium constant of species i, MPa^{-1}
K_P	equilibrium constant

p_i	partial pressure of species i at pressure P (MPa)
p_{0i}	partial pressure of species i at pressure P_0 (MPa)
P	total pressure (MPa)
r	reaction rate (mol/g h)
r_P	reaction rate at pressure P (mol/g h)
r_0	reaction rate at datum pressure (mol/g h)
r_R	reduced rate
T	temperature (K)
V_0	gas flow (l/min)
W	amount of catalyst (g)
y_i	mole fraction of species i
α	degree of conversion of carbon monoxide
β	$p_{CO_2} p_{H_2O} / p_{CO} p_{H_2O} K_p$

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