Intrinsic Kinetics of Dehydrogenation of Isobutane over K_2O-CuO-Cr_2O_3/Al_2O_3 Catalyst

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Abstract. The intrinsic kinetics and mechanism of direct dehydrogenation of isobutane were studied over K-Cu-Cr/Al_2O_3 catalyst. The experiments had been carried out in a fixed-bed reactor with eliminating the influence of both internal and external diffusion at 470-510 ^oC and space velocity of 2500-4000 h^{-1} under atmospheric pressure. Based on the Langmuir-Hinshelwood mechanism, the intrinsic kinetics models were established, and they were verified by statistical analysis. The parameters in the models were estimated by using the method of Simplex-Method (SM) combined with General Global Optimization Algorithm. The results of the kinetics modeling showed that the rate-determining step was the surface reaction process, which was the best one to describe the experimental data. The activation energy of dehydrogenation reaction was obtained. And the models can provide an important basis for the design of industrial reactor.

Introduction

Isobutene was the most versatile chemical intermediates among all the C_4 olefins. It had been mainly used in the production of gasoline blending stocks such as methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) through etherification with methanol and ethanol, respectively. With the development and application of new technologies, the catalytic dehydrogenation of isobutane to isobutene had become an important way to increase the production [1-2]. The process of dehydrogenation could be classified into two types: direct dehydrogenation and oxidative dehydrogenation. As we all knew, direct dehydrogenation of isobutane had already realized industrialization, and chromium supported on alumina or silica were used as the industrial catalysts. The structure and activity of Cr catalysts had been researched extensively in an attempt to understand better catalytic process of the catalysts [3-5].

In the recent years, the study on the kinetics and mechanism of the dehydrogenation of light alkanes had been explored and several kinetic models were proposed in these articles, which based on the mechanisms of Langmuir-Hinshelwood, Eley-Rideal or Mars-van Krevelen type and played an important role on the study of catalytic mechanism. However, due to the use of different catalyst system, reaction conditions and experimental means, different mechanisms, different rate-determining steps and, thus, different kinetic models had been obtained. So far, the kinetics and mechanism of isobutane dehydrogenation with different catalysts had been studied [6-8]. Most of them were on oxidative dehydrogenation which used O_2 or CO_2 as the oxidant. However, studies on the intrinsic kinetics of direct dehydrogenation of isobutane were rare.

In the previous studies by our group, we developed the K-Cu-Cr/Al_2O_3 catalyst, which was found that the catalytic activity was high and it showed high stability and regeneration performance in 100 hours. Therefore, in this work, the dehydrogenation of isobutane on K-Cu-Cr/Al_2O_3 catalyst was studies to clarify the reaction intrinsic kinetics of alkane dehydrogenation. The models of kinetics were derived on the basis of Langmuir-Hinshelwood mechanism, and rate-determining steps and suitable models were tested.

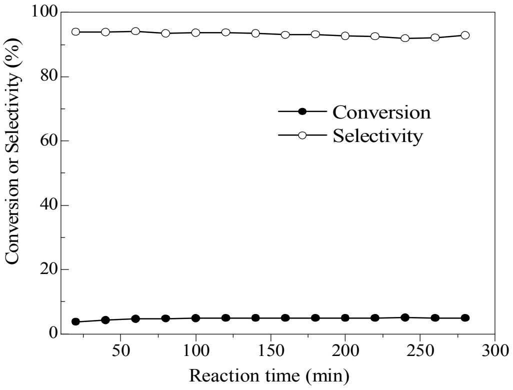
Experimental

Catalyst preparation

The 2%K_2O-1%CuO-10%Cr_2O_3/Al_2O_3 (K-Cu-Cr/ Al_2O_3) catalysts were prepared by impregnation method. Mixed solution of $Cr(NO_3)_3$, KNO_3, $Cu((NO_3)_2$ was simultaneously added into γ-Al_2O_3. After impregnated 4-5 h, the catalysts were dried at 110 °C for 12 h and calcined at 500 °C for 4 h.

Evaluation of catalyst performance

The catalytic performance for the direct dehydrogenation was carried out in a fixed-bed quartz tubular reactor with inner diameter of 6.0 mm at atmospheric pressure, catalyst loading was 0.3 mL. The products were temperature programmed analyzed on line by a gas chromatograph equipped with a packed column Rt-Al_2O_3(30 m×0.53 mm×10.0 μm) and a flame ionization detector (FID). The gas products, such as CO, CH_4 and CO_2, were analyzed by another gas chromatograph equipped with a packed column of GDX-502(3 m×2 mm) and a thermal conductivity detector (TCD) (Shimadzu GC-2014) with He as the carrier gas.



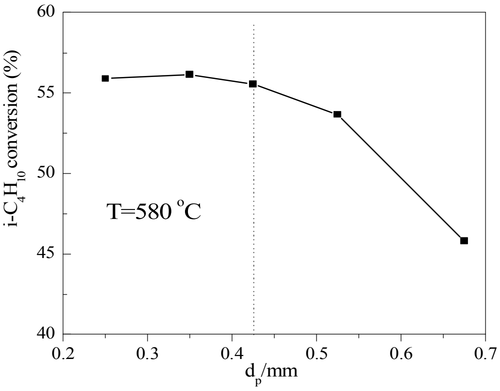


Fig. 1 Stability of K-Cu-Cr/Al_2O_3 catalyst after aging

Fig.2 Internal diffusion test of catalyst particles

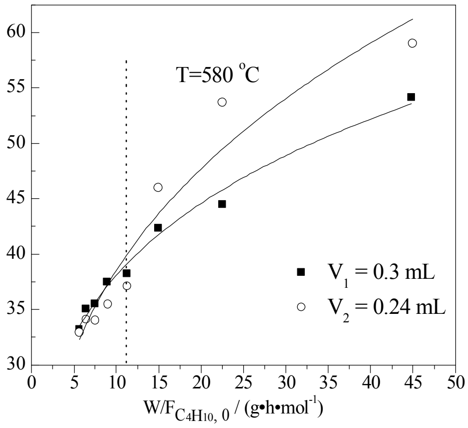


Fig. 3 External diffusion test of catalyst particles

Catalyst stability

The aging treatment of the K-Cu-Cr/Al_2O_3 catalyst was carried out before the dehydrogenation reaction due to that the stability of fresh catalyst was poor in its preliminary stage. The experiment of aging treatment was performed, which was continuous reaction for 2 h at 580 °C with 4000 h^{-1} space velocity. The stability of the aged catalyst was investigated at 510 °C. The curves of isobutane conversion and product selectivity with reaction time were shown in Figure 1. It could be seen from Figure 1 that the activity of the catalyst remained stable after aging. Thus, the effect caused by the deactivation of the catalyst could be excluded in the kinetic experiments.

Elimination of internal and external diffusion

The effect of internal diffusion was eliminated by changing particle size of the catalyst. And the influence of external diffusion with different catalyst loading was eliminated by changing the space velocity. The results were shown in Figs. 2 and 3. It can be seen from Fig. 2 that the effect of internal diffusion had been eliminated when the average particle size of the catalyst was 0.425 mm (40-45 mesh). Therefore, it could make sure that the internal diffusion was not present for using the catalyst with an average particle size of 0.35 mm (45-60 mesh) in the intrinsic kinetics experiments. As shown in Figure 3, when the space velocity over 2000 h^{-1} ($W/F_{C_4H_{10},0}$ = 11.25 g·h·mol^{-1}), it was sufficient to eliminate the influence of external diffusion. Finally, we selected the space velocity of 2500 h^{-1} ($W/F_{C_4H_{10},0}$ = 8.98 g·h·mol^{-1}) in the intrinsic kinetics experiments to ensure that the external diffusion had no effect.

Experimental conditions

According to the performance of the experimental device and preliminary experimental results, and combining with the requirements of intrinsic kinetic experiment, the kinetic experimental conditions were determined as follows: catalyst loading 0.3 mL, particle size 45~60 mesh, temperature 470-510 °C, GHVS 2500-4000 h^{-1}.

Results and discussion

Experimental datas

According to the theory of plug flow reactor, the equation $(-r) = dC_{C_4H_{10}}/d(W/F_{C_4H_{10},0})$ can be obtained. The equation suggested that the reaction rate $(-r)$ was the slope of the isothermal line shown by $C_{C_4H_{10}} \sim W/F_{C_4H_{10},0}$. Basing on the above calculation, the experimental data were processed to get the reaction rate, and the results were shown in Table 1.

Table 1 The experimental data for intrinsic kinetics of direct dehydrogenation over K-Cu-Cr/Al_2O_3

T (^oC)	GHSV (h^{-1})	Distribution of major products (%)							i-C_4H_{10} conversion (%)	i-C_4H_8 selectivity (%)	$r_{exp}\cdot10^{-3}$ ($mol\cdot g^{-1}h^{-1}$)
		i-C_4H_{10}	i-C_4H_8	H_2	C_3H_8	C_3H_6	CH_4	CO			
470	2500	96.68	3.05	0.64	0.05	0.07	0.05	0.86	3.32	91.87	3.149
	3000	96.90	2.89	0.56	0.05	0.03	0.02	0.71	3.04	93.42	3.163
	3500	97.22	2.60	0.37	0.05	0.05	0.03	0.3	2.84	93.31	3.169
	4000	97.44	2.38	0.39	0.05	0.06	0.04	0.43	2.56	92.97	3.177
480	2500	94.92	4.31	0.88	0.06	0.08	0.07	1.01	4.68	92.09	3.800
	3000	95.90	3.81	0.51	0.06	0.07	0.05	0.34	4.10	92.93	3.822
	3500	96.30	3.43	0.50	0.05	0.06	0.04	0.39	3.83	92.17	3.829
	4000	96.50	3.25	0.46	0.05	0.06	0.04	0.36	3.50	92.86	3.842
490	2500	93.16	6.28	1.22	0.06	0.09	0.08	1.16	6.84	91.81	4.526
	3000	93.68	5.90	0.87	0.05	0.06	0.04	0.67	6.32	93.35	4.557
	3500	93.95	5.32	0.92	0.06	0.09	0.06	0.86	6.14	92.75	4.568
	4000	94.53	5.07	0.7	0.06	0.08	0.06	0.46	5.47	92.69	4.586
500	2500	91.49	7.73	1.33	0.07	0.15	0.12	1.29	8.51	90.83	5.942
	3000	92.12	7.13	1.05	0.07	0.14	0.09	0.82	7.65	91.24	5.995
	3500	92.57	6.66	1.09	0.05	0.15	0.11	0.98	7.43	92.33	6.014
	4000	93.28	6.17	0.91	0.06	0.13	0.07	0.69	6.72	91.82	6.045
510	2500	86.30	12.02	1.76	0.11	0.2	0.17	1.06	13.70	87.78	9.071
	3000	87.12	11.54	1.49	0.08	0.14	0.1	0.67	12.48	90.89	9.194
	3500	88.05	11.02	1.51	0.08	0.16	0.11	0.81	12.13	92.17	9.240
	4000	88.88	10.37	1.55	0.09	0.22	0.17	1.21	11.12	93.26	9.312

Establishment of intrinsic kinetics model

The process of catalytic dehydrogenation under high temperature was accompanied by complex side reactions. In the experimental conditions, there was a low conversion of isobutane and a high selectivity of isobutene over 90%. Thus, in the study of kinetics, we only considered the main reaction of isobutane dehydrogenation.

According to the previous study of Airaksinen S. M. K.[8] on isobutane dehydrogenation, who proposed four mechanisms for the catalytic dehydrogenation of isobutane. Considering the complexity of the dehydrogenation process, the research of the catalytic dehydrogenation process was simplified as three steps, i.e.: adsorption, surface reaction and desorption. Taking each step as the rate-determining, and the reaction rate equation were obtained, respectively. The reaction rate equation was based on the Langmuir-Hinshelwood mechanism and shown in Table 2.

Table 2 The rate-determining step and corresponding equations

Models	Rate-determining steps	Equations of reaction rate
(a)	i-C_4H_{10} (g) + * □ i-C_4H_{10}*	$r=\frac{k(P_{C_4H_{10}}-K_{C_4H_8}K_{H_2}P_{C_4H_8}P_{H_2}/K_pK_{C_4H_{10}})}{1+K_{C_4H_8}P_{C_4H_8}+K_{H_2}P_{H_2}}$
(b)	i-C_4H_{10}* □ i-C_4H_8* + H_2*	$r=\frac{k(P_{C_4H_{10}}-P_{C_4H_{10}}P_{H_2}/(K_p))}{(1+K_{C_4H_{10}}P_{C_4H_{10}}+K_{C_4H_8}P_{C_4H_{10}}+K_{H_2}P_{H_2})^2}$
(c)	i-C_4H_8* □ i-C_4H_8 + *	$r=\frac{k(K_pK_{C_4H_{10}}P_{C_4H_{10}}/K_{H_2}P_{H_2}-P_{C_4H_8}/K_{C_4H_8})}{1+K_{C_4H_{10}}P_{C_4H_{10}}+K_pK_{C_4H_8}P_{C_4H_{10}}/K_{H_2}P_{H_2}+K_{H_2}P_{H_2}}$
(d)	H_2* □ H_2 + *	$r=\frac{k(K_pK_{C_4H_{10}}P_{C_4H_{10}}/K_{C_4H_8}P_{C_4H_8}-P_{H_2}/K_{H_2})}{1+K_{C_4H_{10}}P_{C_4H_{10}}+K_pK_{C_4H_{10}}P_{C_4H_{10}}/K_{C_4H_8}P_{C_4H_8}+K_{C_4H_8}P_{C_4H_8}}$

Estimation of parameters and identification

The kinetics equations established were nonlinear. The parameters in the models were estimated by using the method of Simplex-Method (SM) combined with General Global Optimization Algorithm. And the corresponding objective function was founded as Eq. 1.

$$FUNC = \frac{1}{n}\sum_{i=1}^{n}\left(r_{i,cal} - r_{i,\exp}\right)^2 \qquad \text{(Eq. 1)}$$

Where, n was the number of experimental points, r_{cal} was the calculated reaction rate. In order to make the parameters accurate and reliable, the chemical equilibrium constant K_p was calculated with the data from literature [9], $K_p = 3.045\times 10^{11}e^{-145744.42/RT}$.

The kinetics parameters were calculated at each temperature, and then basing on the Van't Hoff equation and Arrhenius equation, Eqs. 2- 5 were deduced as follows:

$k = k_0 \exp(-E_1/RT)$ (Eq. 2) $KC_4H_{10} = KC_4H_{10},0 \exp(QC_4H_{10}/RT)$ (Eq. 3)

$KC_4H_8 = KC_4H_{8,0} \exp(QC_4H_8/RT)$ (Eq. 4) $KH_2 = KH_{2,0} \exp(QH_2/RT)$ (Eq. 5)

Table 3 Activation energy (adsorption heat) and pre-exponential factors

Model		k	KC_4H_{10}	KC_4H_8	KH_2
(a)	pre-exponential factor	2.97×10^{8}	5.02×10^{-4}	4.68×10^{-3}	1.66×10^{-9}
	Activation energy(adsorption heat)	142.09	58.84	47.81	127.30
(b)	pre-exponential factor	1.67×10^{6}	6.34×10^{-2}	2.41×10^{-4}	8.20×10^{-5}
	Activation energy(adsorption heat)	101.31	31.59	64.78	57.90
(c)	pre-exponential factor	1.73×10^{6}	6.42×10^{-10}	5.24×10^{-9}	5.72×10^{-9}
	Activation energy(adsorption heat)	124.73	142.84	131.43	120.45
(d)	pre-exponential factor	1.75×10^{6}	2.59×10^{-3}	1.15×10^{-2}	7.08×10^{-10}
	Activation energy(adsorption heat)	124.80	50.13	41.24	133.80

Ploting with ln$k$, lnKC_4H_{10}, lnKC_4H_8, lnKH_2 versus 1/T, respectively, then the activation energy or adsorption heat was acquired, as well as the corresponding pre-exponential factors and shown in Table 3.

Test of intrinsic kinetic models

The results of statistical test for the intrinsic kinetic models were shown in Table 4.

F was the proportion of regression sum of mean square to residual error sum of mean square:

$$F = \frac{\left[\sum_{\mathrm{i}}^{M} r_{i,\exp}^{2} - \sum_{i}^{M}\left(r_{i,\exp} - r_{i,cal}\right)^2\right] \Big/ M_{\mathrm{P}}}{\sum_{i}^{M}\left(r_{i,\exp} - r_{i,cal}\right)^2 \Big/ \left(M - M_{\mathrm{P}}\right)} \qquad \text{(Eq. 6)}$$

ρ^2 was the key parameter, calculated by:

$$r^2 = 1 - \sum_{i=1}^{M}\left(r_{i,\exp} - r_{i,cal}\right)^2 \Big/ \sum_{i-1}^{M} r_{i,\exp}^2 \qquad \text{(Eq. 7)}$$

$F_{0.05}$ was the value of F table corresponding to 5% significant level. Normally, the model was suitable when $F > 10F_{0.05}$, $\rho^2 > 0.9$ [10]. It can be seen from Table 4, when both prerequisites ($F > 10F_{0.05}$, $\rho^2 > 0.9$) were satisfied, the values of intrinsic kinetic model calculated based on the Langmuir-Hinshelwood type were consistent with the experimental values.

Table 4 Statistic results of the kinetic models

Model	Mp	M-Mp	ρ^2	F	$10F_{0.05}$
(a)	8	22	0.9876	219.12	24.5
(b)	8	22	0.9904	282.60	24.5
(c)	8	22	0.9919	338.76	24.5
(d)	8	22	0.9919	338.66	24.5

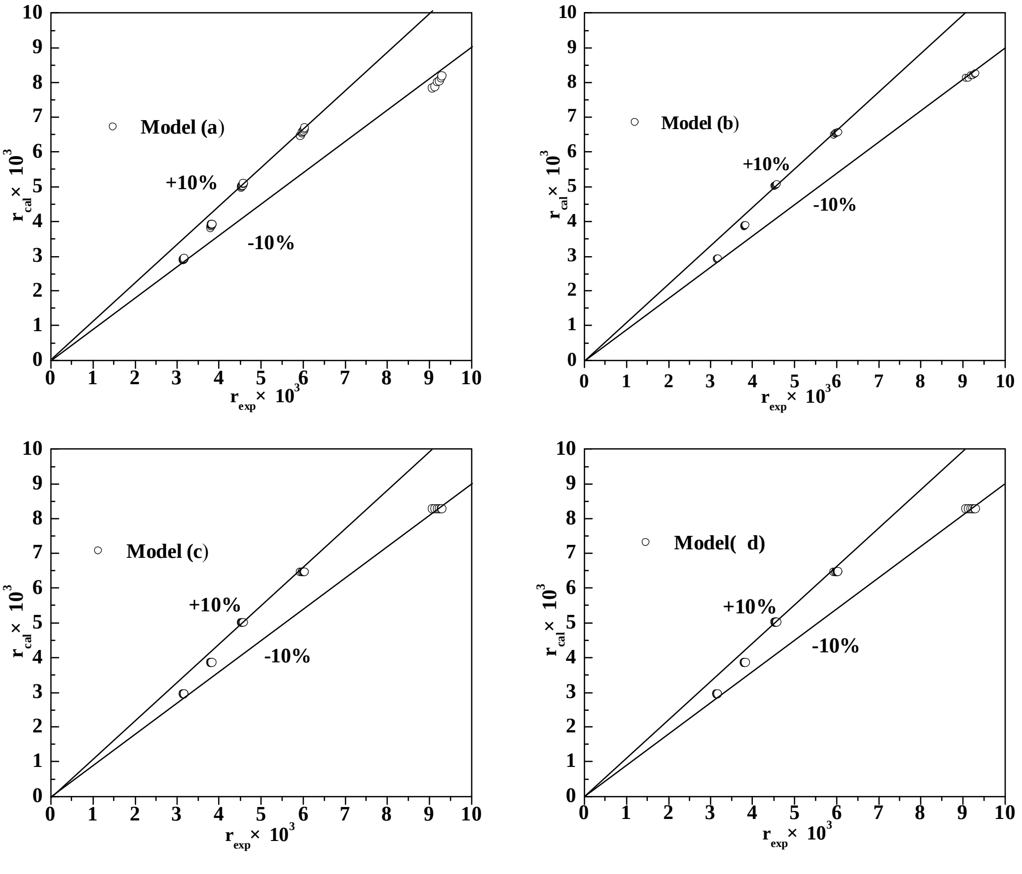


Fig.4 Comparison of the rates between experimental and calculated

The calculated reaction rates were compared with the experimental values and shown in Fig.4. It could be found from the graph, most of the data points were distributed evenly on both sides of the diagonal, and fell within the lines of ± 10% error, which illustrated that the calculated reaction rates were good agreement with the experimental results.

In order to make the models most approximate to the reality, a further inspection for models (a)-(d) was made, in accordanc with the criteria which gave a reasonable determination of kinetics brought by Boudart et al[11]: ① $\Delta S < 0$ ② $|\Delta S| < S_g$ ③ $|\Delta S| > 41.8$ ④ $|\Delta S| < 51.0 - 0.0014\ \Delta H$. Where, S_g was the standard entropy, ΔS was the adsorption entropy change, ΔH was the adsorption enthalpy. Changing $K_i = K_{i,0}e^{Q_i/RT}$ into $K_i = e^{\Delta S/R}e^{-\Delta H/RT}$ to get ΔS and ΔH, the tested results were shown in Table 5.

It could be seen from the further inspection results that only the model (b) was fully consistent with the criteria, so the model (b) was desirable. According to model (b), it could be found that the rate-determining step was surface reaction during the process of isobutane dehydrogenation.

Table 5 The investigation results for intrinsic kinetic models

Model		$i\text{-}C_4H_{10}$	$i\text{-}C_4H_8$	H_2
(a)	ΔH	-58.84	-47.81	-127.30
	ΔS	-63.16	-44.61	-168.06
	Sg	295.50	293.20	130.68
	51.0 - 0.0014 Δ*H*	133.37	117.94	229.21
(b)	ΔH	-31.59	-64.78	-57.90
	ΔS	-22.93	-69.26	-78.22
	Sg	295.50	293.20	130.68
	51.0 - 0.0014 Δ*H*	95.23	141.69	132.06
(c)	ΔH	-142.84	-131.43	-120.45
	ΔS	-175.98	-158.51	-157.79
	Sg	295.50	293.20	130.68
	51.0 - 0.0014 Δ*H*	250.98	235.00	219.63
(d)	ΔH	-50.13	-41.24	-133.80
	ΔS	-49.53	-37.13	-175.16
	Sg	295.50	293.20	130.68
	51.0 - 0.0014 Δ*H*	121.18	108.73	238.32

And the kinetics rate equation was as follows:

$$r=\frac{1.67\times10^{6}e^{-1.01\times10^{5}/RT}(P_{i-C_4H_{10}}-P_{i-C_4H_{10}}P_{H_2}/3.045\times10^{11}e^{-1.46\times10^{5}/RT})}{(1+6.34\times10^{-2}e^{3.16\times10^{4}/RT}P_{i-C_4H_{10}}+2.41\times10^{-4}e^{6.48\times10^{4}/RT}P_{i-C_4H_{10}}+8.20\times10^{-5}e^{5.79\times10^{4}/RT}P_{H_2})^2}$$

Activation energy was E = 101.31 KJ/mol

Conclusions

(1) The intrinsic kinetics of direct dehydrogenation over the K-Cu-Cr/Al_2O_3 catalyst had been investigated in a continuous flow fixed-bed reactor. Under the experimental conditions, the dehydrogenation reaction follows Langmuir-Hinshelwood mechanism, and the results showed that the process of surface reaction was the rate-determining step. The rate equation of intrinsic kinetics was obtained, and the activation energy was E=101.31 KJ/mol.

(2) The parameters in the models were estimated by using the method of Simplex-Method (SM) combined with General Global Optimization Algorithm. The obtained intrinsic kinetics model could well describe the experimental data of isobutane dehydrogenation over the K-Cu-Cr/Al_2O_3 catalyst, and it would plays an important role on the design of catalyst engineering and industrial reactor.

Acknowledgment

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Nomenclature

T	Reaction temperature, K	K_p	Constant of chemical equilibrium
C	Conversion, %	E	Activation energy, $kJ\cdot mol^{-1}$
S	Selectivity, %	Q_i	Heat of adsorption, $J\cdot mol^{-1}$
d_p	Catalyst particle, mm	*	Active site
W	Catalyst loading, g	M	Number of experiments
$FC_4H_{10,0}$	Isobutane flow rate, $mol\cdot h^{-1}$	M_p	Number of parameters in the equation of model
r_{exp}	Experimental rate reaction, $mol\cdot(g\cdot h)^{-1}$	ρ^2	Key parameter
r_{cal}	Calculated rate reaction, $mol\cdot(g\cdot h)^{-1}$	ΔS	Adsorption entropy, $kJ\cdot(mol\cdot K)^{-1}$
K_i	Constant of adsorption equilibrium	S_g	Standard entropy, $kJ\cdot(mol\cdot K)^{-1}$

$K_{i,0}$	Pre-exponential factor of K_i	ΔH	Adsorption enthalpy, kJ·mol^{-1}
P_i	Pressure of component *i*, MPa		

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