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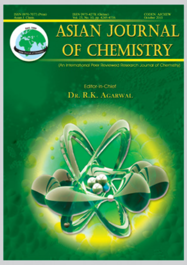

Kinetic Study of the CO_2 Reforming of CH_4 to Synthesis Gas Over Carbonaceous Catalyst

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The CO_2 reforming of CH_4 over carbonaceous catalyst was performed in a plug flow reactor (PFR) at temperatures range from 1223-1323 K, the ratio of $CH_4/CO_2 = 1$ and residence time 3-30 s under normal pressure. The outlet gas was analyzed by gas chromatogram (GC-960TCD and GC-950TCD), the carbonaceous catalyst was analyzed with element analyzer and specific surface area analyzer. The experimental results show that the conversion of CH_4 and CO_2 increases with the increase of the reaction temperature and residence time, but the conversion of CO_2 was significantly higher than the conversion of CH_4 at the same reaction condition, which indicate that the gasification reaction of the carbonaceous catalyst and carbon dioxide was occurred during the reforming process. At 1323 K and residence time over 20 s, the conversion of CH_4 and CO_2 can be expected over 90 %. The carbonaceous catalyst is a highly promising catalyst for the CO_2 reforming of CH_4 to synthesis gas. The kinetics of the CO_2 reforming of CH_4 on carbonaceous catalyst was described in a rate law, which the experimental data was analyzed in non-linear regression. The apparent activation energy E_a and the pre-exponential factor A were solved. A comparison is made between calculation data and experimental data of the CH_4 conversion, which illustrates the rationality of the kinetic model.

Key Words: Kinetic, Carbon dioxide reforming of methane, Carbonaceous catalyst.

INTRODUCTION

Methane is the main composition of natural gas, coal bed gas and coke oven gas. The CO_2 reforming of CH_4 provides a practical method for effectively combines CH_4 utilization with CO_2 transforming, since both methane and carbon dioxide are the main greenhouse gas and the reaction gets raw gases for Fischer-Tropsch, methanol and carbonyl synthesis[1-3]. In recent years, the CO_2 reforming of CH_4 has received considerable attention worldwide. There are four major kinds of catalysts which are transitional metals catalysts, composite metal oxide catalysts, supported metal sulfide catalysts and supported noble metal catalysts[4-6], but carbonaceous catalyst has attracted the attention of most researchers who are engaged CO_2 reforming of CH_4 reaction, the carbonaceous catalyst is both cheap and abundantly available in the word and can not lead to catalyst poisoning. Yan-bing *et al.*[7], studied the influence of different chars and operation parameters on reactant gas conversion and the results show that Tongchuan char with the lowest ash concentration exhibits the highest activity and all the char samples show similar behaviours. A higher conversion is always achieved at the beginning and then it decreases and levels off at a stable value after 0.5 h. Zhang *et al.*[8], studied the effects of the coal char catalyst pretreatment and the ratio of CO_2/CH_4, experimental results showed that the coal char is an effective catalyst for production of synthesis gas and the product gas ratio of H_2/CO is strongly influenced by the feed ratio of CO_2/CH_4. It is also reported the effect of coke on the steam and carbon dioxide reforming reactions of methane at 700-1300 ºC. The results showed that the conversion of methane to produce synthesis gas obviously increased with the presence of coke in the reactor[8].

In the present work, the CO_2 reforming of CH_4 over the Da Tong carbonaceous catalyst was performed in a plug flow reactor. The effect of the reaction parameters on the carbonaceous catalyst activity for CO_2 reforming of CH_4 were studied and the kinetic behaviour was investigated as functions of the reaction temperature and residence time.

EXPERIMENTAL

The CO_2 reforming of CH_4 over the Da Tong carbonaceous catalyst was performed in a plug flow reactor at temperatures range from 1223-1323 K, the ratio of $CH_4/CO_2 = 1$ and residence time 3-30 s under normal pressure. The reactor (internal diameter 20 mm; length 100 mm) was horizontal heated in a furnace. A weighed amount (15 g) of carbonaceous catalyst was loaded in the middle of the reactor. The CH_4 and CO_2 gas flow rates were measured and controlled by mass flow controllers (flow control range 0-200 mL/min). The outlet gas was analyzed by gas chromatogram (GC-960TCD and GC-950TCD), the carbonaceous catalyst was analyzed with element analyzer and specific surface area analyzer.

Preparation and characterization of the catalyst: The carbonaceous catalyst was prepared by pyrolysis of Da Tong coal at 800 ºC for 2 h, crushing the catalyst mass to 80-100 mesh-size particles. The carbonaceous catalyst was dried in muffle furnace for 12 h at 900 ºC in nitrogen. The proximate analysis and ultimate analysis of carbonaceous catalyst were shown in Table-1.

RESULTS AND DISCUSSION

Effect of carbonaceous catalyst on the CO_2 reforming of CH_4: The carbonaceous catalyst activated was investigated at the reaction temperatures range from 1073-1323 K with $CH_4/CO_2 = 1$. Fig. 1 shows the conversion of CO_2 and CH_4 change with the reaction temperature.

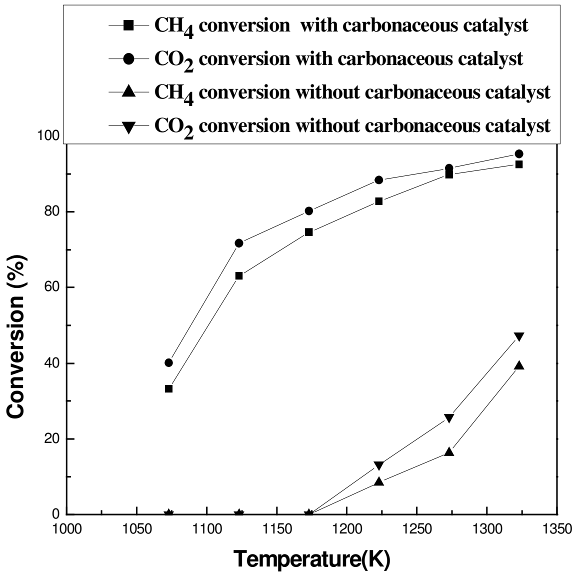
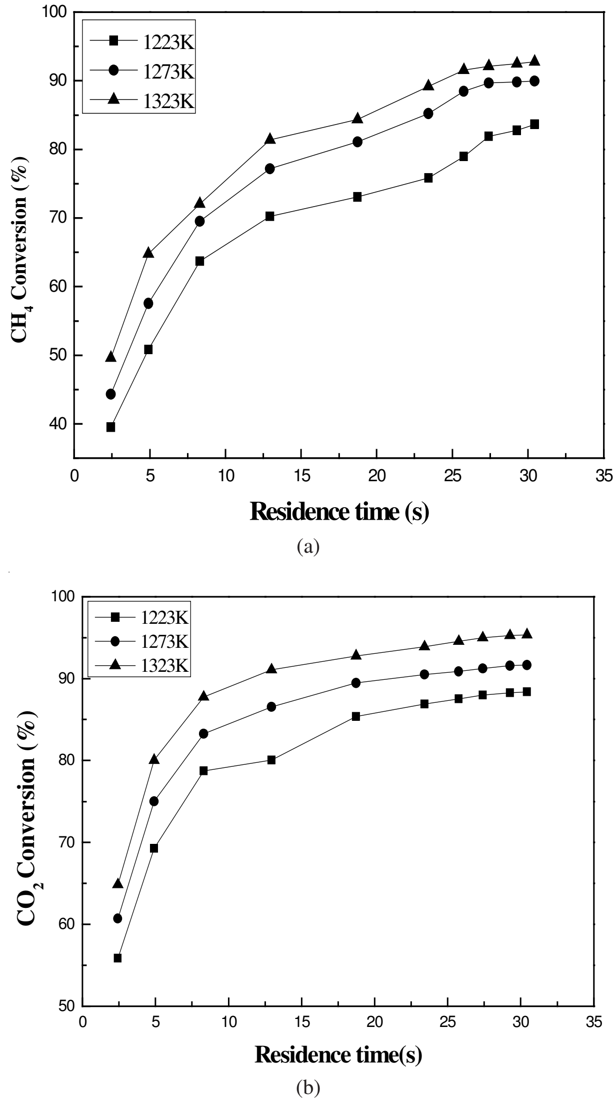


Fig. 1. Effect of carbonaceous catalyst on the CO_2 reforming of CH_4

As can be seen from Fig. 1, the initial reaction temperature of CO_2 reforming of CH_4 without catalyst is 1223 K, while the conversion of CH_4 and CO_2 were 33.2 and 40.1 %, respectively with carbonaceous catalyst at 1073 K, it can be also found from comparison that conversion of methane and carbon dioxide over carbonaceous catalyst is much higher than uncatalyst. The results show that the carbonaceous catalyst has obvious promote conversion of CH_4 and CO_2.

Effect of residence time and reaction temperature on CH_4 and CO_2 conversion: The residence time was varied by changing the feed gases flow. The effect of residence time on CH_4 and CO_2 conversion at different the reaction temperatures was shown in Fig. 2.



(a)

(b)

Fig. 2. Effect of residence time and reaction temperature on CH_4 and CO_2 conversion

As can be seen from Fig. 2, with the increase of residence time, the conversion of CH_4 and CO_2 have increased rapidly then leveled off. When the residence time from 3 to 30 s in reaction temperature 1223 K, the conversion of CH_4 can be increased from 40 to 83 %, but the conversion of CO_2 can be increased from 60 to 93 %, the result shown that the conversion of CO_2 was significantly higher than the conversion of CH_4 at the same condition of residence time and reaction temperature, which indicate that the gasification reaction of the carbonaceous catalyst and carbon dioxide was occurred during the reforming process.

It can be seen also from Fig. 2 that the conversion of CH_4 and CO_2 increases with the increase of the reaction temperature. The conversion of CH_4 and CO_2 were 82.8 % and 88.4 %

TABLE-1
PROXIMATE ANALYSIS AND ULTIMATE ANALYSIS OF CARBONACEOUS CATALYST

Sample	Proximate analysis (w %, ad)			Ultimate analysis (w %, daf)				
	M	A	V	C	H	N	S	O (diff)
Da-Tong coal	3.10	12.20	29.00	87.70	4.96	1.27	0.42	5.36
Carbonaceous-catalyst	1.20	13.30	4.50	94.60	1.47	0.99	0.17	2.36

in the reaction temperature 1223 K and the residence time 30 s. However the reaction temperature arrived 1323 K under the same condition, the conversion of CH_4 and CO_2 can be expected 92.8 % and 95.4 %, respectively. The experimental data show that the reaction temperature was in favour of the CO_2 reforming of CH_4, which promotes the conversion of CH_4 and CO_2.

Effect of the temperature on distribution of the reactants and products: The reactants and products are shown in Fig. 3. (experimental conditions: $CH_4/CO_2 \approx 1$, reaction temperature: 973 to 1473 ºC, residence time: 6 s).

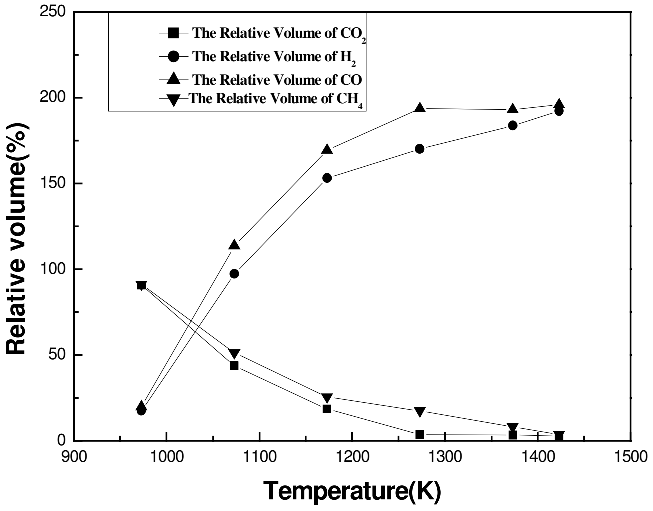


Fig. 3. Distribution diagram of the reactants and products

It can be seen from Fig. 3, the content of CO was significantly higher than H_2 when the temperature is lower than 1373 K. With the increase of the reaction temperature, there is no change in the content of products. When the reaction temperature exceeds 1273 K, the conversion of CO_2 has exceeded more than 95 % and in the gas products, CO relative volume content of up to 200 %. If all carbon and hydrogen that the CO_2 reforming of CH_4 in the gas turn into CO and H_2, then the relative volume content of CO and H_2 should be the same in the gas result, while the relative volume content of H_2 is lower than the relative volume content of CO, it indicate that the gasification reaction of the carbonaceous catalyst and carbon dioxide was occurred during the reforming process.

Kinetic model: The kinetics of the CO_2 reforming of CH_4 on carbonaceous catalyst was described in conversion of CH_4 by a rate law[9]. The basic assumption of kinetic model are as follows: The CO_2 reforming of CH_4 is the dominating reaction; the reaction temperature and the content in feed of CH_4 and CO_2 have considered, nothing to do with the intermediate. Molar content in feed and concentration distribution of CH_4 and CO_2 are same in CO_2 reforming of CH_4.

The conversion of CH_4 defined as:

$$x_{CH_4} = 1 - \frac{[CH_4]}{[CH_4]_0} \qquad (1)$$

where $[CH_4]_0$ is content of CH_4 in feed, mmol/L; $[CH_4]$ is content of CH_4 in outlet, mmol/L.

$$[CH_4] = \frac{P}{RT_0} \qquad (2)$$

where P is partial pressure of CH_4, Pa.

The rate for the transformation of CO_2 reforming of CH_4 can be expressed as follows:

$$-\frac{d[CH_4]}{dt} = k[CH_4]^a[CO_2]^b \qquad (3)$$

where k is the reaction rate constant; a and b are the reaction orders for CH_4 and CO_2, respectively.

Taking into account eqns. 1 and 3 the global rate for CH_4 conversion is represented in eqn. 4

$$\frac{d[CH_4]_0(1-x_{CH_4})}{dt} = k[CH_4]_0^{a+b}(1-x_{CH_4})^{(a+b)} \qquad (4)$$

Which can be integrated between t = 0 and t = t, yielding:

$$x_{CH_4} = 1-[1+(n-1)k[CH_4]_0^{n-1}t]^{\frac{1}{1-n}} \qquad (5)$$

where $n = a + b$ is the overall reaction order.

Using some basic mathematic models, after adjusting the experiment data, the kinetic equations are created in origin multi-parameter curve fitting. Fig. 4 shows curve fitting of different reaction temperatures.

The result as Fig. 4 shown, the coefficient of multiple determination (R^2)was above 0.92, indicating the goodness of fit. Assuming an Arrhenius temperature dependence, the reaction rate constant can be expressed as:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \qquad (6)$$

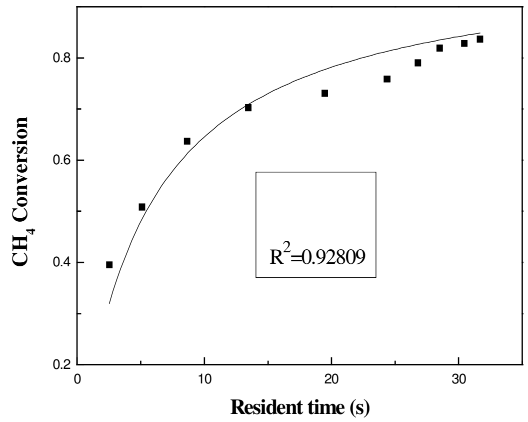
where A is the pre-exponential factor, E_a is the apparent activation energy (J mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the reaction temperature (K).

The kinetic parameters were estimated by linear regression of the experimental data using the least squared method, the pre-exponential factor A and the apparent activation energy E_a were obtained, Fig. 5 shows the ln k *versus* 1/RT relation. The activation energy and the pre-exponential factor were 109.9 kJ/mol and 1765 min L/mol, respectively.

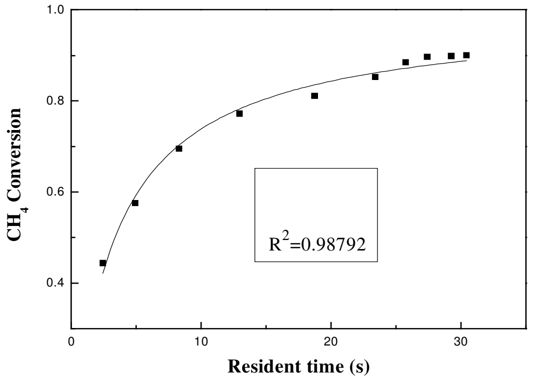
$$k = 1765\exp\left(-\frac{109.9 \pm 10.1KJ}{RT}\right)$$

Comparison between calculation data and experimental data: In order to compare between calculation data and experimental data, the conversion of CH_4 and CO_2 were calculated in different residence time and reaction temperature. Fig. 6 shows a comparison between calculation data and experimental data of conversion of CH_4 and CO_2.

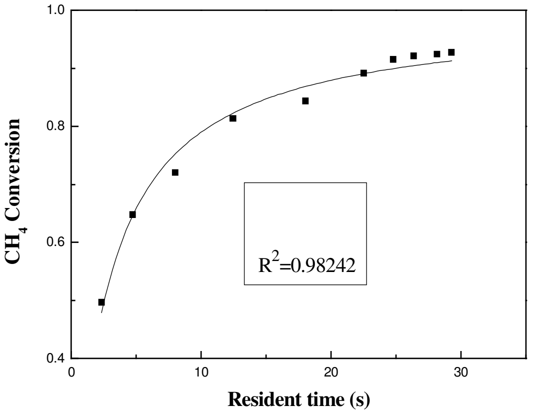
The result (Fig. 6) shows, the calculation data of CH_4 conversion are close to the experimental data, the maximum error of which is 7.3 %, which illustrates the rationality of the kinetic model. However, the calculation data of CO_2 conversion of the simulation had a gap when compared to the experimental data and the maximum error of which is up to 20 %, one of the reasons for the error is caused by dynamic equation which is the established in an ideal condition and the experiment conditions were assumed, which ignored the effect of single particle in the diffusion and mass transfer on reforming reaction, the second reasons for the error is caused by the gasification reaction between carbonaceous catalyst and carbon dioxide.



(a) T = 1223k



(b) T = 1273k



(c) T = 1323k

Fig. 4. Kinetic curves of CH$_4$ conversion of different temperatures

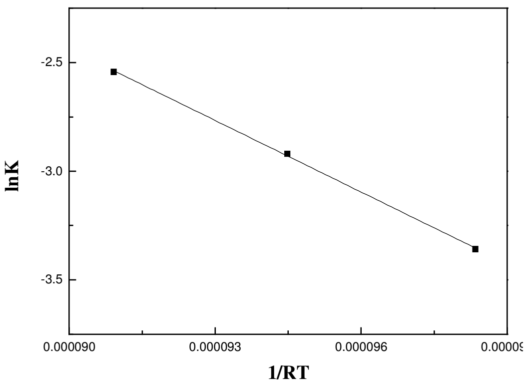
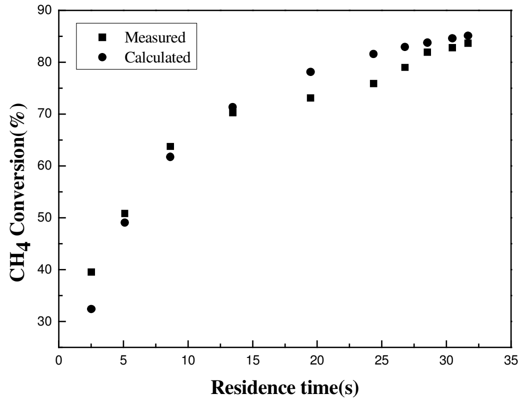
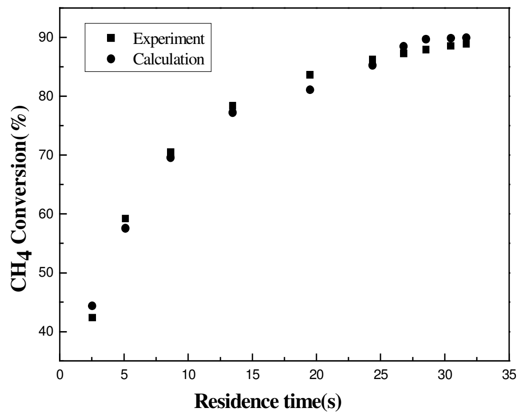


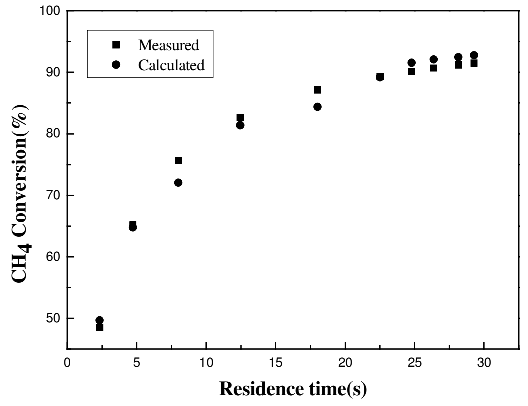
Fig. 5. ln k *versus* 1/RT relation



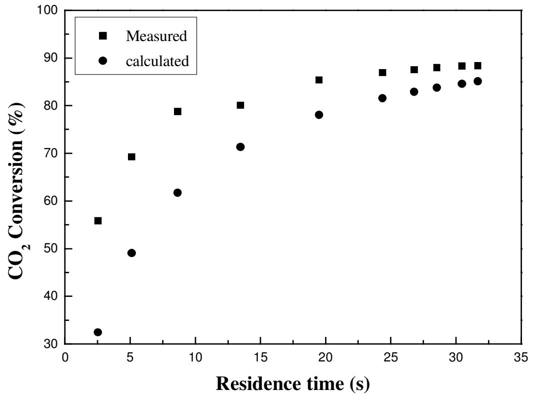
(a) T = 1223 K



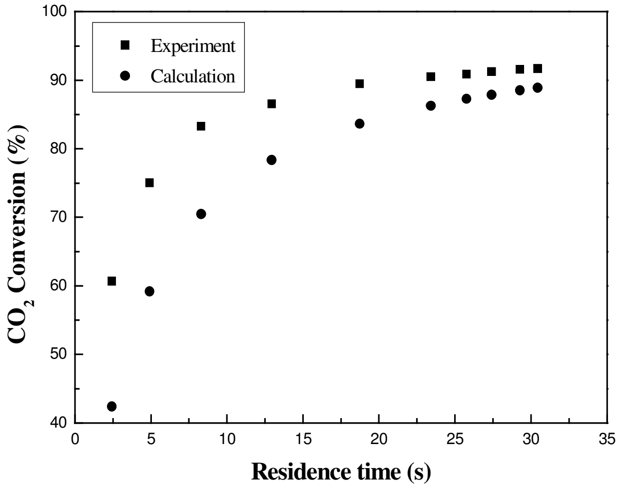
(b) T = 1273 K



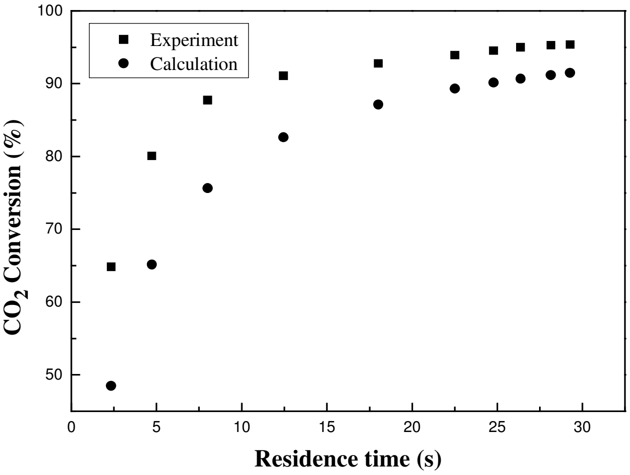
(c) T = 1323 K



(d) T = 1223 K



(e) T = 1273 K



(f) T = 1323 K

Fig. 6. Comparison between calculation and experiment of CO_2 reforming of CH_4 in different temperature

Conclusion

The conversion of CH_4 and CO_2 increased with the residence time and reaction temperatures increasing, compared with blank test. The results show that the carbonaceous catalyst has obvious promote conversion of CH_4 and CO_2. The conversion of CO_2 was significantly higher than the conversion of CH_4, which indicate that the gasification reaction of the carbonaceous catalyst and carbon dioxide was occurred during the reforming process. The experimental data show that the increase the reaction temperature was in favour of the CO_2 reforming of CH_4, which promotes the conversion of CH_4 and CO_2.

The conversion of CH_4 and CO_2 are all relatively high in the initial stage and then decays to a relatively fixed value after a period of time. Shows that the activity of carbonaceous catalyst is relatively high in the section of the initial, with the extension in reaction time, the activity of the carbonaceous catalyst reduces and tends towards stability gradually.

A comparison is made between calculation data and experimental data of the CH_4 conversion, which illustrates the rationality of the kinetic model. The rate constant was as follows:

$$k = 1765 \exp\left(-\frac{109.9 \pm 10.1 \mathrm{KJ}}{\mathrm{RT}}\right)$$

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