A method to determine the relative value of the barriers of carbon chain growth and termination in Fischer–Tropsch synthesis: elementary reaction kinetics for chain growth

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A method is established, by which the difference of the reaction activation barriers of carbon chain growth and termination in Fischer–Tropsch (FT) synthesis can be determined from experiments. A FT synthesis is carried out on Fe/Zn catalyst. We apply the method to analyze the experimental result and obtain the difference of reaction activation barriers of carbon chain growth and termination of α-olefins on the catalyst.

Keywords: Fischer–Tropsch synthesis; reaction activation barrier; carbon chain growth and termination; kinetics

1. Introduction

Many work has been done on the mechanism and kinetics of Fischer–Tropsch synthesis [1,2]. During the synthesis, the C–C chain growth and termination steps play important roles. The formation of hydrocarbons is believed to proceed by the elementary steps outlined in fig. 1, where k_p is the propagation rate constant, k_t and $k_{t'}$ are the termination rate constants of alkanes and olefins. We know little about the reaction activation barriers of these elementary steps, although there were some theoretical estimations [3,4].

$$\begin{tikzcd}
 & C_2H_4 & C_3H_6 & \\
C_1 \arrow[r, "k_p"] \arrow[d] & CC \arrow[r, "k_p"] \arrow[u, "k_{t'}"'] \arrow[d, "k_t"] & CCC \arrow[r, "k_p"] \arrow[u, "k_{t'}"'] \arrow[d, "k_t"] & \text{etc.} \\
CH_4 & C_2H_6 & C_3H_8 &
\end{tikzcd}$$

Fig. 1. Conceivable elementary reaction steps of formation of hydrocarbons in FT synthesis.

Here we present a method, by which we can determine the relative value of the reaction activation barriers of the chain growth and termination steps from FT synthesis experiments.

2. Method

Generally, there is only one carbon chain growth mechanism in the formation of hydrocarbons during FT synthesis. The chain growth probability factor is given by

$$\alpha = \frac{k_p}{k_p + \sum_i k_{t_i}} . \tag{1}$$

If there is only one termination mechanism such as the formation of α-olefins, we have

$$\alpha = \frac{k_p}{k_p + k_t} . \tag{2}$$

From Arrhenius theory,

$$k_p = A_p \exp(-E_p/RT) , \tag{3}$$

$$k_t = A_t \exp(-E_t/RT) , \tag{4}$$

we obtain

$$\alpha = \left[1 + \frac{A_t}{A_p} \exp\left(\frac{E_p - E_t}{RT}\right)\right]^{-1} , \tag{5}$$

$$\frac{1-\alpha}{\alpha} = \frac{A_t}{A_p} \exp\left(\frac{E_p - E_t}{RT}\right) , \tag{6}$$

$$\ln\frac{1-\alpha}{\alpha} = \ln\frac{A_t}{A_p} + \frac{E_p - E_t}{R}\frac{1}{T} . \tag{7}$$

Formula (7) predicts a linear plot of $\ln[(1-\alpha)/\alpha]$ versus $1/T$. Its slope is $(E_p - E_t)/R$, from which the difference $E_p - E_t$ is determined. The intercept is $\ln(A_t/A_p)$, from which the ratio A_t/A_p is obtained.

3. Experimental

The catalyst consists of Fe/Zn ultrafine particles. It is prepared by the method of degradation of organic coordination complex in our laboratory. Its composition is Fe/Zn = 1 : 3 (mole ratio).

Table 1
Influence of reaction temperature on α

	Reaction temperature (K)						
	533	543	553	563	573	583	593
α	0.748	0.727	0.679	0.637	0.699	0.681	0.642
$(1-\alpha)/\alpha$	0.337	0.376	0.473	0.570	0.431	0.468	0.558
$\ln[(1-\alpha)/\alpha]$	−1.09	−0.978	−0.749	−0.562	−0.742	−0.759	−0.583
$1/T\,(10^{-3}\,\mathrm{K}^{-1})$	1.88	1.84	1.81	1.78	1.75	1.72	1.69

Before reaction, the catalyst was reduced in a pure hydrogen stream of 50 cm^3/min at 573 K and 0.2 MPa for 32 h. The reaction was carried out in a stainless steel tube fixed-bed reactor (2.1 cm o.d., 70 cm long), at a pressure of 1.0 MPa and at temperatures of 533, 543, 553, 563, 573, 583 and 593 K. Products from the reactor were analyzed by two Shimadzu gas chromatographs GC-9A.

4. Results and discussion

The chain growth factors for α-olefins under different reaction temperatures are listed in table 1. The plots of $\ln[(1-\alpha)/\alpha]$ versus $1/T$ are shown in fig. 2.

Table 1 shows that the growth factor is highly dependent on the reaction temperature. α decreases with increasing reaction temperature. From this and formula (5), we deduce that the reaction activation barrier of the chain growth is lower than that of the chain termination.

In fig. 2 a linear relation of $\ln[(1-\alpha)/\alpha]$ versus $1/T$ is observed. But, in the

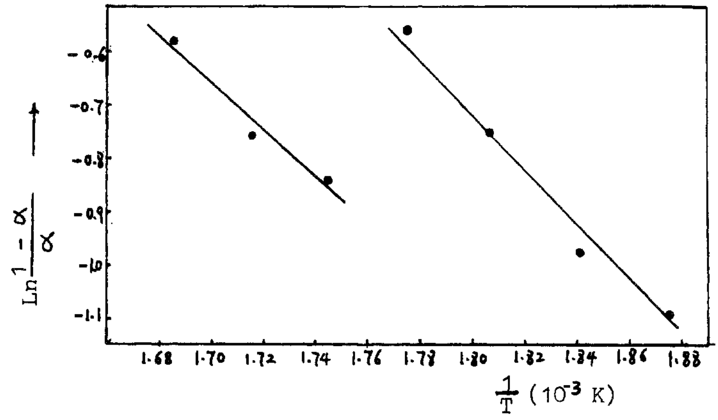

Fig. 2. Relation between $\ln[(1-\alpha)/\alpha]$ and $1/T$.

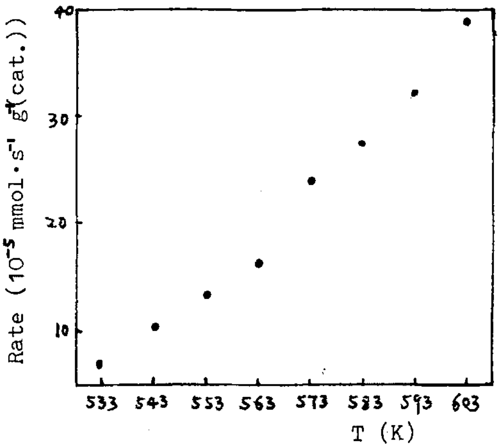

Fig. 3. Methane productive rate against reaction temperature.

range of the investigated temperature two straight lines instead of one appear for $\ln[(1-\alpha)/\alpha]$ versus $1/T$. One is in the range of 533–563 K, and the other is in the range of 573–593 K. This may be due to the fact that, when the reaction temperature arrives around 573 K, the properties of the catalyst change, which influences the barriers of the chain growth and termination. The change is also suggested by some other experimental results, such as the dependence on the reaction temperature of the methane productive rate or of the methane content in hydrocarbons (see figs. 3 and 4). The change of catalyst properties with reaction temperature during FTS has been reported earlier [5–7]. For example, in a study on Fe–Mn catalyst, Maiti found that the phase composition of the catalyst began to change when temperature reaches 573 K [7]. We can imagine that, if the investigated temperature range is wide enough, there may be more straight lines in the plots of $\ln[(1-\alpha)/\alpha]$ versus $1/T$.

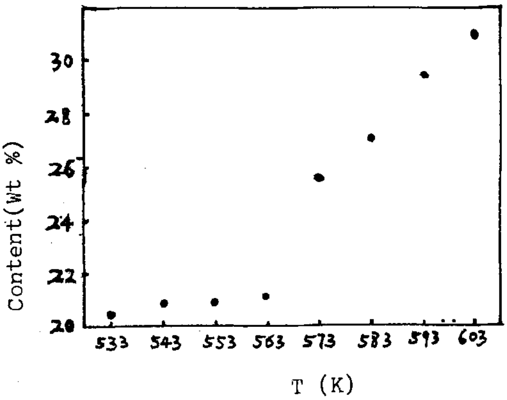

Fig. 4. Methane content in hydrocarbons against reaction temperature.

Table 2
$E_p - E_t$ and A_t/A_p of α-olefins of FT products on Fe/Zn catalyst

	Reaction temperature (K)	
	533–563	573–593
slope (K)	-5.42×10^3	-4.38×10^3
$E_p - E_t$ (kJ/mol)	−45.1	−36.4
intercept	9.06	6.79
A_t/A_p	8.56×10^3	8.85×10^2

From the slopes and the intercepts of the straight lines in fig. 2, the difference $E_p - E_t$ and the ratio A_t/A_p are obtained (listed in table 2). In 1990, Shustorovich estimated the elementary reaction activation barriers in FT synthesis on some metals by applying bond-order-conservation-Morse-potential-approach [3]. In his results, the $E_p - E_t$ for C_2H_4 on Fe(110) is −33.4 kJ/mol. Comparing with our experimental results (listed in table 2), the agreement is very encouraging indeed, although the catalysts are somewhat different.

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