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Reaction behaviors and mechanisms of catalytic pyrolysis of C4 hydrocarbons

Li Li [*], Jinsen Gao, Chunming Xu, Xianghai Meng

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing 102249, China

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Abstract

Catalytic pyrolysis of C4 hydrocarbons over a modified ZSM-5 zeolite was investigated in a fixed bed reactor. The effects of reaction temperature and dilution ratio on product yields and distribution were studied, ethylene yield goes up monotonously with the enhancement of reaction temperature; meanwhile, propylene yield shows a maximum at about 580 °C. As dilution ratio increases, the yield of propylene increases until a dilution ratio of 2.0 is reached, and then changes slightly, and that of ethylene passes through a maximum at about 2.0. For catalytic pyrolysis of *n*-butylene, two reaction pathways have been proposed, the monomolecular reaction mechanism and the bimolecular reaction mechanism. With the analysis of these two reaction pathways and the experimental data, a conclusion is drawn that catalytic pyrolysis of *n*-butylene follows the bimolecular reaction mechanism. According to this mechanism, *n*-butylene catalytic pyrolysis involves two successive reaction steps: the dimerization of *n*-butylene and the cracking of the dimers.

Keywords: Catalytic pyrolysis; C4 hydrocarbons; Propylene; Ethylene; Butylene; Reaction behaviors; Mechanism

1. Introduction

The market demand for ethylene and propylene is growing very quickly, mainly due to the high growth rate of polyethylene and polypropylene use [1]. Ethylene and propylene are traditionally produced by steam cracking, and usually the propylene production is low. The conflict between the low production capacity of ethylene and propylene and their rapid increasing market demand becomes more and more serious [2]. To solve this problem, various technical studies on the production of ethylene and propylene have attracted great interest [3,4]. From the viewpoint of the cost of investment and production, catalytic pyrolysis of C4 and C5 hydrocarbons is considered as one of the most attractive approach [5].

In some countries, especially in some developing countries, the chemical utilization ratio of C4 hydrocarbons is low at present, and C4 hydrocarbons are comparatively surplus [6]. Catalytic pyrolysis of C4 hydrocarbons to produce ethylene and propylene will not only meet the swift growth of the market demand for ethylene and propylene, but also open up a new field on the effective chemical use of C4 hydrocarbons. Up to now, lots of catalysts and technologies on catalytic pyrolysis of C4 hydrocarbons have been studied [7–10].

Buchanan et al. [11] studied the relative cracking rates of C5–C8 olefins over ZSM-5 at 510 °C in terms of the carbonium ion mechanism, and found that the cracking rate increases dramatically with increasing carbon number of olefins, and the cracking rate of octene is about 20 times of that of hexene. Meng et al. [12] studied the reaction mechanisms of heavy oil catalytic pyrolysis, and made a conclusion that the acting percentages of the free radical mechanism and the carbonium ion mechanism account for about 64% and 36%, respectively, for Chinese Daqing atmospheric residue catalytic pyrolysis on catalyst CEP-1 at 660 °C. However, the reaction mechanism of C4 hydrocarbons catalytic pyrolysis is still unclear.

In this paper, catalytic pyrolysis of C4 hydrocarbons was studied on a modified ZSM-5 catalyst, and the influence of operating conditions on product yields and product distribution was analyzed. Based on the experimental investigation, the reaction mechanisms of *n*-butylene catalytic pyrolysis were proposed and discussed.

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[*] Corresponding author. Tel.: +86 10 8973 3775; fax: +86 10 6972 4721.
E-mail address: liliupc@163.com (L. Li).

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Table 1
Feed component

Component	Content (wt%)	Component	Content (wt%)
C_2H_4	0.02	t-2-Butene	18.36
C_3H_8	0.04	1-Butene	51.06
Cyclopropane	0.02	*i*-Butene	0.08
C_3H_6	0.23	c-2-Butene	11.85
i-C_4H_{10}	4.05	1,3-Butadiene	0.13
n-C_4H_{10}	13.61	C5 hydrocarbons	0.09
Propadiene	0.04	C6 hydrocarbons	0.42

2. Experimental

2.1. Feedstock and catalyst

C4 hydrocarbons, taken from Jinshan Petrochemical Corporation, Sinopec, are used as the feedstock, and the components are listed in Table 1. The total content of C4 hydrocarbons is 99.14 wt%, and those of *n*-butylene (including 1-butylene, t-2-butylene and c-2-butylene) and butane are 81.27 wt% and 17.66 wt%, respectively.

The catalyst used is a modified ZSM-5, which is specially developed for catalytic pyrolysis of C4 hydrocarbons in a fixed-bed reactor. The columned catalyst has a diameter and length of about 1.1 mm and 2.0 mm, respectively, with a particle density of 1.37 g/cm^3 and a bulk density of 0.69 g/cm^3. The preparation of the catalyst can be seen in literature [13].

2.2. Apparatus

The experiments of C4 hydrocarbons catalytic pyrolysis were performed in a fixed-bed reactor, illustrated in Fig. 1. It is comprised of six sections: feedstock and dilution nitrogen input mechanisms, a reaction zone, a product separation and collection system, a pneumatic control system and a temperature control system. In experiments, nitrogen is used as the dilution gas to decrease the partial pressure of hydrocarbons, and to reduce the rates of undesirable reactions, such as polymerization, aromatization and condensation of olefins. Six grams of catalysts were loaded into the reactor and nitrogen was used as a carrier gas. The feed was injected through a pump, and the mass of C4 hydrocarbons injected into the reactor was measured by an electronic balance. The space velocities and the dilution ratios (the mole ratio of nitrogen to C4 hydrocarbons) were varied by changing the flow rates of C4 hydrocarbons and nitrogen. The experiments were carried out at temperatures between 450 °C and 650 °C, with C4 hydrocarbons weight hourly space velocity and dilution ratios varying in 1–5 and 0–5, respectively.

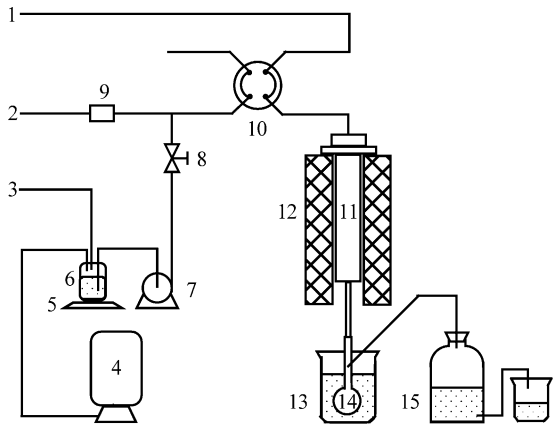


Fig. 1. Schematic diagram of the experimental apparatus. (1) Sweeping nitrogen; (2) dilution nitrogen; (3) constant pressure nitrogen; (4) feed tank; (5) electronic balance; (6) surge tank; (7) plunger pump; (8) counterbalance valve; (9) mass flow controller; (10) four-port valve; (11) reactor; (12) heater; (13) condenser; (14) collecting bottle for liquid products; (15) gas-collect tank.

2.3. Analytical methods

An Agilent 6890 gas chromatograph (having a FID and a TCD detectors) with Chem Station software was used to measure the volume percentage of the components of cracked gas. The equation of state for ideal gases converts these data to mass percentage. The collected liquid samples were analyzed by an AC gasoline component analyzer to give the weight percent of paraffinic, naphthenic, olefinic and aromatic hydrocarbons.

3. Reaction behaviors

For catalytic pyrolysis of C4 hydrocarbons, we investigated the variation laws of product yields and distribution with reaction temperature and dilution ratio.

3.1. Influences of reaction temperature

The effect of reaction temperature from 450 °C to 650 °C on product yields and distribution was investigated, keeping C4 hydrocarbons weight hourly space velocity and dilution ratio constant at 3.14 h^{-1} and 2.97, respectively.

3.1.1. Influence on the percent conversion

Table 2 gives the percent conversions of C4 hydrocarbons. The percent conversion of butylene is much higher than that of butane, indicating that butylenes are much easier to react than butanes. The percent conversion of 1-butylene is higher than that of t-2-butylene, which is slightly higher than that of c-2-butylene. The percent conversion of *n*-butane is higher than that of *i*-butane.

As reaction temperature goes up, the percent conversions of various butylenes pass through minima at about 580 °C, while those of butanes increase monotonously. The percent conversion of *i*-butane under 600 °C and that of *n*-butane under 550 °C are negative. This shows that butanes are products at low reaction temperatures due to the hydrogen transfer reactions of butylenes and the secondary cracking reactions of intermediate liquid products. The percent conversion of *i*-butane is much lower than that of *n*-butane at low reaction temperatures, indicating that the isomerization reactions play an important role. The percent conversion of butane is positive at high reaction temperatures because high reaction temperature can accelerate the

Table 2
Percent conversion of C4 hydrocarbons (%)

	Temperature (°C)								
	450	480	500	530	550	580	600	630	650
1-Butylene	92.47	91.49	90.89	89.82	89.14	88.33	88.13	88.34	88.87
t-2-Butylene	66.41	65.07	64.44	62.89	62.21	61.64	62.32	64.95	67.56
c-2-Butylene	61.69	58.92	57.65	55.94	55.59	55.58	56.77	59.93	63.02
i-Butane	−58.67	−41.89	−33.40	−25.12	−19.92	−11.98	−5.15	8.87	18.72
n-Butane	−6.92	−4.54	−3.11	−2.10	−0.65	2.50	6.36	15.20	22.01

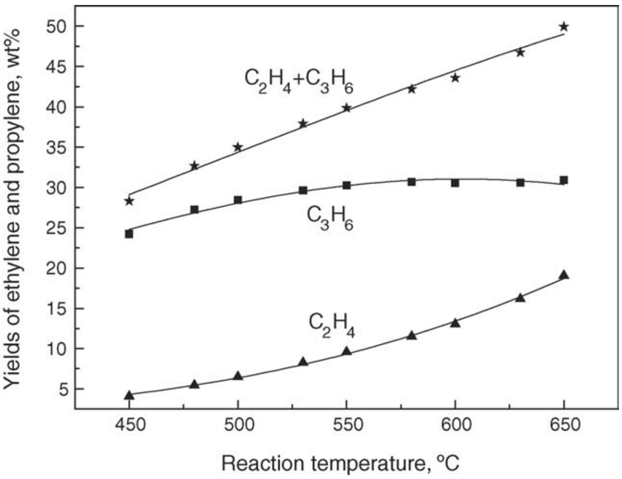


Fig. 2. Effect of reaction temperature on the yields of ethylene and propylene.

thermal cracking of butanes and does not favor the isomerization reactions of butylenes.

3.1.2. *Effect on the yields and the selectivity of ethylene and propylene*

The selectivity is defined as the ratio of the yield of light olefins to the percent conversion of the feedstock. The influences of the reaction temperature on the yields and the selectivity of ethylene and propylene are illustrated in Figs. 2 and 3, respectively. As reaction temperature goes up, the yields of ethylene and ethylene plus propylene increases monotonously, while that of propylene shows a maximum at about 580 °C. Ethylene selectivity goes up with the enhancement of reaction temperature, propylene selectivity reaches the highest 58.87% at about 570 °C, while the selectivity of ethylene plus propylene increases until a reaction temperature of 580 °C is reached, and then changes slightly.

3.1.3. *Effect on the yields of hydrogen and light alkanes*

Hydrogen, methane, ethane and propane are the by-products of catalytic pyrolysis of C4 hydrocarbons. The yields of these by-products are very low in experimental scope, and the total yield of hydrogen, methane and ethane is only 4.25 wt% at 650 °C, as listed in Table 3. As reaction temperature goes up, the yields of hydrogen, methane and ethane increase, and that of propane decreases. From 450 °C to 650 °C, the yields of hydrogen, methane and ethane increase by 0.34 wt%, 2.72 wt% and 1.10 wt%, respectively. Methane yield is very low, and the methane content in cracked gas below 530 °C is too low to be detected by the gas chromatograph.

3.1.4. *Components of liquid products*

Liquid yield decreases with increasing reaction temperature, from 23.46 wt% at 450 °C to 5.21 wt% at 650 °C. The components of liquid products at 530 °C and 580 °C are listed in Table 4. In experiments, the dilution ratio and C4 hydrocarbons weight hourly space velocity were kept fixed at 1.5 and 2.0 h^{-1}, respectively.

The key components in liquid products are olefins and aromatic hydrocarbons. The primary components of olefins are pentene and hexene, and the main components of aromatics are toluene, C8 and C9 aromatic hydrocarbons. This explains that the feeds of polyreactions are various olefins, of course including butylene. There is only a small amount of large molecular olefins and alkanes in liquid products, because the olefins and alkanes with carbon number above 7 are easy to undergo further reactions, such as cracking, aromatization and dehydrocyclization, generating light olefins, alkanes and aromatic hydrocarbons.

3.2. *Effects of dilution ratio*

The influence of dilution ratio on product yields and distribution was investigated, keeping reaction temperature and total

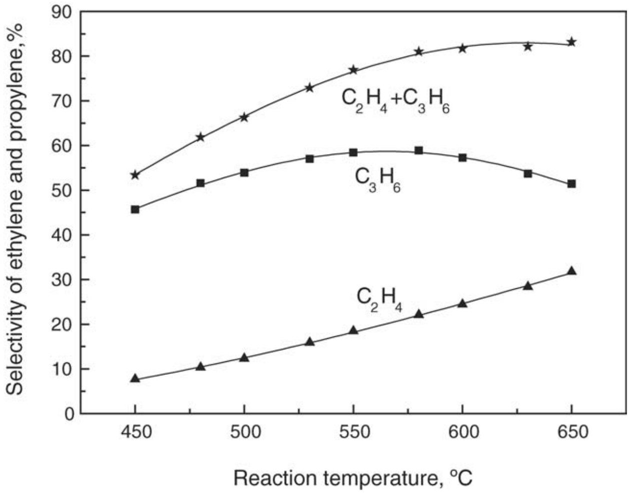


Fig. 3. Effects of reaction temperature on the selectivity of ethylene and propylene.

Table 3
Effect of temperature on the yields of light alkanes (wt%)

	Temperature (°C)								
	450	480	500	530	550	580	600	630	650
Hydrogen	0.04	0.05	0.06	0.08	0.10	0.14	0.19	0.28	0.38
Methane	0	0	0	0	0.33	0.65	1.02	1.85	2.72
Ethane	0.05	0.08	0.11	0.17	0.23	0.37	0.52	0.85	1.15
Propane	1.55	1.38	1.29	1.18	1.13	1.09	1.06	1.02	1.00

Table 4
Components of liquid products

Temperature (°C)	C-number	Paraffins	Olefins	Naphthenics	Aromatics	Total
530	5	5.62	53.32	0.18	–	59.12
	6	0.24	13.35	0.46	0.77	14.82
	7	0.11	0.71	0.60	6.90	8.32
	8	0.23	0.48	0.05	10.28	11.04
	9	0	0.24	0.04	4.62	4.90
	10	0	0.04	0	0.68	0.72
	11	0	0.22	0	0	0.22
	12+	0.03	0	0.03	0.80	0.86
	Total	6.23	68.36	1.36	24.05	100
580	5	2.51	38.37	0.13	–	41.01
	6	3.27	9.11	0.24	2.34	14.96
	7	0.09	0.65	0.24	18.52	19.5
	8	0.06	0.41	0	16.06	16.53
	9	0	0.16	0.06	5.77	5.99
	10	0	0.02	0	0.89	0.91
	11	0	0	0	0	0
	12+	0	0	0.13	0.97	1.10
	Total	5.93	48.72	0.80	44.55	100

volume velocity of nitrogen and C4 hydrocarbons fixed at 580 °C and 945 ml/min, respectively.

Fig. 4 shows the influence of dilution ratio on the yields of ethylene and propylene. As dilution ratio raises from 0 to 2.0, propylene yield increases by about 5 wt%, and changes slightly when dilution ratio is over 2.0, while the yields of ethylene and ethylene plus propylene reach maxima at about 2.0. The reason for these experimental results will be discussed later.

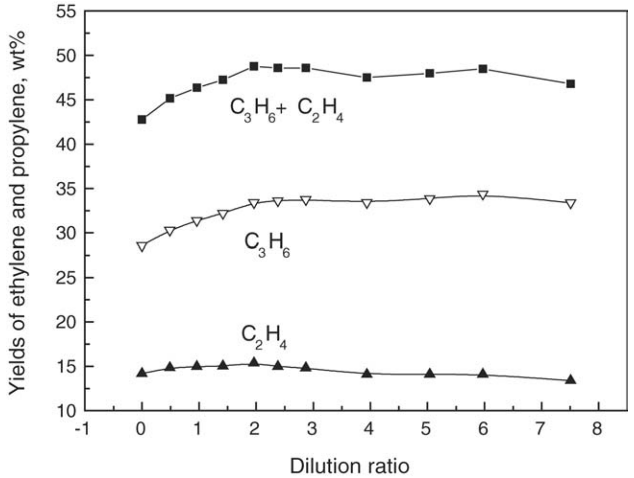


Fig. 4. Effects of dilution ratio on the yields of ethylene and propylene.

4. Reaction mechanism

The contents of *n*-butylene and butane in the feedstock are 81.27 wt% and 17.7 wt%, respectively. Experimental results show that butane can react only at high temperature, and butane is a product below 580 °C. In the process of C4 hydrocarbons catalytic pyrolysis, *n*-butylene is the predominant reactant; therefore, we lay emphasis on the reaction mechanisms of *n*-butylene in this paper.

It is through carbonium ions that the reactions of *n*-butylenes take place on the catalyst's active sites. Under the operating conditions, carbonium ions can undergo such reactions as hydrogen transfer, isomerization and polymerization, in addition to cracking. Upon that, two possible reaction mechanisms of *n*-butylene catalytic pyrolysis are proposed. They are monomolecular reaction mechanism (a), *n*-butylene directly cracking to light products, and bimolecular reaction mechanism (b), *n*-butylenes firstly dimerizing to intermediate liquid products, and then the intermediate products cracking to light products.

4.1. Monomolecular reaction mechanism

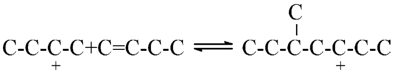
Fig. 5 shows the reaction network for *n*-butylene catalytic pyrolysis following by the monomolecular reaction mechanism. There are two cracking directions, A1 and A2, in addition to a skeletal isomerization to *i*-butylene (A3). Judging from the stability of carbonium ions, we can draw a conclusion that the reaction step a2 runs slowly. Absorbing abundant energy is the only driving force for the formation of ethyl carbonium ion and methyl carbonium ion in the steps a4 and a5. From a thermodynamic point of view, *n*-butylene can hardly crack into such light products as ethylene and propylene directly following the monomolecular mechanism.

There must be a certain amount of methane and ethane when *n*-butylenes crack to propylene and ethylene directly, following by the monomolecular reaction mechanism shown as Fig. 5. However, the experimental data listed in Table 3 shows that the yields of methane and ethane are very low, and in particular, there is almost no methane generated under 530 °C. This is not accord with the monomolecular reaction mechanism.

According to the above analysis, *n*-butylene can hardly crack to ethylene and propylene directly. And then, does the reactions of *n*-butylene catalytic pyrolysis certainly follow the bimolecular mechanism?

4.2. Bimolecular reaction mechanism

It is reported that *n*-butylene can easily dimerize to octyl carbonium ions on H-ZSM-5 zeolites with a high number of acid sites [14]. The bimolecular reaction mechanism suggests that *n*-butylenes firstly dimerize to 3-methylheptyl or 3,4-dimethylhexyl carbonium ions, as shown in expressions (1) and (2).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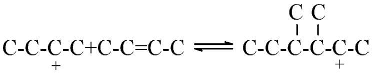
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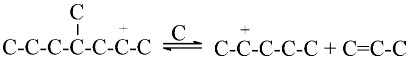
The above two carbonium ions isomerize to all other octyl carbonium ion isomers, which then crack according to β-rule. The 13 possible cracking reactions are shown in expressions (3)–(15) [11,15,16].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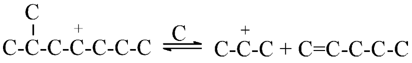
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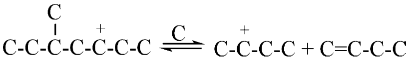
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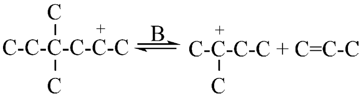
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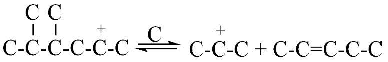
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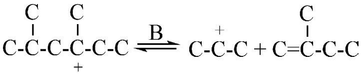
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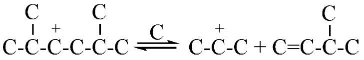
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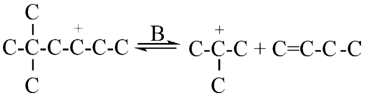
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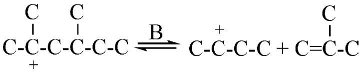
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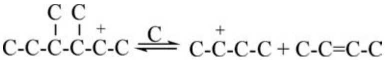
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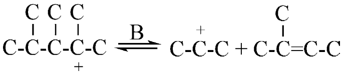
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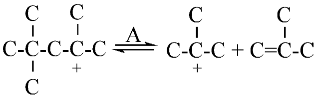
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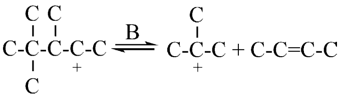
$$\mathrm{C\text{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}\text{-}\overset{\overset{C}{|}}{C}\text{-}\underset{+}{C}\text{-}C \overset{B}{\rightleftharpoons} C\text{-}\underset{+}{\overset{\overset{C}{|}}{C}}\text{-}C + C\text{-}C{=}C\text{-}C} \qquad (15)$$

Only the cracking of tertiary and secondary octyl carbonium ions is given in the above expressions. The cracking of primary octyl carbonium ions is not listed because they are not stable and can quickly isomerize to tertiary or secondary octyl carbonium ions. The symbols A–C represent three reaction types of β-cracking. Reaction type A shows the cracking reactions involving two tertiary carbonium ions, reaction type B refers to the cracking reactions involving one tertiary carbonium ion and

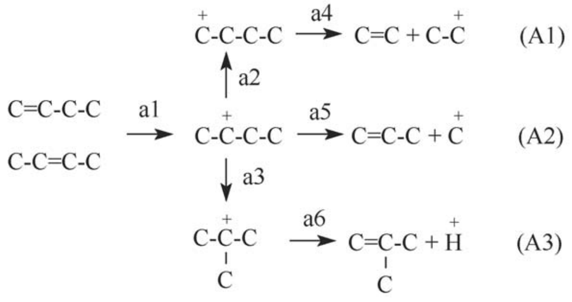

Fig. 5. Reaction network of the monomolecular reaction mechanism.

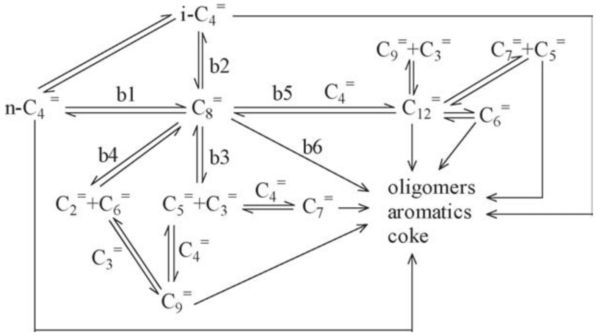

Fig. 6. Reaction network of the bimolecular reaction mechanism.

one secondary carbonium ion, and reaction type C represents the cracking reactions involving two secondary carbonium ions. According to the stability of carbonium ions, the cracking rate of reaction type A is the fastest, and that of reaction type C is the lowest.

Propylene and pentene or the respective carbenium ions can be produced via seven cracking reactions (three of reaction type B and four of reaction type C), whereas isobutene or an isobutyl carbenium ion can be formed via four cracking reactions (three of reaction type B and one of reaction type A). Besides, two cracking reactions are the reverse reaction of dimerization (expressions (5) and (12)). If other influencing factors were neglected, the ratio of propylene yield to *i*-butylene yield would be less than 7:5.

The pore structure of molecular sieves has significant influence on the cracking rate, and the effect cannot be neglected. Literature [17] says that there is no reaction of tertiary carbonium ions in the pores of ZSM-5 zeolite. As for the process of *n*-butylene catalytic pyrolysis, octyl carbonium ions with three and more branched chains can be hardly formed in the pores of ZSM-5. However, the formation of *i*-butylene are mostly from the cracking of the carbonium ions with more branched chains. Therefore, the yield of *i*-butylene is less than that of propylene, which agrees well with the experimental results (Table 2 and Fig. 2). Cejka et al. [18] studied the mechanism of skeletal isomerization of *n*-butylene to *i*-butylene over H-ferrierite molecular sieves, and found that the bimolecular mechanism is responsible for the formation of propylene, pentene and other by-products.

According to the bimolecular reaction mechanism, the cracking reactions of *n*-butylene involve two successive steps, the dimerization of *n*-butylene and the cracking of the dimer. The in-process products of dimerization can isomerize, and the light olefins of cracking can undergo secondary reactions, such as hydrogen transfer and aromatization. All of these result in varieties of the end products. Following the bimolecular reaction mechanism, there will be much propylene and *i*-butylene in cracked gas, as well as much pentene and aromatic hydrocarbons in cracked liquid. This also agrees well with the experimental results.

Under the experimental conditions of low reaction temperature and small space velocity, the temperature in reactor goes up during the initial feeding time, indicating that the exothermic polymerization reactions do take place. However, under the experimental conditions of high reaction temperature and large space velocity and dilution ratio, there is a temperature drop in the reactor during the initial feeding time, explaining that the endothermic cracking reactions do take place. All these experimental results and phenomena are the strong evidences of the bimolecular reaction mechanism for *n*-butylene catalytic pyrolysis.

4.3. Reaction network for n-butylene catalytic pyrolysis

Following the bimolecular reaction mechanism, a reaction network for *n*-butylene catalytic pyrolysis is proposed, as illustrated in Fig. 6, with literature [14] being used for reference. This reaction network only includes the major reactions, while the minor reactions such as hydrogen transfer reactions of olefins to alkanes and the cracking reactions of alkanes to olefins are not involved. In the process of catalytic pyrolysis, *n*-butylenes first dimerize to C_8-units, and then C_8-units crack directly or crack after isomerization, shown as steps b2, b3 and b4, which are competitive with each other. According to the carbonium ion mechanism, the reaction velocity of step b4 is low, while it becomes high at high reaction temperature. Furthermore, C_8-units can react with butylene generating C_{12}-units and oligomers, or aromatize to aromatic hydrocarbons, or condensate to coke. The cracking, polymerization and aromatization of C_8-units are also competitive each other. C_{12}-units can also undergo such reactions as isomerization, cracking, polymerization, aromatization and condensation.

Increasing reactant concentration can accelerate the reaction velocity of step b1, as well as those of steps b5 and b6, but the reaction velocities of steps b5 and b6 speed up more quickly than that of step b1. Therefore, the yield of liquid product increases, and those of ethylene and propylene decrease with the enhancement of the reactant concentration. From this point of view, the introduction of nitrogen into feedstock to reduce the reactant concentration will favor the formation ethylene and propylene. However, high dilution ratio is not suggested because the high dilution ratio also reduces the reaction speed of step b1, resulting in the low yields of ethylene and propylene.

5. Conclusions

(1) Catalytic pyrolysis of C4 hydrocarbons on a modified ZSM-5 zeolite was investigated in a fixed bed reactor. As temperature increases, ethylene yield goes up monotonously, and propylene yield passes through a maximum at about 580 °C. With increasing dilution ratio, the yield of propylene increases until a dilution ratio of 2.0 is reached, and then changes slightly, while that of ethylene reaches maximum at about 2.0.

(2) For catalytic pyrolysis of C4 hydrocarbons, *n*-butylene is the major reactant. The yields of hydrogen and light alkanes are very low, while that of liquid product is high, reaching 23.46 wt% at 450 °C. The main components of liquid products are pentene, hexene and aromatic hydrocarbons.

(3) For *n*-butylene catalytic pyrolysis, two possible reaction mechanisms, the monomolecular reaction mechanism and the bimolecular reaction mechanism, were proposed. The theoretic analysis and the experimental results show that *n*-butylene catalytic pyrolysis follows the bimolecular mechanism.

(4) According to the bimolecular mechanism, *n*-butylene catalytic pyrolysis involves two successive reactions, the dimerization of *n*-butylenes and the cracking of the intermediate dimers. The reaction network of *n*-butylene catalytic pyrolysis is illustrated and some reactions in the network are discussed.

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