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Reaction Pathway of 1-Decene Cracking to Produce Light Olefins over H-ZSM-5 at Ultrahigh Temperature

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ZSM-5, and the catalytic cracking dominated even at 750 °C. With the increase in temperature, the yields of ethylene and propylene gradually increased, and the yields of alkanes and aromatics also increased. The low WHSV was favorable for the yield of light olefins. With the increase of the WHSV, the yields of ethylene and propylene decrease. H

olefins. With the increase of the WHSV, the yields of ethylene and propylene decrease. However, at low WHSV, secondary reactions were accelerated, and the yields of alkanes and aromatics increased significantly. In addition, the possible main and side reaction routes of the 1-decene cracking reaction were proposed based on product distribution.

1. INTRODUCTION

Ethylene and propylene were important chemical raw materials.^{1–3} At present, light olefins mainly come from steam cracking and fluid catalytic cracking (FCC) units in the industry.^{4,5} However, the steam cracking process requires high reaction temperatures and consumes large amounts of energy. For the FCC unit, it is difficult to produce ethylene.^{6–9} Therefore, we developed an FCC process for targeted cracking to light olefins (TCO), which was aimed at producing ethylene and propylene while ensuring low methane selectivity.¹⁰ The key of TCO technology is the cracking reaction of C_5^+ olefins, and its reaction mechanism is different from that of pentene. Therefore, the 1-decene cracking reaction is studied in this paper.

At present, there are many research studies on the cracking of C_4-C_6 olefins to ethylene and propylene.^{12–17} Monomolecular and bimolecular cracking mechanisms are widely accepted in C_4-C_6 olefin cracking.^{18–20} For the cracking of short-chain olefin over zeolite, it is generally believed that monomolecular and bimolecular cracking mechanisms coexist. When the carbon chain gradually increases, the reaction mechanism is mainly monomolecular cracking. Lin et al. studied the effect of acid strength on the cracking paths of butene and pentene over H-ZSM-5.^{13,14} It was found that the olefin cracking pathway can be regulated by changing the acid strength. The strong acid site of zeolite is favorable for the pathway of ethylene formation, and the weak acid site is favorable for the pathway of propylene formation. Sun et al. studied the effect of acidity and reaction temperature on the cracking path of hexene at 460–580 °C. It was found that high temperature promoted the monomolecular cracking of hexene, and the selectivity of propylene increased with the increase in temperature.²¹

Compared with the catalyst modification method to improve the yield of light olefins, changing the reaction conditions was a more convenient method.²² Some researchers have discussed the effect of temperature on olefin cracking to produce light olefins.^{23–27} Zhang et al. studied the influence of thermodynamic factors on the equilibrium distribution of olefin cracking reaction. They found that olefin systems with different carbon numbers exhibit similar thermodynamic equilibrium distributions. The equilibrium composition of ethylene increases with the increase in reaction temperature, and the equilibrium composition of propylene reaches the maximum at 850–950 K

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6 h-1





Figure 1. Catalytic cracking experimental equipment.



Figure 2. Conversion and main product yields of the 1-decene cracking reaction varied with temperatures over (a) quartz sand and (b) H-ZSM-5.

under 0.1 MPa.²⁷ It showed that high temperatures are more conducive to the formation of light olefins in thermodynamics.

In the past, the research temperature of olefin cracking was mainly focused on 450-600 °C, and the reaction followed the carbenium ion mechanism.^{21,28,29} If we want to further improve the yield of light olefins, we may need to increase the reaction temperature. When the reaction temperature exceeds 600 °C, it is still controversial whether the cracking reaction over the zeolite is still dominated by the catalytic cracking reaction mechanism.³⁰ Earlier, our research group proposed a thermal/catalytic cracking proportion model for pentene cracking and discussed the mechanism of pentene cracking mechanism of 1-decene at ultrahigh temperature was discussed using the model established by our previous research.

2. EXPERIMENTAL SECTION

2.1. Materials. H-ZSM-5 zeolite was provided by the Sinopec Research Institute of Petroleum Processing. H-ZSM-5 were crushed and sieved into 20–40 mesh particles and hydrothermally treated at 800 °C for 4 h. The properties of the catalyst can be referred to in our previous article.¹¹ 1-Decene (96%, the rest are olefin isomers) was purchased from Alfa Aesar.

2.2. Catalytic Cracking of 1-Decene. The evaluation of 1-decene was carried out on the fixed-bed reactor in the laboratory. The experimental equipment is shown in Figure 1. The catalyst (1 g, 20–40 mesh) was loaded into the quartz tube reactor (inner diameter 6 mm). Quartz cotton was placed at the bottom of the reaction tube to prevent the catalyst from falling.

1-Decene (1.7 g) was injected into the reactor through a syringe pump, and the feed was driven by nitrogen to pass through the catalyst bed. The reacted product enters the liquid



Figure 3. P/E, ethylene/methane molar ratio (E/M), and methane yield as a function of reaction temperature (a) propene/ethylene molar ratio (b) methane yield, and ethylene/methane molar ratio.

collecting bottle and is cooled by a cooling tank (-19 °C). The gas product is collected in the gas collecting bottle, and the volume of cracked gas is calculated by weighing the discharged water. The liquid phase product is collected in the liquid collecting bottle. The gaseous products were analyzed by an Agilent 7890A gas chromatograph (Agilent J&W HP-PLOT Al_2O_3 KCl column) and the liquid products were analyzed by Agilent 7890A (Agilent J&W HP-PONA column). The conversion and yield are calculated as shown in eqs 1 and 2.

conversion (%) =
$$\left(1 - \frac{\text{decene mass in the product}}{\text{decene feed mass}}\right)$$

× 100% (1)

yield
$$(C_x H_y) = \frac{C_x H_y \text{ mass}}{\text{decene feed mass}} \times 100\%$$
 (2)

where $C_x H_v$ was the hydrocarbon in the product.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature and WHSV on Product Distribution. 3.1.1. Effect of Reaction Temperature on the Main Product Yields of 1-Decene Cracking. The cracking reaction of 1-decene is endothermic and requires a high temperature, so the effect of temperature is crucial to the cracking reaction. At present, the temperature of olefin cracking is mainly concentrated in the range of 450-600 °C. To obtain higher ethylene, the reaction temperature must be increased. Therefore, the study of 1-decene cracking was carried out in a higher temperature range in this paper. The 1decene cracking reaction temperature was set in the range of 500-750 °C. The thermal cracking reaction of hydrocarbons may occur when the reaction temperature was above 600 °C. To clarify the role of thermal cracking reaction and catalytic cracking reaction, the pyrolysis reaction of hydrocarbons at different temperatures was carried out with quartz sand and H-ZSM-5, respectively. The effects of reaction temperature on the conversion and product yield were investigated by fixing the WHSV at 90 h^{-1} .

The effect of reaction temperature on 1-decene cracking over quartz sand is shown in Figure 2a. It was observed that

the yields of ethylene, propylene, butene, and conversion increased with the growth of temperature. The thermal cracking reaction was not very obvious at temperatures below 600 °C, but when the reaction temperature exceeded 600 °C, the conversion increased significantly. The reaction conversion was as high as 56.61% at the reaction temperature of 750 °C.

Conversion and main product yields of the 1-decene cracking reaction varied with temperatures over H-ZSM-5 as shown in Figure 2b. Different from the monotonous increase of all products over quartz sand, the reaction products of 1decene over H-ZSM-5 showed different trends. As shown in Figure 2, the yields of ethylene and propylene both increased with the increase in the reaction temperature, but the upward trend of the two was not consistent. The growth rate of ethylene yield was relatively slow in the early stage, and when the temperature exceeded 650 °C, the growth rate of the yield becomes faster. The difference was that the change rule of propylene was just the opposite. In the early stage, the growth rate of propylene yield was fast, but when the temperature exceeded 650 °C, the growth rate of that slowed down. The butene yield over H-ZSM-5 changed relatively gently in the low-temperature section, but when the temperature increased to the high-temperature section, the butene yield decreased significantly.

The yields of ethylene and propylene showed an increasing trend with the increase in the reaction temperature, but the increasing rates of the two were different. Increasing the temperature was more favorable for the formation of ethylene. Also, the thermodynamic equilibrium distribution of ethylene was more favorable with the increasing temperature. It can also be seen from Figure 3a that the value of the molar ratio of propylene to ethylene (P/E) decreased significantly with the increase in the reaction temperature. However, the rate of decline changes around 650 °C, and the value of P/E decline began to decrease at the temperature above 650 °C.

The yields of ethylene and propylene increased with the increase in reaction temperature. Moreover, the yield of methane also increased at the same time. The increase in methane yield results in a great waste of hydrogen resources in petroleum. To evaluate the relationship between the growth rate of ethylene and methane, we put forward the evaluation index ethylene/methane molar ratio (E/M). Figure 3b depicts the variation of methane yield and ethylene–methane molar ratio with temperature. With the increase in temperature, the E/M value decreased obviously, but the yield of methane increased rapidly. Considering the reaction temperature and the value of E/M comprehensively, the reaction temperature around 610 °C has a better atom economy.

The olefin product yield of 1-decene cracking over H-ZSM-5 as a function of temperature is shown in Figure 4. It can be



Figure 4. Olefin product yields of the 1-decene cracking reaction vary with temperatures over H-ZSM-5.

seen that with the increase in temperature, the yield of longchain olefins becomes less, and the whole product distribution tends to shorten the carbon chain. The olefin carbon number of the whole product was mainly distributed between C_1-C_6 . The proportion of olefins in the 1-decene cracking product was about 85–90%. It showed that the side reaction occupies a considerable proportion in 1-decene cracking. The rest of 1decene will generate some aromatics, alkane coke, and other products. The side reactions of 1-decene cracking are discussed below.

The cracking of 1-decene was a relatively complex reaction. While the main cracking reaction occurs, there were also many side reactions, including oligomerization, hydrogen transfer, cyclization, aromatization, alkyl transfer, and other reactions. Some major side products of 1-decene cracking over quartz sand and H-ZSM-5 are shown in Figure 5. The yields of the main byproducts over the quartz sand all increased with the increase of the reaction temperature. The product yield did not exceed 0.5% when the reaction temperature was lower than 600 °C. The yields of methane and ethane increased linearly and rapidly after the reaction temperature exceeded 600 °C. The yields of propane and aromatics also started to increase significantly after 600 °C, but the growth rate was relatively slow. The total aromatic produced by the reaction of 1-decene over quartz sand was the highest at 750 °C, but only about 1%. This indicated that olefins were not easy to generate aromatics in quartz sand. Butane had been maintained at relatively low levels.

The side product yield on the catalyst as a function of the reaction temperature is illustrated in Figure 5b. As can be seen from Figure 5b, with the increase in reaction temperature, the vields of methane and ethane started to increase slowly and then sharply, those of propane and butane increased sharply and then fell sharply, and that of hydrogen increased slowly. The variation trends of methane and ethane were very similar over quartz sand and H-ZSM-5. It showed that the methane and ethane produced by thermal cracking may occupy a considerable proportion in the cracking of 1-decene. Propane and butane were produced by hydrogen transfer reactions for 1-decene cracking over H-ZSM-5.31,32 Initially, the yields of propylene and butene increased with the increase in reaction temperature, and parts of propylene and butene were converted to propane and butane through hydrogen transfer reaction, respectively. The hydrogen transfer reaction is exothermic. As the reaction temperature continues to increase, the hydrogen transfer reaction was greatly inhibited, resulting in a decrease in the yields of propane and butane.

1-Decene produced almost no aromatization over quartz sand, but a significant aromatization reaction occurred over H-



Figure 5. Side product yields of the 1-decene cracking reaction vary with temperatures over (a) quartz sand and (b) H-ZSM-5.

ZSM-5. It showed that the aromatization reaction needs to be carried out under acidic conditions. Aromatization reaction is a relatively high proportion of side reactions over H-ZSM-5. The unique pore structure and acid properties of H-ZSM-5 were beneficial to the generation of aromatics.^{33,34}

The yields of major aromatic products for the 1-decene cracking reaction over H-ZSM-5 as a function of reaction temperature are listed in Figure 6. As we can see from Figure 6,



Figure 6. Main aromatic product yields of the 1-decene cracking reaction vary with temperatures over H-ZSM-5.

the temperature rise has an obvious influence on the aromatization activity of the catalysts and the distribution of aromatics. With the increase in temperature, the yields of total aromatics and aromatics for each carbon number increase. The aromatics generated in the 1-decene cracking process were mainly concentrated from C_7 to C_9 aromatics, and when the reaction temperature reaches 650 °C, benzene begins to appear.

The conversion of olefins to aromatics was a very complex reaction. The mechanism of olefins converted to aromatics has not been fully elucidated. However, there was still some consensus that aromatization reactions mainly include oligomerization, cracking, hydrogen transfer, dehydrocyclization, transalkylation, etc.^{35,36} Some researchers believe that short-chain olefins were first polymerized into long-chain olefins and then underwent hydrogen transfer, dehydrocyclization, and other steps to generate aromatics. Unlike short-chain olefins, 1-decene already has a longer carbon chain that does not require further stacking to generate aromatic lengths. Therefore, 1-decene may favor aromatization more than short-chain olefins.

3.1.2. Effect of WHSV on the Main Products Yields of 1-Decene Cracking. The WHSV was an important influencing factor for catalytic cracking reaction, and the study of the effect of the WHSV on the catalytic cracking reaction was of great significance for converting the olefin into light olefin products.³⁷ The effects of the WHSV on the conversion and product yield were investigated by fixing the temperature at 600 °C.

It can be seen from Figure 7 that in the WHSV range of 6- 90 h⁻¹, the conversion of 1-decene was above 99%, and the



Figure 7. Conversion and main product yields of the 1-decene cracking reaction vary with WHSVs over H-ZSM-5.

WHSV had almost no effect on the conversion. However, the yield of the product varies dramatically with the increase in WHSV. With the increase in WHSV, the ethylene yield decreased, and the propene yield first increased and then decreased. It can be seen that the increase in WHSV was unfavorable to the yield of ethylene and propylene, especially the yield of ethylene. It can be seen from Figure 8 that the



Figure 8. P/E of the 1-decene cracking reaction varies with WHSVs over H-ZSM-5.

value of the molar ratio of propylene to ethylene (P/E) increases linearly with the increase in WHSV. Unlike ethylene, propylene has a maximum in the low-WHSV region. This may be because the propylene produced by the reaction further reacts with other substances at low WHSV, resulting in the macroscopically produced propylene amount at low WHSV being lower than the actual amount produced. Compared with propylene, ethylene was more difficult to convert further, so it does not turn around like propylene in the low-WHSV region. Different from propylene, the yield of ethylene decreases monotonically, which may be because some short-chain olefins were more difficult to crack further with the increasing WHSV.

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Figure 9. Olefin yields of the 1-decene cracking reaction vary with WHSVs over H-ZSM-5.

then remained unchanged, and the heavy olefin yield increased, especially C_4 to C_6 olefins. It showed that with the increase in WHSV, some short-chain olefins do not continue to crack. Except for WHSV on 6 h⁻¹, the olefin yields at other WHSVs were kept between 80 and 85%. It showed that in the low-WHSV range, olefins were more prone to some side reactions except cracking.

The variation of the side product yield with WHSV is illustrated in Figure 10. As can be seen from the figure, hydrogen, methane, ethane, and propane all gradually decrease with the increasing WHSV. In addition, methane and ethane dropped significantly in the low-WHSV range, and then the downward trend became slower. Alkanes were mainly formed by hydrogen transfer reactions. It was generally believed that the hydrogen transfer reaction was a bimolecular reaction that



Figure 10. Side product yields of the 1-decene cracking reaction vary with WHSVs over H-ZSM-5.

requires two adjacent active sites to complete the reaction. Increasing the WHSV was unfavorable for the hydrogen transfer reaction. Therefore, the yield of alkanes decreases with the increase of WHSV.

The yields of the main aromatic products for the 1-decene cracking reaction over H-ZSM-5 as a function of WHSV are listed in Figure 11. It can be seen from Figure 11 that the



Figure 11. Main aromatic product yields of the 1-decene cracking reaction varied with WHSVs over H-ZSM-5.

increase in WHSV has a significant impact on the distribution of aromatics generated during the 1-decene cracking process. The yields of aromatics per carbon number and total aromatics decreased with the increasing WHSV. The aromatics generated during the cracking of 1-decene were mainly concentrated in C_6-C_9 aromatics. When WHSV increased to 90 h⁻¹, almost no benzene was formed. Hydrogen transfer and dehydrogenation reactions were two important reactions affecting the formation of aromatics. The hydrogen transfer reaction occurred in two adjacent active sites, and reducing the WHSV was beneficial to the hydrogen transfer reaction to generate aromatics. At the same time, the reduction of WHSV was more conducive to the cyclization and dehydrogenation of olefins.^{38,39} Therefore, a large number of aromatics was generated after WHSV was reduced.

3.2. Radical and Carbocation Reactions of 1-Decene over Quartz Sand and Catalyst. The cracking of hydrocarbons at high temperatures follows the free radical mechanism and carbenium ion mechanism. To better compare the difference between free radical reaction and carbocation reaction, cracking experiments were carried out on quartz sand and catalyst, respectively. It was found that the thermal cracking reaction is very weak in the reaction temperature range of 500–600 °C over quartz sand. When the temperature increases to 650 °C, the thermal cracking reaction begins to intensify.

To evaluate the proportion of thermal cracking and catalytic cracking at high temperatures, we proposed a thermal/catalytic cracking ratio model. For a certain amount of olefin reactants over H-ZSM-5 at high temperatures. The part of chemical adsorption with the acid site was recorded as a, which was speculated to be catalytic conversion or final desorption; the remaining fraction was dissociated, 1 - a, presumed to be

thermally cracked or unreacted. Therefore, the conversion of the reaction can be represented by eq 3. Through eq 3, deformation can yield eq 4.

$$a \times C_{\text{catalytic}} + (1 - a) \times C_{\text{thermal}} = C_{\text{total}}$$
 (3)

$$a = \frac{C_{\text{total}} - C_{\text{thermal}}}{C_{\text{catalytic}} - C_{\text{thermal}}}$$
(4)

where $C_{\text{catalytic}}$ is the conversion of catalytic cracking, C_{thermal} is the conversion of thermal cracking, and C_{total} is the total conversion.

By bringing in the values of each variable, the range of a can be obtained, as shown in Table 1. It can be seen that for the cracking of 1-decene, the carbenium ion mechanism cracking dominates.

Table 1. Value Ranges of $C_{\text{catalytic}}$ and a in 1-Decene Cracking over H-ZSM-5 at 650–750 °C

reaction temperature (°C)	C _{catalytic} (%)	a (%)
650	99.63-100	99.56-100
700	99.69-100	99.52-100
750	99.78-100	99.49-100

3.3. Effect of Temperature on the Reaction Pathway of 1-Decene Cracking. It was generally believed that for the cracking reaction of short-chain olefins, like C_5-C_6 olefins, monomolecular cracking and bimolecular cracking mechanisms coexist. However, for long-chain-length olefins, like C_7^+ olefins, the monomolecular cracking mechanism was dominant. Also, as the temperature increases, it becomes more difficult for bimolecular reactions to occur. Therefore, the bimolecular cracking reaction of 1-decene was not considered in this paper, and only a monomolecular reaction was thought to occur. The process of generating ethylene must involve primary carbenium ions. For long-chain olefins, it was difficult to directly generate primary carbenium ions. Therefore, this paper believes that ethylene was produced by the secondary

cracking of 1-decene cracking products, and the situation that 1-decene directly generates ethylene is not considered.

As the carbon chain grows, the isomers of hydrocarbons increase dramatically. There were 75 isomers of 1-decane, taking into account the position of the double bond, the isomers of 1-decene would increase exponentially. Therefore, this paper did not enumerate the different β -scission modes of 1-decene in detail and only outlines the possible reaction pathways, as shown in Figure 12.

1-Decene and the longer-carbon-chain olefins produced by its cracking can be cyclized to form naphthene. On the one hand, cycloalkanes can be generated by the hydrogen transfer reaction to generate aromatic hydrocarbons and can also be directly generated by the dehydrogenation reaction. At relatively low temperatures, naphthenic hydrocarbons mainly generate aromatics through the hydrogen transfer reaction. However, at relatively high temperatures, the dehydrogenation reaction dominates.⁴⁰ Aromatic can continue to undergo transalkylation, dealkylation, and other reactions, and some aromatic hydrocarbons were further polycondensed into fusedring aromatic hydrocarbons through hydrogen transfer and other reactions, and further react to form coke.

Based on the above reaction network, the main network of the reaction was obtained by appropriate simplification. The mole number of reactants and products was calculated according to the main reaction model, and the proportion of each pathway in the main reaction network at different temperatures was obtained, as shown in Figure 13. Considering the number of variables and equations, this model made appropriate assumptions and simplifications for the cracking process. The alkanes in the product were considered to be the result of olefin hydrogen transfer in the calculations, which were incorporated into olefins of the same carbon number. In the low-reaction-temperature range, it was difficult for pentene to directly generate C1 and C4, so pathway VII was not considered in the low-temperature range.¹¹ At the same time, limited by the number of variables and equations, the pathway with a small proportion was ignored at this time.



Figure 12. Possible main and side reaction network for the cracking of 1-decene. Abbreviations: Isom isomerization; β -scis, β -scission; Cycl, cyclization; Ht, hydrogen transfer; Deh, dehydrogenation; Dea, dealkylation.

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		500°C	550°C	600°C	650°C	700°C	750°C
a $C_3^{=+}C_7^{=} \longrightarrow C_3^{=+}C_7^{=}$	Ι	8.05%	7.72%	4.22%	0.00%	0.00%	0.00%
$C_3^{=+}C_4^{=+}C_4^{=-}$	Π	28.26%	33.04%	47.17%	43.41%	39.15%	21.43%
$C_{10} \xrightarrow{\hspace{1cm} b} C_4 \xrightarrow{\hspace{1cm} +} C_6 \xrightarrow{\hspace{1cm} /} C_4 \xrightarrow{\hspace{1cm} +} C_4 \xrightarrow{\hspace{1cm} +} C_2 \xrightarrow{\hspace{1cm} -} C_4 \xrightarrow{\hspace{1cm} +} C_2 \xrightarrow{\hspace{1cm} -} C_2 \hspace{1$	III	7.47%	6.75%	14.73%	9.26%	7.38%	3.30%
c $C_4^{=+}C_6^{=}$	IV	30.07%	24.66%	12.38%	11.22%	7.33%	5.24%
$C_5^{=+}C_5^{=}$	V	27.13%	26.14%	16.48%	15.89%	11.32%	7.78%
$C_5^{=}+C_5^{=} \longrightarrow 2C_2^{=}+2C_3^{=}$	VI	-0.99%	1.69%	5.02%	15.78%	28.46%	48.26%
$2C_1 + 2C_4^{=}$	VII	/	/	/	4.44%	6.35%	13.99%

Figure 13. 1-Decene cracking reaction network.

It can be seen from the reaction network that if higher ethylene and propylene are desired, the temperature should be increased to above 650 °C. At this time, more 1-decene is reacted through pathway c. If you want more butene, you should control the temperature below 650 °C, when more 1decene reacted through pathways a and b.

4. CONCLUSIONS

The reaction of 1-decene at different temperatures was carried out on quartz sand and H-ZSM-5. It was observed that the conversion of 1-decene reacted on quartz sand increased with the increase of the reaction temperature. When the temperature was 600 °C, an obvious thermal cracking reaction started, and the conversion (56.6%) of the reaction was the highest at 750 °C. The conversion of 1-decene over H-ZSM-5 was relatively high. In the range of 500-750 °C, the conversion of 1-decene cracking was always above 99%. Through analysis, the reaction over the H-ZSM-5 catalyst is still dominated by the carbenium ion mechanism even at 750 °C. With the increase in temperature, the yields of ethylene and propylene gradually increased, and the number of alkanes and aromatics also increased. In addition, the increasing rates of ethylene and propylene were not the same, and the value of P/E decreased with the increase in temperature. In addition, when the temperature reaches 650 °C, the amount of ethylene generated by pathway VI begins to increase, and methane is generated by pathway VII.

At a reaction temperature of 600 °C and WHSV of 6-90 h⁻¹, WHSV has little effect on the conversion of 1-decene cracking, which was always maintained above 99%. With the increase in WHSV, the yield of propylene increased first and then decreased, ethylene decreased gradually, and butene increased gradually. The value of P/E increases monotonically, and the increase in WHSV has a greater impact on the yield of ethylene. By adjusting the WHSV of the reaction, the ratio of ethylene to propylene in the product can be flexibly adjusted.

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