Study on the catalytic performance of Ag-P/HZSM-5 Catalyst for n-heptane at different reaction temperature and residence time

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Abstract. One of the key technologies for the catalytic cracking of alkanes to produce low-carbon alkenes is the development of high-efficiency catalyst. This research prepared Ag-P/HZSM-5 and it had good regeneration performance. The continuous reaction regeneration experiment was carried out on the circulating fluidized bed experimental device, and the catalytic performance of n-heptane was investigated under the conditions of different reaction temperature and different residence time. The results showed that the conversion and yield of each product increased gradually with the increase of residence time, and the conversion rate of the reaction increased rapidly with the increase of reaction temperature. This can provide a basis for the research and development of new catalysts.

1. Introduction
For the catalytic cracking reaction of hydrocarbons, catalyst is an important factor affecting the cracking degree and product distribution [1-2]. Therefore, one of the key technologies for the catalytic cracking of alkanes to produce low-carbon alkenes is the development of high-efficiency catalyst. Now, there are two kinds of traditional catalysts, one is metal oxide catalyst, and the other is molecular sieve catalyst [3-5]. In 1960, the metal oxide catalysts was used in the production of low-carbon olefins. The most widely used catalyst is calcium aluminum composite oxide catalyst. 12CaO-7Al2O3-K2CO3 and KVO3-Al2O3 are considered as the excellent catalysts for naphtha catalytic pyrolysis [6]. The catalytic cracking reaction on metal oxides is still essentially the thermal cracking reaction of hydrocarbon molecules, and its reaction still follows the free radical mechanism [7]. The reaction temperature is still high, which is only about 50 ℃ lower than the steam cracking reaction, and the conversion rate improved. However, the distribution of the products hardly changed [8-10]. The selectivity of ethylene in the reaction products is high and the P/E ratio is low. For the zeolite catalyst, the pore structure, acidity, grain size and Si / Al ratio are the main factors affecting its catalytic performance [11].

ZSM-5 zeolite was a three-dimensional shape selective zeolite with MFI structure developed by Mobil Company in the early 1970s [12]. Although ZSM-5 zeolite catalyst has been successfully used in many processes, its catalytic activity and molecular diffusion ability still need to be further improved [13-15]. In order to develop the advantages of ZSM-5 molecular sieve in catalysis, different ways of modification have been studied to improve its hydrothermal stability and acid properties [16-18].
The distance between the metal active sites and the acid sites of ZSM-5 is minimized in this research, and the dehydrogenation active sites are introduced into the molecular sieves by the way of metal modification of molecular sieves [19-20]. This research prepared a kind of bifunctional catalyst for cracking and dehydrogenation which was HZSM-5 modified by silver and phosphorus. The continuous reaction regeneration experiment was carried out on the circulating fluidized bed experimental device, and the catalytic performance of n-heptane was investigated under the conditions of different reaction temperature and different residence time.

## 2 Experimental method

### 2.1 Circulating fluidized bed experimental device

Continuous reaction regeneration evaluation was performed with a circulating fluidized bed apparatus. The device mainly includes a feeding system, a reaction regeneration system, an oil and gas condensate collection and measurement system, a flue gas collection and measurement system, and a total control system. The n-heptane feedstock enters the riser reactor from the middle and reacts with the catalyst. The reacted oil and gas enters the subsequent condensation collection and metering system, and the catalyst enters the regenerator for regeneration. The regenerated catalyst enters the reactor for the next reaction.

### 2.2 Analysis of reaction products

The resulting gas products were analyzed by brooke Dalton's 450-gc gas chromatograph. The contents of hydrogen, nitrogen, oxygen, CO and CO2 in the products were analyzed by TCD detector, and the compositions of C1–C5 hydrocarbons in the products were analyzed by FID flame ion detector. The composition of liquid products was analyzed by Agilent4890 gas chromatograph.

The composition of dry gas includes hydrogen, methane, ethane, and ethylene. The composition of liquefied gas includes propane, propylene, butane, and butene. The calculation formulas of reaction conversion rate, yield and selectivity of each product were as follows.

\[
\text{Conversion} = \frac{\text{mass of n-heptane converted}}{\text{mass of n-heptane}} \times 100\%
\]

\[
\text{Yield of product } i = \frac{\text{mass of product } i \text{ formed}}{\text{mass of n-heptane}} \times 100\%
\]

\[
\text{Selectivity of product } i = \frac{\text{yield of product } i}{\text{Conversion of n-heptane}} \times 100\%
\]

## 3 Reaction law of Ag-P / HZSM-5 Catalyst

This research prepared HZSM-5 modified by silver and phosphorus. The continuous reaction regeneration experiment was carried out on the circulating fluidized bed experimental device, and the catalytic performance of n-heptane was investigated under the conditions of different reaction temperature and different residence time.

### 3.1 The influence of reaction temperature

In the experiment, the residence time is 1.45 s, the feed quantity is 0.8 kg/h. Figure 1 shows the conversion rate and the change curve of dry gas, liquefied gas and coke yield with reaction temperature, and Figure 2 shows the change curve of each component yield in dry gas and liquefied gas at different temperatures.
Figure 1. Conversion and yield of dry gas, LPG and coke at different reaction temperatures

Figure 2. Yield of main gas product at different reaction temperatures

With the increased of reaction temperature, the conversion rate of the reaction increased rapidly from 15% at 530 °C to 70% at 610 °C, and the yield of liquefied gas and dry gas also increased. Because there are dehydrogenation reaction and cracking reaction in the process of n-heptane reaction, and both are strong endothermic processes. The increase of reaction temperature is beneficial to the endothermic reaction, so the conversion rate increases rapidly. The increase of conversion rate correspondingly increases the yields of liquefied gas, ethylene, propylene, butene and other products. With the increased of reaction temperature, the thermal cracking reaction intensified and the dry gas yield increased. Figure 1 shows the yield of hydrogen and methane in dry gas increases very little, followed by ethane, and Ethylene changes most. In addition to thermal cracking, the source of ethylene under the catalysis of silver phosphorus modified catalyst include the free radical reaction. Because the oxidation-reduction of silver may promote the free radical reaction. The free radical reaction is an endothermic reaction, so the yield of ethane and ethylene in dry gas increases rapidly.
with the increase of reaction temperature. The yield of coke was almost zero in the whole temperature range, and it remained unchanged with the increased of temperature, which indicated that the silver phosphorus modified catalyst had good carbon deposition resistance.

Figure 3. Selectivity of ethylene, propylene and butylene at different reaction temperatures

Fig. 3 shows that the selectivity of the three alkenes varies greatly with temperature. With the increase of reaction temperature, ethylene selectivity increases linearly, propylene selectivity increases first and then decreases, and butene selectivity decreases monotonously. The increase of ethylene selectivity is the result of thermal cracking and free radical reaction. When the reaction temperature increases, the depth of cracking reaction increases, and the secondary reaction of butene and propene intensifies. Compared with propene, butene is more prone to secondary reaction, so the selectivity of butene decreases with the increase of reaction temperature. It is generally believed that the reabsorption and cracking of butene in the acid center followed the mechanism of dimerization cracking, and part of propylene would be formed during dimerization cracking. Therefore, the selectivity of propylene shows a certain increasing trend. But when the temperature was very high, the degree of secondary reaction of propylene also intensified. The propylene produced by butene cracking was not enough to offset the consumption of propylene cracking, so the selectivity was reduced.

3.2 The influence of residence time
The reaction conditions in the experiment are as follows: the outlet temperature of riser is 590 °C, the ratio of agent to oil is 22.35, and the feed quantity is 0.8 kg / h.

| Residence time, s | 1.04 | 1.43 | 1.94 | 2.50 |
|-------------------|------|------|------|------|
| Conversion, wt%   | 45.34| 52.95| 60.26| 62.89|
| Yield, wt%        |      |      |      |      |
| H₂                | 0.17 | 0.20 | 0.23 | 0.26 |
| CH₄               | 0.62 | 0.66 | 0.81 | 0.91 |
| C₂H₆              | 1.78 | 2.16 | 2.50 | 2.67 |
| C₂H₄              | 4.20 | 4.93 | 5.38 | 5.28 |
| C₃H₆              | 6.12 | 8.97 | 10.97| 11.92|
| C₃H₈              | 10.24| 11.52| 11.98| 11.56|
| C₄H₁₀             | 3.64 | 5.14 | 6.63 | 7.65 |
| C₄H₈              | 6.15 | 6.75 | 7.29 | 7.31 |
| Coke              | 0.07 | 0.10 | 0.14 | 0.19 |
| Dry gas           | 6.77 | 7.94 | 8.92 | 9.12 |
Table 4-8 shows that the conversion and yield of each product increase gradually with the increase of residence time. Because of the prolongation of residence time, the contact time of oil and gas molecules with the active center of catalyst increases. The cracking reaction intensifies, and conversion rate increases, so the yield of corresponding gas products also increases. With the increase of residence time, the secondary reactions of propylene and butene intensify, such as hydrogen transfer reaction. The selectivity of olefins decrease, and the selectivity of butane and propane increase. The retention time is a double-edged sword. If the retention time is prolonged, the catalyst and raw material can react fully and it can improve the conversion rate. However, the secondary reaction of propylene and butene intensified, then the selectivity of the target product decreased. Therefore, the selection of residence time must meet both conversion and olefin selectivity.

Previous studies showed that high temperature and short residence time were beneficial to the formation of low-carbon olefins. Compared with the results of fixed bed reaction under the same conditions, the results of riser amplification experiment are different. At the temperature of 590 °C and residence time of 1 s, the conversion of riser reaction was 45.34%, the selectivity of ethylene, propylene and butene were 9.26%, 22.53%, and 13.55% respectively. While the conversion of fixed bed reaction was 53.49%, the selectivity of ethylene, propylene and butene were 11.32%, 24.91%, and 13.55% respectively. The contact efficiency of circulating fluidized bed was worse than that of fixed bed, which may be the reason why the conversion rate was low under the same conditions, but its selectivity was also low. In the experiment, the temperature of regenerator was maintained at 500 °C. The secondary reactions of olefins intensified when the reactants passed through the settler at 500 °C, such as hydrogen transfer reaction. This results in the decrease of olefin selectivity and the increase of alkane selectivity.

4. Conclusion
This research prepared a kind of bifunctional catalyst for cracking and dehydrogenation. The results of the circulating fluidized bed experiment shows that Ag-P/HZSM-5 catalyst has good regeneration performance. At the temperature of 590 °C and residence time of 1 s, the conversion of riser reaction was 45.34%, the selectivity of ethylene, propylene and butene were 9.26%, 22.53%, and 13.55% respectively. But due to the low control temperature of the precipitator in the reaction process, the olefin selectivity still has a certain gap compared with the results of the fixed bed reaction.

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