Catalytic Pyrolysis of Polyethylene for the Selective Production of Monocyclic Aromatics over the Zinc-Loaded ZSM-5 Catalyst

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ABSTRACT: The transformation of waste plastics into value-added aromatics could incentivize better waste plastic management. The reported studies had low selectivity for monocyclic aromatics because more polycyclic aromatic hydrocarbons and carbon residues were generated. The effects of temperature, pressure, and catalyst on monocyclic aromatic selectivity were explored using a central composite design (CCD) followed by the response surface methodology (RSM) at a high ramp rate of 15 °C/min. The liquid product yield and selectivity to aromatic hydrocarbons were enhanced by regulating the acidic properties of the catalyst and processing parameters. The proportion of monocyclic aromatics in the liquid product was up to 90%, and the yield of monocyclic aromatics based on the reactant mass was 51% at the optimized condition. The carbon deposit production was low (only approximately 1%), which allowed higher liquid yields. In addition, the coupling mechanism of multiple factors on the depolymerization/aromatization reactions was proposed. This conversion of polyethylene into high-yield monocyclic aromatics provides a viable plastic recycling approach.

1. INTRODUCTION

Plastics have been widely used in various aspects associated with human production and life because of their excellent properties such as natural plasticity, chemical stability, and insulation. The annual production of plastics reached an alarming 330 Mt in 2016, and it has also been predicted that the annual production growth rate of plastics is about 4%, implying that waste plastics will be produced in an increasing pace. Because waste plastics are difficult to degrade under natural conditions, their improper disposal will cause a series of environmental problems. Landfill treatment can be used to deal with waste plastics; however, land resources will be wasted, and a severe threat will also be posed to biological organisms. Recently, it has been found that microplastic particles are threateningly distributed in the snow cover of the Antarctic continent, warning the footprints of plastics all over the world. However, data statistics show that only 9% of plastic waste is recycled, while 12% is incinerated and 79% flows into the land and marine ecosystems. Therefore, the appropriate disposal and recycling of waste plastics have become an urgent demand. From 1990 to 2014, the plastic recovery rate increased at a rate of 7%, which will reach 44% in 2050 with the continuing growth rate.

To utilize recycled waste plastics, researchers have done a substantial amount of research. The current recycling methods include incineration, mechanical recycling, and chemical recycling. The recovery based on incineration leads to the generation of toxic gases such as dioxins and nitrogen oxides, which quickly causes secondary pollution. Mechanical recycling is the most commonly used technique for recycling waste plastics since it can directly process waste plastics into plastic products without a significant sacrifice of their...
Table 1. Summary of the Critical Information on the Catalytic Conversion of Plastics to Aromatics

| raw material | test apparatus | test condition | catalyst | product distribution | ref |
|--------------|----------------|----------------|----------|----------------------|-----|
| mixed plastics (PE, PP, PS, PVC, PET, etc.) | fluid bed (filler: fine sand; HCl adsorbent: CaO) | temperature: 685–738 °C | none | gas: 38–44 wt %, liquid: 44–50 wt % (BTX + styrene: 23–37%), distillation residue: 6–7 wt %, ash + filler: 5–6 wt % | 20 |
| PE and PP (2–3.35 mm) | fluid bed | temperature: 650–750 °C | none | | |
| PE (mainly waste plastic bags) (4 × 4 mm) | three kinds of semi-batch reactors: 1) catalyst in gas phase, 2) catalyst in liquid phase, 3) catalyst in gas-liquid phase | temperature: 500, 600, 700, and 800 °C | ZSM-5 (SiO₂/Al₂O₃ = 30:1) | gas: 700 °C—gas: 21 wt %, liquid: 73 wt % (BTX 11%), solid: 6 wt % | 15 |
| PE (mainly waste plastic bags) (4 × 4 mm) | two kinds of semi-batch reactors: 1) catalyst in the liquid phase, 2) catalyst in the gas-liquid phase | temperature: 500, 600, 700, and 800 °C | pristine fly ash and the fly ashes calcinated at 600, 700, 800, and 900 °C | | |
| 59 wt % PE + 22 wt % PP + 19 wt % PVC | tube furnace | raising the temperature to 500 °C at a rate of 20 °C/min and keeping it at 500 °C | 1) Zn/C-I (one-step solution impregnation), 2) Zn/C-II (two-step solution impregnation), 3) Zn/C-III (two-step microemulsion impregnation) | gas: 25 wt %, liquid: 73 wt % (BTEX 22%), solid: 2 wt % | 16 |
| PE | pyrolysis—catalysis two-stage fixed bed | pyrolysis stage: raising the temperature to 550 °C at a rate of 20 °C/min and keeping it at 550 °C for 5 wt % | P/WC = 0.1, 0.2, 0.3, 0.4, and 0.5 | P to wood chips ratio = 0.4, a residence time of 3 s—gas: 56.4 wt %, liquid: 37.5 wt % (aromatics: 30%, monocylic aromatics: 23.8%), coke: 6.1 wt % | 18 |
| HDPE (5 mm in particle size) | pyrolysis—catalysis two-stage fixed bed | pyrolysis stage: raising the temperature to 600 °C at a rate of 10 °C/min and keeping it at 600 °C for 30 min | 1) Y zeolite, 2) 1.0 wt % transition metal-loaded Y zeolite, 3) 5.0 wt % transition metal-loaded Y zeolite | gas: 36 wt %, liquid: 45 wt % (aromatic hydrocarbon: 79%), coke: 10 wt % | 19 |
| | | catalyst stage: 600 °C | | | |
| | | catalyst-to-feedstock ratio: 2.5:1 | | | |
| | | residence time: 1, 2, 3, 4, and wt % | | | |
| | | catalyst-to-feedstock ratio: 1:2 | | | |
properties through the procedures of screening, impurity removal, crushing, and melting regeneration. The phase separation after the co-melting of different kinds of plastics would adversely affect the performance of products. Besides, mechanical recycling presents high restrictions on raw materials for pyrolysis, which may be only suitable for thermoplastics. Compared with mechanical recovery, chemical recovery is more applicable. All thermoplastics, thermosetting plastics, and even mixed plastics can be pyrolyzed.

As a petroleum-based product, the monomer of plastics comes from petroleum hydrocarbons. The massive combustion of fossil fuels causes climate change. Thus, restrictions on the exploitation of chemical fuels should be implemented, but the shortage of carbon sources will then be an essential problem facing society in the future. The generation of fuel oil and chemical raw materials from waste plastics can help to solve both the problems of white pollution and possible carbon source shortage.

The most common plastic materials include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), among which PE production is the highest, accounting for approximately 48%. Therefore, in many studies, PE is selected as the raw material for pyrolysis. At present, the primary researches involving the pyrolysis of waste plastics focus on the preparation of fuel oil, such as gasoline, diesel oil, and jet fuel. However, due to the complex composition of waste plastics, the high process costs to distinguish them, and the complicated reforming and purification procedures that are involved in the preparation of fuel oil by pyrolysis, it is challenging to produce fuel oil that fully meets the gasoline and diesel standards only by adjusting process conditions. A high concentration of aromatics as the target product can be prepared by catalytic cracking of the waste plastics. The monocyclic aromatics and other components in the liquid products are separated, which can continually be used as industrial chemicals for further production.

So far, a few studies have been conducted on the catalytic pyrolysis of plastics, with monocyclic aromatic hydrocarbons as the target product, as summarized in Table 1. Gaurh and Pramanik employed ZSM-5 to catalyze the pyrolysis of PE to prepare aromatic hydrocarbons and explored the influence of three different structures (catalyst contacting with the gas phase, liquid phase, or gas–liquid phase reactant) in the semi-batch reactor on the distribution of pyrolysis products. The results revealed that the highest BTX content (35.06 wt %) was detected in the fuel oil produced by the pyrolysis reaction in the two-phase catalytic reactor at 700 °C, which is about 6 times of that without a catalyst. Based on previous studies, Gaurh and Pramanik further explored the calcined fly ash as a catalyst to catalyze the pyrolysis of PE to prepare aromatic hydrocarbons. The results also showed that the BTEX content in fuel oil was increased in the two-phase catalytic reactor, which was measured to be 22.12 wt % at the pyrolysis temperature of 700 °C with the fly ash calcined at 800 °C as the catalyst. The BTEX content was 22.12 wt % at 700 °C. Finally, the physical and chemical properties of the fuel, such as calorific value and carbon residue, were characterized in detail to evaluate its end-use applications. The two studies of Gaurh and Pramanik demonstrated that the catalyst was not in close contact with gaseous hydrocarbons, which was not conducive to the formation of high content aromatics. In contrast, due to the aggregation state of hydrocarbons in the liquid phase, the short-chain hydrocarbons continued to aromatize on the acid sites of the catalyst, resulting in more aromatic products. On the other hand, some studies show that the content of the resulting aromatics can be controlled by incorporating transition metals to the catalyst, changing the contact form of the catalyst and reactant, and adjusting the temperature and other operating conditions. Sun et al. used three ZnCl₂-activated biochar catalysts that were prepared through different impregnation methods, and results showed that the highest fuel yield (43.7%) was obtained with the help of Zn/C-III catalysts (prepared from the two-step microemulsion impregnation method), in which a relatively high selectivity to two-ring aromatics (87.7%) was observed. Next, H₃PO₄-activated carbon was chosen as the catalyst for pyrolysis of waste polyethylene, and the highest content of monocyclic aromatics was up to 23.8% when the residence time was 3 s and the P/WC ratio was 40%. Moreover, a high P loading quantity on carbon would result in more aromatized species. Akubo et al. adopted a two-stage fixed bed capable of pyrolysis and catalysis to study the catalytic conversion of HDPE to aromatic hydrocarbons. The experimental results indicated that compared with bare Y zeolite, 1.0 wt % metal-loaded Y zeolite led to a reduction of the liquid yield but an increase in the content of aromatic hydrocarbons in the liquid products. With the increase of the metal loading to 5.0 wt %, the Y zeolite exhibited a debased catalytic effect on the production of aromatic hydrocarbons in the liquid products, as evidenced by a decrease in the content of aromatic hydrocarbons relative to that for 1.0 wt % metal-loaded Y zeolite. After metal loading, a little change was found in the gas yield, whereas the proportion of hydrogen (vol %) in the gaseous products and the amount of carbon deposit on the catalyst increased continuously with the increase of metal loading. Kaminsky and Kim employed a fluidized bed to pyrolyze the mixed plastics to prepare BTX and styrene. The influence of temperature and residence time on the product components was explored, and the result was also compared with the industrial process with a longer residence time. The results revealed that the yield of benzene and methane increased significantly with the rise of temperature, while the yield of benzene decreased with the increase of residence time, leading to the formation of branched aromatic hydrocarbons and the decrease of the content of the CI in oil products.

To conclude, the liquid products obtained from the catalytic pyrolysis of PE can be used as the source of monocyclic aromatic hydrocarbons, especially benzene, toluene, xylene, ethylbenzene, and other high-value-added chemical raw materials. However, to the best of our knowledge, the satisfactory selectivity to aromatics has not been achieved, and few studies have been carried out under pressure conditions. Normally, the petrochemical industry turns to pressure conditions since certain pressure conditions are required for hydrocracking and visbreaking to obtain better fuel quality. For PE hydrocracking, increasing hydrogen pressure is helpful to obtain more light components and to reduce the fuel oil viscosity. For visbreaking, the reactants can be maintained in the liquid state under necessary pressure conditions; however, excessive pressure is not conducive to cracking reactions but promotes condensation reactions. Besides, the previous research showed that the pyrolysis product distribution could be changed by pressurizing the pyrolysis process of PE, and the fuel components contained more aromatics and isoalkanes. Therefore, it is of...
considerable significance to explore the impact of high pressure on the reaction process and product distribution.

The zeolite molecular sieve catalyst has a strong hydrogen transferability, which is helpful to the aromatization of intermediate products. Therefore, in this study, ZSM-5 is used as a catalyst to prepare aromatics by catalytic pyrolysis of PE in a high-pressure reactor. By loading zinc on the zeolite molecular sieve catalyst, the acid properties of the catalyst can be regulated. The influences of temperature, pressure, and zinc loading on the yield and aromatics selectivity were investigated. Higher aromatics yield can be achieved over a modified catalyst under low-pressure conditions. Finally, the mechanism of the pressurized catalytic pyrolysis of PE was proposed by comparing the product changes under different reaction conditions.

2. EXPERIMENT

2.1. Raw Materials. The low-density polyethylene (LDPE) used in this study was purchased from Sigma Aldrich Co. Ltd. The M<sub>n</sub> and M<sub>w</sub> of LDPE are 2.048 × 10<sup>3</sup> and 5.412 × 10<sup>3</sup>, respectively, measured by GPC. The ZSM-5 zeolite catalyst adopted in the test was purchased from Alfa Aesar Co. Ltd., with ammonium groups and a silicon-to-aluminum ratio of 23, which was denoted as NH<sub>4</sub>-ZSM-5. The NH<sub>4</sub>-ZSM-5 catalyst was dried in an oven at 120 °C for 12 h before being calcinated in a tubular furnace. The calcination conditions were provided as follows: at the airflow rate of 30 mL/min/g<sub>catalyst</sub>, the catalyst was heated to 120 °C at a rate of 3 °C/min for 2 h and then to 550 °C at a rate of 1 °C/min and finally kept at 550 °C for 4 h. For zinc loading, the H-ZSM-5 catalyst was immersed in a Zn(NO<sub>3</sub>)<sub>2</sub> solution in an equal amount. Then, through the above drying and baking procedures, zeolite catalysts with different zinc loading amounts were obtained, which were termed as Zn(x)-ZSM-5, where x was the mass percentage of zinc.

2.2. Testing Apparatus. The catalytic pyrolysis of PE was carried out in a high-pressure reactor under stirring, and the specific device is shown in Figure 1, which mainly consists of four parts: a 100 mL microreactor (Parr 4590), a PID temperature controller, a high-pressure nitrogen supply device, and a computer used to record temperature and pressure curve. The temperature was measured by a J-type thermocouple, while a pressure sensor measured the pressure value. The temperature and pressure signals were transmitted to the computer to obtain the curves of temperature and pressure vs time. The autoclave was equipped with a magnetic stirrer, with a rotating speed of 200 rpm/min during the test. The amount of the LDPE sample in each test was kept to 6 g, and the mass ratio of LDPE to catalyst was 20:1. After the homogenization, the mixture was put into the bottom of the autoclave. Before the test, the reactor was purged with nitrogen for 20 min to ensure the inert atmosphere during the test. Then, the high-pressure nitrogen was charged into the reactor body until the initial pressure reached 600 °C/min. Afterward, the heater was removed to allow the reactor to be cooled to room temperature by air when the preset final temperature was reached. The gas product was collected with a gas collection bag, and the liquid product, catalyst, and residue were collected in the kettle. Each experiment was repeated three times to observe the experimental error.

2.3. Data Processing and Analysis. 2.3.1. Characterizations of the Prepared Catalyst. Nitrogen isothermal adsorption—desorption measurements were conducted using an ASIQMO002-2 analyzer to illuminate the specific surface area, pore volume, and pore size of the catalyst. The sample was first degassed at 200 °C for 6 h. The specific surface area of the catalyst was calculated by the BET (Brunauer—Emmett—Teller) method, while the pore size distribution was determined using the BJH (Barrett—Joyner—Halenda) model.

Ammonia adsorption—temperature programmed desorption (NH<sub>3</sub>-TPD) was performed with the following procedures: the acidic strength and concentration of the catalyst surface were first measured on a fully automatic temperature-programmed chemical adsorption instrument (AutoChem II 2920). First, 0.1 g of the sample was conditioned in a helium (20 mL/min) atmosphere at 500 °C for 2 h to remove the adsorbed water and impurities. After cooling to 100 °C, a 10% NH<sub>3</sub>/He mixture was injected for 30 min to saturate the adsorption. Pure helium (20 mL/min) was continually purged for 30 min to remove the physically adsorbed ammonia. Finally, the temperature was increased to 600 °C at a rate of 10 °C/min.

For the pyridine IR measurement, a Fourier infrared spectrometer (Nicolet 5700) was employed, and pyridine was adopted as the probe for the determination of the relative content of L-acid and B-acid. The self-supporting plate with the catalyst (20 mg) was put into the IR in situ cell, which was then purified for 2 h at 350 °C under vacuum (2.5 × 10<sup>−2</sup> Pa) to remove the water and impurities from the sample, and the IR spectrum was recorded before adsorption. After the temperature dropped to room temperature, the pyridine vapor was charged. Upon 90 min adsorption equilibrium, the temperature was raised to 150 °C, and the physically adsorbed pyridine was removed from the sample under vacuum for 3 h before the IR spectrum of the sample adsorbed with pyridine was recorded.

2.3.2. Calculation of Product Yield. The test products include gas, liquid, residue, and carbon deposits on the catalyst. The gas products were determined using GC. The internal standard method was used to calculate the molar amount of each gas, including C<sub>1</sub>—C<sub>6</sub> hydrocarbons and hydrogen. The molar amount of nitrogen was derived from the actual gas equation of state. Then, the molar amount of each gas product

![Figure 1. Testing apparatus used for the catalytic pyrolysis of PE. (1) Nitrogen gas cylinder. (2) Pressure reducing valve. (3) Air inlet valve. (4) Autoclave body. (5) Heater. (6) Air outlet valve. (7) Magnetic stirrer. (8) Pressure gauge. (9) Reaction controller. (10) Computer. (11) Gas collection bag.](https://doi.org/10.1021/acsomega.1c05401)
was obtained based on the component ratios detected by GC. The mass of each of the C1–C6 hydrocarbons and hydrogen was calculated by the equation \( m = n \cdot M \), respectively, and the sum was the mass of the total gas product, denoted as \( m_{GP} \). The gas yield was calculated according to eq 1. The mixed solid and liquid products in the reactor were transferred out with the excess dichloromethane, and the solid product was separated by filtration to obtain a mixed liquid. Then, the dichloromethane solution was dried at 40 °C to obtain the final liquid product, which was weighted to determine the mass of the liquid oil. The liquid yield was calculated by eq 2. The mass \( (m_C) \) of carbon deposits on the catalyst was calculated by thermogravimetry, and the production rate of the carbon deposits was calculated according to eq 3. Because it was difficult to collect most of the pyrolysis residues in the upper pipe of the autoclave, the residue yield was obtained by the subtraction method according to eq 4. The production yields of carbon deposits on the catalyst, gas, liquid, and residue were calculated using the following equations:

\[
Y_G = \frac{m_{GP}}{m_{LDPE}} \times 100\% \tag{1}
\]

\[
Y_L = \frac{m_L}{m_{LDPE}} \times 100\% \tag{2}
\]

\[
Y_C = \frac{m_C}{m_{LDPE}} \times 100\% \tag{3}
\]

\[
Y_R = 1 - Y_G - Y_L - Y_C \tag{4}
\]

2.3.3. Product Analysis Method. The gas product distribution was determined by the refinery GC (Agilent 7890N), which was equipped with two thermal conductivity detectors (TCDs) and one hydrogen flame ionization detector (FID). Standard gas (including C1–C6 hydrocarbon gas and hydrogen) was used for calibration, and all gaseous products were analyzed qualitatively and quantitatively.

The product distribution of pyrolysis oil was determined by GC–MS (TRACE 1300ISQ), with the chromatographic conditions described as follows: (1) an HP-5 capillary column \((30 \times 0.25 \text{ mm ID})\) was adopted; (2) a sample volume of 1 \( \mu L \) was considered; (3) helium was used as the carrier gas at a flow rate of 0.8 mL/min; (4) the GC furnace was kept at 40 °C for 5 min and then heated to 290 °C at 7 °C/min followed by maintaining at 290 °C for 10 min; and (5) for the MS method, ionization mode EI was adopted, with an ionization energy of 70 eV and ion source temperature of 230 °C. Compared with the NIST 14 MS library, the products were identified, and BTEX was calibrated by the external standard method.

The number of carbon deposits on the zeolite catalyst was determined by a thermal analyzer (SDT650). For the test, 5 mg of the catalyst sample with carbon deposits was put into the analyzer. Air (oxidant) was used as the carrier gas at a flow rate of 50 mL/min, and the TG curve was recorded for the heating process at the heating rate of 15 °C/min over the range of 25 to 800 °C.

2.3.4. Modeling the Response Surface Methodology (RSM). RSM is a combination of mathematical and statistical methods, and it is also a comprehensive application of experimental design, mathematical statistics, and parameter optimization. The primary purposes of RSM are to (i) express implicit function by approximately constructing a polynomial with a clear expression form, (ii) use multiple quadratic regression equations to fit the functional relationship between factors and response values in the multi-factor experiment, and (iii) solve the multivariable problem.

A comprehensive study of the selected test parameters under the condition of limited test times and time can be realized by RSM, resulting in accurate results and optimal process parameters as obtained via analyzing the response surface graph. In this study, a face central composite design (FCD) was employed, with pyrolysis temperature, pressure, and zinc loading of the catalyst as the main factors. Based on eq 5, 20 test points were designed using the Design Expert 10 software, including 8 cube (factorial) points, 6 axial points, and 6 center points. For the selection of the range of independent variables, first of all, preliminary experiments were conducted to probe the emergence of the liquid products that appeared when the pyrolysis test was performed at 340 °C. Second, unlike the pressure conditions of the petrochemical industry, the actual requirements could be met with a lower pressure value in our case due to the macromolecular characteristics of PE. When the catalyst without calcination was used for pyrolysis, the production yield of carbon deposits was calculated to be about 7–10 wt %.

### Table 2. Experimental Factors and Levels

| variables | experimental levels |
|-----------|---------------------|
| a: temperature (°C) | 340 380 420 |
| b: pressure (bar) | 1 4 7 |
| c: zinc loading contents (wt %) | 1 2 3 |

established with liquid and monocyclic aromatics yields as response values. The second-order polynomial can be expressed as eq 6.

\[
N = 2^a + 2n + n_i = 2^2 + 2 \times 3 + 6 = 20 \tag{5}
\]

where \( N \) represents the number of tests, \( n \) is the number of factors, and \( n_i \) is the number of repeated tests at the center point.

\[
Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_i X_i^2 + \sum_{i=1}^{n} \sum_{j>i}^{n} \beta_{ij} X_i X_j \tag{6}
\]

where \( Y \) represents the test response value; \( n \) is the number of tests; \( \beta_0, \beta_i, \beta_{ij} \) and \( \beta_{ij} \) denote the coefficients of constant, primary, secondary, and interaction terms in the fitting formula, respectively; and \( X_i \) and \( X_j \) are the coding values of independent variables.

3. RESULTS AND DISCUSSION

3.1. Characterizations of the Prepared Catalyst. 3.1.1. \( N_2 \) Adsorption–Desorption Measurements. The specific surface area, pore volume, and pore diameter of the catalyst are provided in Table 3. It can be noted that the pristine catalyst NH₄-ZSM-5 possesses the largest specific surface area (590 m²/g). After calcination, the specific surface area of the resulting H-ZSM-5 catalyst decreases slightly. After loading the zinc element and recalcination, the specific surface area was reduced to 360 m²/g. These results indicate that the addition of NaOH, followed by calcination and loading of zinc, affects the structure and properties of the H-ZSM-5 catalyst.

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area is debased to a more significant degree, especially for the Zn(3)-ZSM-5 catalyst with the lowest (351 m²/g). In general, the pore volume of the zinc-loaded catalyst is lower than that of NH₄-ZSM-5. The pore size of Zn(1)-ZSM-5 is basically the same as that of NH₄-ZSM-5. The pore sizes of Zn(2)-ZSM-5 and Zn(3)-ZSM-5 are more extensive than that of NH₄-ZSM-5, with the largest average pore size of 3.88 nm found for Zn(3)-ZSM-5. After the introduction of zinc and two calcination procedures, some of the microporous pores collapsed, which dramatically reduced the specific surface area of the catalyst. Then, some pores with a larger pore size were formed, resulting in an increase in pore volume and pore size. All of these demonstrated that the catalysts loaded with the zinc element are enriched with mesopores.

3.1.2. Characterization of NH₃-TPD. Table 4 shows the acid strength and acid quantity of different ZSM-5 catalysts measured by NH₃-TPD. For NH₄-ZSM-5, two desorption peaks appear near 209 and 441 °C corresponding to weak acid and strong acid centers, respectively. The temperature of the second desorption peak is decreased by 100 °C for the H-ZSM-5 sample as compared with that for the NH₄-ZSM-5 sample, while the temperature of the second desorption peak was maintained at about 320 °C for all the three zinc-supported catalysts, along with the significantly decreased acid strength. After calcination, the number of strong acid centers becomes approximately 1/4 of the NH₄-ZSM-5 catalyst, revealing that the strength of the acid and the number of strong acid centers are decreased significantly after calcination. In addition, it can be noted from Table 4 that, after calcination, the strength and quantity of weak acid center are also decreased to a certain extent. However, the decreasing range is found to be lower than that of the strong acid center, with the quantity of weak acid center being about 3/5 of the pristine catalyst.

3.1.3. Pyridine-IR Characterization. Figure 2 shows the IR spectrum of different catalyst samples adsorbed with pyridine. Characteristic peaks indexed to pyridine adsorption can be found at 1450, 1490, and 1540 cm⁻¹ for all the catalysts. The characteristic peaks at 1450 and 1540 cm⁻¹ can be indexed to the pyridine adsorption on L-acid and B-acid sites of the ZSM-5 catalyst, respectively, while the sum of the characteristic peaks, assigned to L-acid and B-acid sites, can be observed at 1490 cm⁻¹. For the cracking reaction of alkanes, both B-acid and L-acid are needed. Table 5 presents the calculated quantity of B-acid and L-acid for each catalyst. After calcination of the NH₄-ZSM-5 catalyst once, the B-acid and L-acid contents of H-ZSM-5 are decreased and increased, respectively, along with a decrease of the B/L value from 1.0 to 0.6. However, after zinc loading, the B-acid content of the catalyst is promoted significantly, and the higher the zinc loading is, the higher is the B-acid content. The loading zinc firstly increases the amount of zinc ions (L-acid sites) on the catalyst surface, and then L-acid sites are converted to the more active B-acid sites due to the action of water. Therefore, the introduction of zinc ultimately increases the acidity of the catalyst. Accordingly, with the increase of zinc loading, the B/L value of the catalyst rises from 1.6 to 3.8. The L-acid contents of the Zn(1)-ZSM-5 and Zn(2)-ZSM-5 catalysts are basically the same as that of H-ZSM-5, while the L-acid content of the Zn(3)-ZSM-5 catalyst decreases by about 1/3.

3.2. Response Surface Methodology (RSM). 3.2.1. Significance Analysis of FCD Design Scheme and Model. For RSM analysis, the monocyclic aromatic ratio (monocyclic aromatic hydrocarbon ratio in the liquid product) and monocyclic aromatic yield (proportion of monocyclic aromatic yield to the starting PE) are selected as response values. The FCD design scheme and test results are presented in Table 6. Multiple regression fitting on the test data shown in Table 6 was performed using the Design Expert 12 software, resulting

Table 3. Textural Properties of Different Catalysts

| catalyst     | specific surface area (m²/g) | pore volume (cm³/g) | pore diameter (nm) |
|--------------|-----------------------------|-------------------|-------------------|
| NH₄-ZSM-5    | 590                         | 0.38              | 2.59              |
| H-ZSM-5      | 530                         | 0.39              | 2.75              |
| Zn(1)-ZSM-5  | 377                         | 0.24              | 2.57              |
| Zn(2)-ZSM-5  | 381                         | 0.26              | 2.95              |
| Zn(3)-ZSM-5  | 351                         | 0.34              | 3.88              |

Table 4. NH₃-TPD Results of Different Catalysts

| catalyst     | peak number | temperature at maximum (°C) | quantity (cm³/g STP) |
|--------------|-------------|-----------------------------|----------------------|
| NH₄-ZSM-5    | 1           | 209                         | 25.9                 |
|              | 2           | 441                         | 22.4                 |
| H-ZSM-5      | 1           | 178                         | 16.3                 |
|              | 2           | 344                         | 5.0                  |
| Zn(1)-ZSM-5  | 1           | 184                         | 14.5                 |
|              | 2           | 320                         | 5.7                  |
| Zn(2)-ZSM-5  | 1           | 183                         | 15.2                 |
|              | 2           | 320                         | 5.9                  |
| Zn(3)-ZSM-5  | 1           | 181                         | 15.2                 |
|              | 2           | 322                         | 6.1                  |

Table 5. Amount and Distribution of B- and L-Acid Sites Determined by Pyridine Absorption

| catalyst     | amount of acid sites (μmol/g) | B | L | B + L | B/L |
|--------------|------------------------------|---|---|-------|-----|
| NH₄-ZSM-5    | 80.1                         | 77.6|157.6|1.0    |
| H-ZSM-5      | 55.6                         | 96.2|151.7|0.6    |
| Zn(1)-ZSM-5  | 159.6                        | 98.5|258.1|1.6    |
| Zn(2)-ZSM-5  | 248.0                        | 98.9|346.9|2.5    |
| Zn(3)-ZSM-5  | 265.9                        | 70.2|336.1|3.8    |
Table 6. FCD Experimental Design Matrix and Response

| runs | factor A: temperature (°C) | factor B: pressure (bar) | factor C: zinc loading content (wt %) | response (%) |
|------|---------------------------|--------------------------|---------------------------------------|-------------|
| 1    | 380 0                     | 4 0                      | 2 0                                   | R_{MA} 80.6 Y_{MA} 51.0 |
| 2    | 380 0                     | 4 0                      | 2 0                                   | 78.0 53.5   |
| 3    | 380 0                     | 4 0                      | 2 0                                   | 84.7 49.3   |
| 4    | 380 0                     | 4 0                      | 2 0                                   | 79.2 51.6   |
| 5    | 340 −1                    | 7 1                      | 3 1                                   | 61.8 25.5   |
| 6    | 380 0                     | 4 0                      | 2 0                                   | 84.1 49.5   |
| 7    | 380 0                     | 4 0                      | 2 0                                   | 81.5 49.0   |
| 8    | 340 −1                    | 1 1−1                    | 1 −1                                  | 45.6 13.9   |
| 9    | 420 1                     | 1 1−1                    | 1 −1                                  | 82.8 40.0   |
| 10   | 340 −1                    | 1 4 0 2 0               | 56.5 21.9                             |
| 11   | 380 0                     | 4 0 1 −1                | 75.0 46.0                             |
| 12   | 420 1                     | 1 1−1                    | 3 1                                   | 84.5 39.2   |
| 13   | 380 0                     | 7 1 2 0                 | 77.1 48.4                             |
| 14   | 340 −1                    | 7 1 1 −1                | 72.1 28.6                             |
| 15   | 380 0                     | 1 1−1                    | 81.4 47.6                             |
| 16   | 420 1                     | 7 1 3 1                 | 77.0 37.7                             |
| 17   | 420 1                     | 4 0 2 0                 | 84.8 42.0                             |
| 18   | 420 1                     | 7 1 1 −1                | 81.7 40.4                             |
| 19   | 340 −1                    | 1 1−1                    | 69.3 22.4                             |
| 20   | 380 0                     | 4 0 3 1                 | 80.5 51.7                             |

in the quadratic polynomial regression equation between each factor and response value, as described by eqs 7 and 8.

\[
R_{MA} = 80.34 + 10.55A + 0.61B + 1.60C - 3.44AB - 2.05AC - 5.06BC - 8.21A^2 - 0.43B^2 - 1.08C^2 \tag{7}
\]

\[
Y_{MA} = 50.13 + 8.70A + 1.76B + 0.78C - 2.36AB - 1.10AC - 1.68BC - 17.45A^2 - 1.37B^2 - 0.55C^2 \tag{8}
\]

The results obtained via the analysis of variance of model $R_{MA}$ and $Y_{MA}$ are provided in Tables 7 and 8. The $F$ value of the model $R_{MA}$ is 9.99 (Table 7), indicating that the model exhibits significance. Besides, the $p$ value is less than 0.05, revealing the significance of the model item. The lack-of-fit $F$ value is 4.85, which indicates that it is not significant in contrast to the pure error, and it is necessary to have a nonsignificant term. The $F$ value (55.98) and lack-of-fit $F$ value (2.46) of the model $Y_{MA}$ are similar to those of the model $R_{MA}$. A $p$ value of less than 0.05 indicates the significance of the model item. In contrast, a $p$ value of greater than 0.1 implies that the model item is not significant. For the model $R_{MA}$, the significant model terms are A, BC, and $A^2$, and their $F$ values are 54.19, 9.96, and 9.02, respectively. Therefore, the item that exerts an influence on the monocyclic aromatic ratio is given in the order of impacting extent as follows: A > BC > $A^2$. For the model $Y_{MA}$, the significant model items are also A, B, AB, and $A^2$, among which $A^2$ is the essential item, with an $F$ value of 161.63. In addition, the $R^2$ values of model $R_{MA}$ and $Y_{MA}$ are 0.8999 and 0.9805, together with adjusted $R^2$ values of 0.8099 and 0.9630 (both greater than 0.8), respectively. Variations of only 19.01 and 3.7% can be noted for the model $R_{MA}$ and $Y_{MA}$. Therefore, the model has high reliability and can be used to analyze and predict the experimental results.

3.2.2. Influence of Three Factors on the Product Yield.

Before the analysis of the change of the product yield, the product distribution of pressure-assisted catalytic pyrolysis of PE was elucidated. In this paper, the experiment is denoted as "the initial temperature—the initial pressure—the zinc loading of catalyst". Figure 3 shows the average yield of two repeated experiments. Pyrolysis products include gas, liquid, residue, and carbon deposits on the catalyst. Among them, residue refers to PE wax that is not cracked into oil and gas, which exhibits a white color and viscous state. Based on the NH$_3$-TPD characterization, the prepared catalysts with the lower acid strength were adopted in the present study; the deep deposition product from methanol is low (only approximately 1%), which is lower than that of other studies listed in the first part.\textsuperscript{15,17,19} Guisnet et al.\textsuperscript{25} reported that using Pt/H-ZSM-5 and Ga/H-ZSM-5 to catalyze the pyrolysis of short-chain alkanes produced more coke in comparison with H-ZSM-5, which further led to the deactivation of the catalysts. In our case, the acid strength of the catalysts with Pt and Ga; therefore, it is desirable to reduce the carbon deposit on the catalyst. The fewer amounts of carbon deposits in our case can be due to the fact that the acid strength of the active site was reduced on the pristine catalyst after being calcinated twice, resulting in losing many useful catalytic active sites of the condensation of aromatics. As a consequence, the

Table 7. ANOVA for the Monocyclic Aromatic Ratio Response Model

| source      | sum of squares | df  | mean square | $F$ value | $p$ value | remark          |
|-------------|----------------|-----|-------------|-----------|-----------|-----------------|
| model       | 1846.86        | 9   | 205.21      | 9.99      | 0.0006    | significant     |
| A           | 1112.60        | 1   | 1112.60     | 54.19     | <0.0001   |                 |
| B           | 3.77           | 1   | 3.77        | 0.1836    | 0.6774    |                 |
| C           | 25.50          | 1   | 25.50       | 1.24      | 0.2911    |                 |
| AB          | 94.46          | 1   | 94.46       | 4.60      | 0.0576    |                 |
| AC          | 33.50          | 1   | 33.50       | 1.63      | 0.2304    |                 |
| BC          | 204.53         | 1   | 204.53      | 9.96      | 0.0102    |                 |
| $A^2$       | 185.18         | 1   | 185.18      | 9.02      | 0.0133    |                 |
| $B^2$       | 0.5182         | 1   | 0.5182      | 0.0252    | 0.8769    |                 |
| $C^2$       | 3.21           | 1   | 3.21        | 0.1565    | 0.7007    |                 |
| residual    | 205.33         | 10  | 20.53       |           |           |                 |
| lack of fit | 170.21         | 5   | 34.04       | 4.85      | 0.0541    | not significant |
| pure error  | 35.12          | 5   | 7.02        |           |           |                 |
| cor total   | 2052.19        | 19  |             |           |           |                 |
Temperature has a significant influence on the product yield of PE. As the temperature increases, the liquid yield decreases, while the gas yield increases. The solid yield decreases with increasing reaction temperature. Specifically, the PE is first broken into liquid hydrocarbon molecules. With the further increase of temperature, the liquid product continues to be degraded into volatile gas products. Therefore, a temperature point exists at which the maximum liquid yield can be obtained. In the set initial pressure range (1–7 bar), the liquid and solid yields are promoted and decreased slightly with the rise of pressure, respectively. This is because the rising pressure changes the boiling point of hydrocarbon intermediates and results in more intermediate molecules deposited at the bottom of the reactor in the early stage of the reaction, thus increasing the contact time between the reactant and the catalyst at actually higher temperatures. Meanwhile, the acid sites on the catalyst promote the C–C bond breaking reaction and other secondary reactions.

3.2.3. Influence of Three Factors on the Ratio of Monocyclic Aromatics in Liquid Products and the Yield of Monocyclic Aromatics. In this paper, a three-dimensional (3D) response surface is used to show the influence of each variable on the response value. Although the 3D response surface cannot show the influence of all variables on the test results, it can fully show the impact of the change of the remaining two variables on the response value by keeping one variable unchanged. Figure 4 presents the response surface diagram of the influence of temperature, initial pressure, and zinc load of the catalyst on the content of monocyclic aromatic hydrocarbons in liquid products, and the variation trend of the influence of each variable on the response value can be directly analyzed. Pyrolysis temperature is the most significant factor affecting the proportion of monocyclic aromatics. With the increase of temperature, the fracture of reactants is intensified, and the intense molecular collision in the reactor occurs. Meanwhile, the cyclization of chain hydrocarbons and the generation of diene from small olefin gas are improved, accompanied by the intensified dehydrogenation of cycloolefins with the increase of temperature. As a result, the generated monocyclic aromatics further undergo condensation reaction, leading to carbon deposits.

Temperature has a significant effect on liquid yield, while pressure and zinc loading exert an insignificant influence on liquid yield, which is consistent with the results of variance analysis. At the same 2 wt % zinc loading and 4 bar initial pressure, with the rise of pyrolysis temperature from 340 to 420 °C, the wax yield gradually decreases from 42.7 to 4.1 wt %; however, the liquid yield firstly increases from 38.7 to 58.2 wt % and then decreased to 49.5 wt %. This is due to the endothermic reaction for breaking the PE chain. Hence, the rise of temperature promotes the fracture of the C–C bond. The solid yield decreases with increasing reaction temperature. Specifically, the PE is first broken into liquid hydrocarbon molecules. With the further increase of temperature, the liquid product continues to be degraded into volatile gas products. Therefore, a temperature point exists at which the maximum liquid yield can be obtained. In the set initial pressure range (1–7 bar), the liquid and solid yields are promoted and decreased slightly with the rise of pressure, respectively. This is because the rising pressure changes the boiling point of hydrocarbon intermediates and results in more intermediate molecules deposited at the bottom of the reactor in the early stage of the reaction, thus increasing the contact time between the reactant and the catalyst at actually higher temperatures. Meanwhile, the acid sites on the catalyst promote the C–C bond breaking reaction and other secondary reactions.

Table 8. ANOVA for the Monocyclic Aromatic Yield Response Model

| Source     | Sum of Squares | df | Mean Square | F Value | p Value | Remark       |
|------------|----------------|----|-------------|---------|---------|--------------|
| Model      | 2609.92        | 9  | 289.99      | 55.98   | <0.0001 | significant  |
| A          | 756.91         | 1  | 756.91      | 146.10  | <0.0001 |              |
| B          | 30.86          | 1  | 30.86       | 5.96    | 0.0348  |              |
| C          | 6.03           | 1  | 6.03        | 1.16    | 0.3061  |              |
| AB         | 44.59          | 1  | 44.59       | 8.61    | 0.0149  |              |
| AC         | 9.72           | 1  | 9.72        | 1.88    | 0.2007  |              |
| BC         | 22.58          | 1  | 22.58       | 4.36    | 0.0634  |              |
| A²         | 837.36         | 1  | 837.36      | 161.63  | <0.0001 |              |
| B²         | 5.19           | 1  | 5.19        | 1.00    | 0.3403  |              |
| C²         | 0.8266         | 1  | 0.8266      | 0.1596  | 0.6980  |              |
| Residual   | 51.81          | 10 | 5.18        |         |         |              |
| Pure Error | 36.83          | 5  | 7.37        | 2.46    | 0.1729  | not significant |
| Cor Total  | 2661.72        | 19 |             |         |         |              |

Figure 3. Yield distribution of the products obtained via the catalytic pyrolysis of PE.
as high as 90.0% over the ZSM-5 catalyst with 3 wt % zinc at 420 °C and initial pressure of 1 bar, in which the aromatics accounted for 84.5%. The highest proportion of monocyclic aromatics in the liquid product was 85.0% over the ZSM-5 catalyst with 2 wt % zinc at 420 °C and initial pressure of 4 bar. The increase in temperature can improve the concentration of aromatics in the liquid, and the following two factors can be used to explain this finding: First, the temperature can promote the aforementioned aromatization reactions and increase the aromatics production. Second, with the increase of temperature, some of the intermediate products other than aromatics continue to be cracked into gases, allowing the concentration of other hydrocarbons in the liquid products to be reduced. It is worth mentioning that although the increase in temperature enhanced the production of monocyclic aromatic hydrocarbons, the excessively high temperature reduced the liquid yield. It can be seen from Figure 4 that the proportion of monocyclic aromatic hydrocarbons increased as the zinc loading increased. The pressurized condition had a relatively small effect on the proportion of monocyclic aromatics.

Figure 4. (a) Response surface of three factors that affect the content of monocyclic aromatic hydrocarbons in fuel: interactions between temperature and pressure (a), between temperature and zinc load (b), and between pressure and zinc load (c).

Figure 5 shows the response surface diagram of the impact of temperature, initial pressure, and zinc loading of the catalyst on the yield of monocyclic aromatics. The temperature has a noticeable impact on the yield of monocyclic aromatic hydrocarbons, partly due to its influence on the liquid yield and the degree of aromatization. As the temperature increases, the yield of monocyclic aromatics first increases and then decreases because the increase in temperature promotes the aromatization reactions and the conversion of waxes to liquid products. However, as the temperature continues to increase, more gases are generated and the liquid yield decreases, resulting in a decrease in the total amount of aromatic hydrocarbons. The increase of zinc loading imparts the ratio of B/L acid to be increased, which promotes the aromatization of chain hydrocarbons and thus generates more monocyclic aromatic hydrocarbons. Akubo et al.19 employed a pyrolysis–catalysis two-stage fixed bed to study the catalytic conversion of HDPE to aromatic hydrocarbons. Their experimental results showed that, compared with the Y zeolite without metal loading, the content of monocyclic aromatic hydrocarbons in
liquid products increased when 1 wt % metal was incorporated, along with an increase in the proportion of hydrogen in gas products, consistent with the results of our experiment. The increasing pressure promotes an increase in the liquid yield, as the contact time of the liquid with the catalyst at a higher temperature is increased, and the conversion of wax to liquid is promoted. Although the proportion of aromatics is slightly reduced, the yield of aromatics based on the mass of polyethylene is generally improved. The macromolecular characteristics of PE endow it with a high boiling point, indicating that, unlike the catalytic reforming of petroleum, only a low pressure that is required for the catalytic cracking of PE exerts a significant impact on the product distribution.

3.2.4. Product Contribution at Optimized Conditions. To maximize the yield of monocyclic aromatics, the temperature, pressure, and zinc loading of the catalyst were maintained in the range of the aforementioned conditions, while the response of monocyclic aromatic yield was maximized. The solution result indicates that the set temperature of 388.5 °C, the ZSM-5 catalyst with 1 wt % zinc, and the initial pressure of 6.9 bar were sufficient to produce the optimum monocyclic aromatic yield of 51.7%. Three repeated experiments under the above conditions were conducted, and the product contribution is shown in Table 9. The obtained average yield of monocyclic aromatics recorded (51.0%) is consistent with the predicted

Table 9. The Experimental and Predicted Values at Optimized Condition

| run | temperature (°C) | pressure (bar) | zinc loading content (wt %) | the yield of monocyclic aromatics (%) |
|-----|-----------------|----------------|-----------------------------|-------------------------------------|
| 1   | 388.5           | 6.9            | 1                           | 49.3                  | $1.7$ |
| 2   | 388.5           | 6.9            | 1                           | 53.1                  | $1.7$ |
| 3   | 388.5           | 6.9            | 1                           | 50.6                  | $1.7$ |
| average |                 |                |                             | 51.0                  | $1.7$ |
value. Therefore, this result confirms the adequacy of the quadric model for the yield of monocyclic aromatics.

3.3. Distribution of Products from the Catalytic Pyrolysis. 3.3.1. Liquid Product Distribution. Table 10 shows the composition of liquid products in the body-center and face-center tests. The primary liquid products obtained from these tests are composed of aromatics (57.1–89.0%), among which monocyclic aromatics account for 56.5–84.8%. Thus, liquid products can be changed obviously under different test conditions. The monocyclic aromatic hydrocarbons mainly consist of toluene and xylene with high added value, with a relatively low content of benzene and ethylbenzene. In addition, liquid products contain a small number of n-alkanes, isoalkanes, alkenes, cycloalkanes, and cycloalkenes. The comparison between the body-center test and the corresponding face-center test shows that temperature is the main factor affecting the content of aromatics in liquid products. With the increase of temperature, the contents of monocyclic and polycyclic aromatic hydrocarbons increase at the same time, and the contents of other alkanes and alkenes decrease monotonously. This is because the increase in temperature promotes the cyclization of chain hydrocarbons, diene synthesis, and the dehydrogenation of cyclohydrocarbons, respectively. Furthermore, the content of benzene, toluene, and xylene increases with the rise of temperature. The content of ethylbenzene and other benzenes with mono branched-chain increases first and then declines, indicating that the higher temperature inhibits the formation of longer branched aromatic hydrocarbons. With the increase of pressure, the concentration of aromatics in the liquid shows a decreasing trend, and reversely, an increasing trend can be found for the concentration of other hydrocarbons. This is because more reactants stay at the bottom of the reactor due to pressure, which cannot be efficiently catalytically converted due to the limited number of catalysts. Moreover, the finite contact time between reactants and catalyst causes an incomplete aromatization process. It is worth mentioning that higher pressure reduces the aromatic content in the liquid but increases the aromatic yield based on the raw material. Under the conditions of 380 °C and 4 bar, both monocyclic and polycyclic aromatic hydrocarbons show an upward trend with the increase of zinc loading from 1 to 3 wt %, which indicates that the active sites produced by zinc-loaded catalysts are helpful for the aromatization of alkanes.

3.3.2. Gas Product Distribution. Table 11 shows the composition of the gas products in the body-center and face-center tests. The gas product is mainly composed of hydrogen and C1–C4 small molecule alkane gas. A small amount of hydrogen is produced by the fracture of the C–H bond during the pyrolysis of PE. In contrast, a more significant proportion of hydrogen is generated by the dehydrogenation of cyclohydrocarbon. Besides, a small amount of hydrogen can also be formed during the condensation of aromatics. Considering that both monocyclic aromatics and hydrogen are the target products with high added value, it is favorable for the formation of monocyclic aromatics in the reaction process. In addition, compared with alkane gas, the proportion of olefin gas in this experiment is relatively low, which is due to the fact that the instability of small olefin causes the generation of aromatic hydrocarbon mainly from the diene synthesis reaction.

| Table 10. The Distribution of Liquid Products from Body and Face Center Experiments |
|---------------------------------|---|---|---|---|---|---|---|
|runs  | 11  | 1  | 17  | 16  | 5  | 12  | 7  |
| reaction conditions  | 340-4-2  | 380-4-2  | 420-4-2  | 380-7-2  | 380-1-2  | 380-4-1  | 380-4-3  |
| aromatics  | 57.1  | 82.8  | 89.0  | 83.7  | 78.9  | 77.2  | 83.1  |
| benzene  | 4.3  | 5.9  | 5.6  | 4.4  | 4.2  | 4.8  |
| toluene  | 11.7  | 21.0  | 25.2  | 24.9  | 19.8  | 17.4  | 21.6  |
| ethylbenzene  | 3.6  | 4.5  | 4.1  | 4.3  | 4.3  | 4.2  | 4.4  |
| xylene  | 19.5  | 25.8  | 26.4  | 25.7  | 24.5  | 23.3  | 25.6  |
| other MAHs  | 21.7  | 25.1  | 23.3  | 20.9  | 24.1  | 26.0  | 24.1  |
| PAHs  | 0.6  | 2.2  | 4.2  | 2.3  | 1.8  | 2.2  | 2.6  |
| other hydrocarbons  | 42.9  | 16.5  | 10.1  | 16.0  | 20.8  | 22.2  | 16.1  |
| n-paraffins  | 13.9  | 6.3  | 4.5  | 6.8  | 7.9  | 7.8  | 6.2  |
| iso-paraffins  | 13.1  | 5.6  | 2.8  | 5.0  | 7.0  | 8.0  | 5.5  |
| olefins  | 4.10  | 1.0  | 0.9  | 1.5  | 1.2  | 0.9  |
| cycloparaffins  | 9.1  | 3.5  | 2.8  | 3.4  | 4.3  | 5.2  | 3.6  |
| cycloolefins  | 2.7  |  |  |  |  |  |  |

| Table 11. Distribution of Gas Products from Body and Face Center Experiments |
|---------------------------------|---|---|---|---|---|---|---|
|runs  | 11  | 1  | 17  | 16  | 5  | 12  | 7  |
| reaction conditions  | 340-4-2  | 380-4-2  | 420-4-2  | 380-7-2  | 380-1-2  | 380-4-1  | 380-4-3  |
| hydrogen  | 19.3  | 18.2  | 24.2  | 26.2  | 19.1  | 12.9  | 19.2  |
| methane  | 4.1  | 5.5  | 10.1  | 6.9  | 6.0  | 4.1  | 6.1  |
| ethane  | 3.4  | 5.1  | 8.1  | 5.0  | 5.4  | 4.6  | 5.7  |
| ethylene  | 3.5  | 2.0  | 1.7  | 4.1  | 1.9  | 2.7  | 2.1  |
| propane  | 33.7  | 42.7  | 38.1  | 31.3  | 39.5  | 45.8  | 42.1  |
| propylene  | 7.9  | 3.9  | 2.9  | 7.7  | 4.0  | 5.3  | 4.2  |
| butane  | 7.2  | 7.1  | 4.4  | 5.2  | 7.6  | 7.4  | 6.2  |
| isobutane  | 12.8  | 11.3  | 7.9  | 8.1  | 11.4  | 12.0  | 10.2  |
| C5 olefins  | 4.4  | 1.7  | 1.3  | 3.3  | 2.3  | 2.7  | 1.9  |
| C5+, hydrocarbons  | 3.7  | 2.5  | 1.3  | 2.5  | 3.0  | 2.7  | 2.1  |
and from the oligomerization reaction involving a small amount of propane gas. From Table 11, it can be noted that the propane content in the pyrolysis product is much higher than that of methane and ethane owing to the fact that the carbocations undergo a shorter carbon chain after a fracture until the formed C3 and C4 positive carbon ions cannot continue to generate C1 and C2 carbocations. With the increase of temperature, the further fracture of carbon chain occurs, leading to the increased small molecule gas and the decreased larger molecule gas. On the other hand, the increase of pressure results in the debasing of the content of hydrogen and small molecule gas. This is because more reactants deposited on the bottom of the reactor exceed the capacity of the limited number of catalysts. Only confined chain breaking and aromatization reactions occur to generate a certain amount of small molecule gas and hydrogen. Under 380 °C and 4 bar conditions, the increase of zinc loading leads to the promoted hydrogen content, which is also due to the active acid sites as generated by the introduction of zinc to promote the aromatic condensation and generate more hydrogen. Furthermore, the contents of methane and ethane are increased with the rise of zinc loading, while the contents of propane and butane are diminished with the increase of zinc loading. These results indicate that the new active sites generated due to the zinc incorporation are helpful to the end fracture of the C–C bond.

3.4. Analysis of the Mechanism Underlying the Pressure-Assisted Catalytic Pyrolysis of PE to Produce Aromatics over Zinc-Supported ZSM-5. 3.4.1. Reaction Paths. Figure 6 shows the reaction procedures of the conversion of PE to aromatic hydrocarbon. The acid sites on the catalyst surface drive PE to first generate carbocations, some of which generate cycloalkanes through a cyclization reaction, which further gradually dehydrogenate to aromatics over a catalyst. Small olefins undergo diene synthesis to form cycloalkenes, which continue to be converted into aromatics through dehydrogenation. It is worth noting that the macromolecular characteristics of PE facilitate the first catalytic cracking reaction on the catalyst surface, resulting in the formation of small enough molecules that can enter the catalyst channel for continuing chain breaking, cyclization, aromatization, and other reactions. Because the pore size of ZSM-5 is small, p-xylene is easy to diffuse out of the zeolite pores, while m-xylene and o-xylene are difficult to diffuse out. Due to the shape selectivity of the catalyst, the content of p-xylene was higher than that of m-xylene and o-xylene. In addition, PE is pyrolyzed as driven by a free radical mechanism along with the catalytic cracking. The pyrolyzation reaction products are also catalyzed over the active surface sites or inside the pores of the catalyst. Since some of the generated monocyclic aromatics did not get out of the catalyst in time, they continue to condense through the strong acid site of the catalyst to generate polycyclic aromatics. Due to its high boiling point, the large molecular weight polycyclic aromatics are located at the bottom of the reactor and thus are in close contact with the catalyst, leading to the gradual formation of carbon deposits through the aromatic condensation.

3.4.2. The Influence of Processing Conditions. Compared with the gas-phase catalytic pyrolysis with the same residence time, the reaction rate and product conversion rate of the PE reactant can be more significant in the liquid phase under the pressurized conditions. There are two main reasons for explaining this result. First, the higher concentration of reactants on the surface and in the pore of the catalyst can increase the probability of forceful collision between reactants and active sites of the catalyst. Second, carbocations are generated from the liquid hydrocarbons at the active sites. Because the molecules are in the aggregation state, the generated carbocations continue to react with another molecule, generating new carbocations and hence continuing to participate in the reaction. In contrast, it is difficult for the dispersed gaseous molecules to carry out this transfer reaction. Therefore, the catalytic pyrolysis of PE in the gas phase requires more catalyst and a longer residence time to achieve the same conversion rate. Two studies of Gaurhi and Pramanik also showed that the catalytic efficiency for the PE conversion in the liquid phase region is higher than that in the gas phase region. In addition, the change of the boiling point of the product under pressure can ensure that the large molecule stays at the bottom of the reactor to continue the catalytic pyrolysis reaction. In contrast, the generated small molecule product volatilizes to the upper part of the reactor, reducing the contact opportunity with the catalyst. Consequently, the formation of carbon deposits, as a result of the aromatic condensation reaction, can be avoided, thereby improving the required product selectivity. Due to the high boiling point of macromolecular PE, it can meet the reaction requirements only with a little pressure, which thus holds great potential for practical applications.

When the unbaked ZSM-5 is used to catalyze the pyrolysis of PE, higher gas and carbon production yields are obtained. This is because more strong acid sites exist on the catalyst surface, which plays two critical roles: (i) promotion of the excessive cracking of PE and thus generation of more gas products and (ii) condensation of the generated aromatics and then polycyclic aromatic hydrocarbons to form carbon deposits. Most of the strong acid sites on ZSM-5 are removed after calcination, and the weak acid sites can meet the requirements of PE chain breaking and aromatization reactions. Therefore, the excessive acid strength speeds up the coke formation and hence deactivates the catalyst, and only a certain acid strength is desirable for such a reaction. The calcination and the incorporation of zinc can not only control the acid strength of the catalyst but also effectively adjust the ratio of B-acid center to L-acid center of the catalyst to meet the acid demand of the catalyst.

Because PE possesses a long-chain macromolecular structure, it is difficult to diffuse into the catalyst channel at
the beginning of the reaction. In the process of catalytic pyrolysis, the acid sites on the surface of zeolite catalyst first contact with each other, and the C−C bond breaking reaction takes place. At this stage, the acid sites in the molecular sieves channel do not work. Some of the short-chain hydrocarbons formed by surface catalysis continue to break and aromatize on the surface of the catalyst. They can also diffuse into the pores to undergo the above reactions. Therefore, although the total amount of intermediate products with acid sites, thereby enhancing the catalytic effect to a certain extent. In the research of Coelho et al., it was also stated that the hierarchical porous zeolites were more suitable for the catalytic cracking of PE reactants bearing macromolecular properties.28

Temperature is an important factor affecting the reaction rate and product selectivity of the catalytic pyrolysis of PE. The rise of temperature aggravates the fracture of the C−C bond of PE, resulting in a small molecular product. Nevertheless, the excessive temperature causes the excessive cracking of PE into gas products.29 Thus, appropriate temperature conditions are necessary for the desired catalytic pyrolysis of PE. In addition, the rise of temperature enhances the yield of aromatics, which has been described in previous studies. This is because the increase of temperature promotes the cyclization of carbenium ions and the dehydrogenation of cyclohydrocarbons, thus generating more aromatics. However, the higher temperature also causes excessive cracking of reactants into gas products. As for which factor is more significant, it depends on the reaction conditions, such as the acid property of catalyst and the contact time between the intermediate products and catalyst. Therefore, if the above-mentioned second factor plays a decisive role, the rise of temperature only promotes the concentration of aromatics in the liquid products but does not improve the aromatic yield based on the mass of the PE raw materials.

4. CONCLUSIONS

In summary, through the catalyst selection and modification and the optimization of reaction parameters, including heating rate, temperature, and pressure, the transformation of polyethylene into high selectivity monomeric aromatics was obtained. The highest proportion of monocyclic aromatics and BTEX in recovered liquid was 90.0 and 61.5%, respectively. Temperature is a significant factor affecting the cracking/aromatization reactions. The increasing temperature significantly increased the aromatic proportion in the liquid product; however, the liquid yield was reduced due to the excessive cracking of polyethylene into non-condensable products. During the catalytic pyrolysis of polyethylene, the higher pressures change the boiling point of the reactant and inhibit the desorption of the reactants from the catalyst, thus prolonging the contact time between the catalyst and the liquid phase reactants at higher temperatures. The loading of zinc increased the number of different types of acidic sites and increased the B/L acid ratio, which was beneficial to promote the aromatization reactions. In addition, a coupling relationship exists between various factors. We speculate that the lower carbon residue and gas yields of the pyrolysis process can be realized by optimizing the reactor, especially controlling the contact time between the active sites of catalysts and the reactants (affected by the heating rate and the desorption of the intermediates), and the structure of the catalyst pores, so as to obtain higher aromatic yields.

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Notes

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