Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Catalytic pyrolysis of waste polyethylene into benzene, toluene, ethylbenzene and xylene (BTEX)-enriched oil with dielectric barrier discharge reactor

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ARTICLE INFO

Keywords: Plastics Non-thermal plasma Oil BTEX Regeneration

ABSTRACT

The increasing demand for plastics has resulted in significant plastic waste accumulation and environmental pollution. Catalytic pyrolysis is an attractive treatment method to mitigate the plastic waste management problems and recover high-value oil products. In our study, waste polyethylene (PE) was pyrolyzed to produce benzene, toluene, ethylbenzene and xylene (BTEX)-enriched oil a using dielectric barrier discharge plasma catalytic pyrolysis reactor. Ga-modified Hydro-Zeolite Socony Mobile-Five (HZSM-5) was used as a pyrolysis catalyst. The effects of the PE to Ga/HZSM-5 ratio and discharge power on BTEX enhancement and carbon deposition are discussed. The greatest BTEX selectivity (77.04%) and relatively low coke yield (1.37%) were achieved when the PE/(Ga/HZSM-5) ratio was 2:1 with a non-thermal plasma (NTP) discharge power of 20 W. The regeneration effects of conventional thermal oxidation and NTP on the zeolite catalyst were compared. NTP regeneration at a low temperature (150 °C) achieved the same coke removal rate as that of thermal regeneration at high temperatures (500 °C). Ga/HZSM-5 subjected to NTP regeneration showed higher activity for BTEX formation (BTEX selectivity was 40.59%). The NTP synergistic catalytic pyrolysis of plastics over Ga/HZSM-5 was found to be a promising strategy for mitigating the plastic waste management problems and upgrading the quality of oil products.

1. Introduction

The increasing demand for plastics has led to significant environmental concerns (Jie et al., 2020; Zheng and Suh, 2019). In 2019, the global plastic output reached 368 million tons, of which approximately 79% was discarded without proper disposal (Plastics, 2021). Thus, it is necessary to address the environmental pollution caused by plastics wastes. Recently, the conversion of non-recyclable waste plastics into fuel oil rich in benzene, toluene, ethylbenzene and xylene (BTEX) through pyrolysis has attracted intensive interest because of its low cost and high energy recovery efficiency (Inayat et al., 2022; Matsuura et al., 2022; Palos et al., 2022; Parku et al., 2020; Zhang et al., 2020). Compared to other catalysts, Hydro-Zeolite Socony Mobile-Five (HZSM-5) is suitable for producing light aromatic hydrocarbons because of its broad intra-crystalline pore channel structure, narrow micropore diameter, high surface area and strong acidity. López et al. (2011) adopted the acidic HZSM-5 and alkaline red mud for catalyzing plastic pyrolysis. In addition, a BTEX selectivity of 40.8% in the fuel oil was observed when HZSM-5 was used. Other researchers have found that when metals (Ga, Mo, Fe, Ni, Ru, Co, Zn et al.) were loaded onto zeolite catalysts, the aromatics content of the catalytic pyrolysis oil can be enhanced significantly (Akubo et al., 2019; Nishino et al., 2008; Pierella et al., 2005). For example, Nishino et al. (2003) examined the effect of H-gallosilicates on the cracking behavior of polyethylene (PE) and reported a 62 wt% yield of BTEX in the pyrolysis fuel oil. Akubo et al. (2019) reported that 1 wt% Ga loading ratio on Y-zeolite could increase the aromatic content of the pyrolysis oil by 13.1% and the monocyclic aromatic hydrocarbons included chiefly toluene, ethylbenzene, and xylenes.

In addition to catalysts, many researchers have employed nonthermal plasma (NTP) to improve pyrolysis performance. Many studies have found that the synergy of NTP and catalysts can increase the yield of target product species and reduce carbon deposition (George

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https://doi.org/10.1016/j.jenvman.2022.116096

Received 1 June 2022; Received in revised form 20 August 2022; Accepted 22 August 2022 Available online 7 September 2022 0301-4797/© 2022 Elsevier Ltd. All rights reserved.







| Abbreviations | | | |
|---------------|---|--|--|
| PE | Polyethylene | | |
| BTEX | Benzene, toluene, ethylbenzene and xylene | | |
| DBD | Dielectric barrier discharge | | |
| NTP | Non-thermal plasma | | |
| MAHs | Monocyclic aromatic hydrocarbons | | |
| BAHs | Bicyclic aromatic hydrocarbons | | |
| | | | |

et al., 2021; Yao et al., 2021). Song et al. (2021) found that compared to HZSM-5, the synergistic effect of NTP and HZSM-5 may increase the aromatic content by 7.58% at a discharge power of 15 W. Zhao et al. (2018) found that HZSM-5 coking was reduced by 3.74% when NTP was applied to a catalytic biomass pyrolysis system. Moreover, the NTP technology was developed for catalyst generation. Fan et al. (2015) reported that NTP may recover the textural appearance of deactivated HZSM-5 in a catalytic biomass pyrolysis reaction. Li et al. (2020) demonstrated that the skeleton structure of La/Hi-ZSM-5 coked during the catalytic pyrolysis of rape straw was also maintained after NTP regeneration. Astafan et al. (2019) applied NTP to regenerate coked zeolites in the propene transformation reaction and found that the regeneration efficiency was impacted by the accessibility of the active oxygenated species generated under plasma to coke.

It is essential to develop effective and robust catalysts because most previous reported catalysts are suffering from coking and relatively low selectivity after regeneration. In our study, a Ga-modified HZSM-5 catalyst was proposed for obtaining BTEX-enriched fuel oil from waste PE through NTP-assisted catalytic pyrolysis. NTP was generated by a dielectric barrier discharge (DBD) reactor, as reported in many studies (Huang et al., 2022; Xiao et al., 2022). The effects of the PE to Ga/HZSM-5 ratio and discharge power on BTEX enhancement were explored by laboratory experiments. The coking behavior was also examined, and the coke deactivated catalysts were comparatively regenerated by the NTP technology at a low temperature (150 °C) and by high-temperature thermal oxidation (500 °C). Our study provided a new perspective on the energy-efficient low-temperature regeneration of catalysts.

2. Materials and methods

2.1. Materials and catalyst

The PE sample was provided by Meisheng Engineering Plastics Co., China.

The HZSM-5 (SiO₂/Al₂O₃ = 50) support was obtained from Tianjin Yuanli Chemical Co. and the gallium(III) nitrate hydrate was supplied by Aladdin. The Ga/HZSM-5 catalyst was synthesized using a wet-impregnation method. 4 g HZSM-5 was added to 50 mL of Ga(NO₃)₃ hydrate solution to produce 1 wt% of Ga loading ratio by stirring at 80 °C for 5 h. The samples were then dried at 100 °C for 4 h and calcined at 10 °C/min to 550 °C for 5 h in air. Finally, the Ga/HZSM-5 powder was sieved into 200 mesh. The catalyst preparation method was based on the works of Du et al., 2013, Vichaphund et al., 2015, Xiao et al., 2015.

2.2. Catalyst characterization

The specific surface area and pore volume of the catalysts (before and after the synthesis) were evaluated using an analyzer ASAP 2460. As illustrated in Table 1, the surface area decreased from 509.33 m²/g to 381.01 m²/g, and the pore volume declined from 0.21 cm³/g to 0.14 cm³/g with the addition of Ga.

The Ga content in Ga/HZSM-5 was determined using an inductively

| Ta | ble | 1 |
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Textural properties of the catalysts.

| Properties | HZSM-5 | Ga/HZSM-5 |
|--|--|--|
| BET surface area (m ² /g) Internal surface area (m ² /g) External surface area (m ² /g) Total pore volume (cm ³ /g) | $\begin{array}{c} 509.33 \pm 0.96 \\ 446.90 \pm 0.88 \\ 62.42 \pm 0.08 \\ 0.21 \pm 0.01 \end{array}$ | $\begin{array}{c} 381.01 \pm 1.08 \\ 330.87 \pm 0.97 \\ 50.14 \pm 0.11 \\ 0.14 \pm 0.01 \end{array}$ |

coupled plasma optical emission spectrometer (EDS) apparatus (Agilent 720ES), and the actual wt.% of Ga in the catalyst was 0.92%.

Temperature-programmed desorption of ammonia (NH₃-TPD) was performed using Bel Cata II. Before analysis, the samples were pretreated at 500 °C for 60 min in a helium stream and cooled to 100 °C. For the NH₃-TPD, samples were saturated with ammonia at a flow rate of 35 mL/min for 90 min. This was followed by filling with He for 2 h to remove reversibly bound NH₃ from the surface. Finally, the temperature was increased to 600 °C at a rate of 10 °C/min to desorb NH₃.

 $\rm H_2$ temperature-programmed reduction (H₂-TPR) was performed using a Bel Cata II analyzer. Approximately 50 mg of the sample was heated in a quartz reactor at 500 °C for 1 h under He flow (50 mL/min), followed by cooling to 50 °C. Subsequently, the samples were reduced by a 5% H₂/Ar gas mixture (30 mL/min) at a ramping rate of 10 °C/min, up to 800 °C.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific K-Alpha spectrometer with Al K α (1486.60 eV) source radiation. The binding energies were calibrated with the adventitious C 1s line at 284.80 eV for the charging effect. The photoelectron lines of Ga 3d and Ga 2p were recorded.

Transmission electron microscope (TEM) profiles were obtained using an HT-7700 microscope. Energy dispersive X-ray spectroscopy analysis was performed for each sample.

2.3. Experimental setup

The united fixed-bed device used in the experiment is illustrated in Fig. 1. The main components of the system were described in detail in a previous study (Song et al., 2021). An external tube furnace was used to pyrolyze the sample and preserve the heat. The DBD reactor consisted of an alundum tube (φ 25 × 2.5 mm, dielectric constant of 8–11) that acted as the dielectric medium, a stainless steel rod (φ 14 mm) centrally located inside the reactor as the inner electrode and a copper mesh wrapped around the alundum tube used as the outer low voltage electrode. The inner electrode was connected to an AC high-voltage generator and the low-voltage electrode was grounded. The discharge zone was 150 mm long with a gap of 3 mm. A four-channel digital oscillo-scope (MDO3014, Tektronix, USA) was used to record the electrical signals.

When fresh catalyst was used, Ga/HZSM-5 (0.5 g) and PE (1 g) were placed in the alundum tube using quartz wool. Prior to each run, the reactor was purged with N₂ gas. The system was heated to 500 °C at 5 °C/min and maintained for 15 min. The DBD reactor was discharged at the desired power in the temperature range of 300–500 °C. Nitrogen was used as the carrier gas (100 mL/min). Finally, the oil products were condensed in ice -water. The mass difference of the zeolite (before and after the reaction) was assumed to be caused by coke. Gas yield was determined from the mass difference.

The condensed oil was analyzed by the gas chromatography/mass spectrometer (GC/MS-QP2010 SE, Shimadzu, Japan). The TGA Q500 V20.13 was applied to analyze the mass-loss properties of carbon deposition. The exact program settings of the GC/MS and TGA were demonstrated elsewhere (Song et al., 2021).

Thermal catalyst regeneration was achieved by heating 25 mg of Ga/HZSM-5 (PE/(Ga/HZSM-5) at a ratio of 1:2, 20 W) from 20 °C to a terminal temperature of 550 °C (10 °C/min) and maintaining the temperature for 15 min under oxygen flow. NTP catalyst regeneration was



Fig. 1. Schematic diagram of the experimental device.

performed under the same working conditions adopted for thermal regeneration, except for the final temperature of 150 °C and discharge at 50 W during the entire regeneration process. Moreover, the catalytic pyrolysis of the regenerated Ga/HZSM-5 was conducted to illustrate the regeneration effect. In each test, 0.5 g PE and 0.25 g regenerated zeolite were fixed in the reactor in proper order. The tubular furnace was heated to 500 °C at 20 °C/min and maintained for 15 min under a nitrogen flow of 100 mL/min.

3. Results and discussion

3.1. Catalyst characterizations

 NH_3 -TPD characterization was performed to examine the acid concentrations and strength of zeolites. The NH_3 -TPD curve of HZSM-5 commonly shows two peaks centered at low and high temperatures, belonging to weak and strong acid sites, respectively (Matsuura et al., 2003). As shown in Fig. 2(a), both peaks shifted to lower temperature. In addition, the first peak area increased with Ga modification. The acidity declined slightly, and the weak acid content enhanced sharply. The massive increase in the weak acid density was attributed to the



Fig. 2. The profiles of (a) NH₃-TPD, (b) H₂-TPR, (c) XPS curves of Ga 3d and (d) XPS curves of Ga 2p.

appearance of GaO^+ by proton substitution and the generation of new Lewis acid sites on the Ga_2O_3 surface (Espindola et al., 2020; Nowak et al., 2003).

The H₂-TPR curves of the fresh Ga/HZSM-5 are shown in Fig. 2(b). There was only one intense reduction peak near 520 °C, which was attributed to the small Ga₂O₃ species (Liu et al., 2015). Compared to the reduction signal at approximately 507 °C for pure Ga₂O₃, the elevated reduction temperature of Ga/HZSM-5 indicated that the Ga₂O₃ particles were extensively dispersed on the catalyst host (Xiao et al., 2015). There was no reduction peak of GaO⁺ because the Ga species at the cationic positions could barely be reduced by H₂ (Xin et al., 2019).

XPS characterizes the chemical states of Ga on the surface of the catalysts. The Ga 3d and Ga 2p XPS spectra for the fresh and used zeolites are shown in Fig. 2(c) and (d), respectively. As shown in the XPS curves of the fresh catalyst, the first peak at approximately 21 eV of the Ga 3d curve was caused by Ga (III) with tetrahedral coordination (Ga₂O₃). Dehydrogenation of volatiles has reported to be catalyzed by Ga₂O₃ sites (Seo et al., 2003). The second peak at 1118.5 eV in the Ga 2p spectra suggests the appearance of GaO⁺ on the zeolites (Nowak et al., 2003). Espindola et al., 2020 reported that the GaO⁺ species were capable of substituting the Brønsted acid sites of HZSM-5 to produce strong Lewis acidity in the form of Si–O(GaO⁺)- at non-framework positions on the zeolite surface, and the alkylation and aromatization reactions could be promoted by Lewis acid sites. As shown in Fig. 2(c), there was a small shift in the binding energy for the used Ga/HZSM-5, suggesting the stability of the Ga₂O₃ sites. As shown in Fig. 2(d), the Ga 2p binding energy for Ga in the used zeolite was less than that in the fresh zeolite, illustrating a weaker interaction between the GaO⁺ species and HZSM-5 catalyst.

3.2. BTEX enhancement by different PE/(Ga/HZSM-5) ratio

Fig. 3 shows the oil composition and product yield at various PE/ (Ga/HZSM-5) ratio. The yields of pyrolysis products are presented in Fig. 3(a). Compared to the high coke yield of modified micro Zn-zeolites (14.64%) reported by Pierella et al., 2005, coke production in our study was relatively low. The coke over Ga/HZSM-5 increased from 0.76% to 1.87% when the PE/(Ga/HZSM-5) ratio changed form 4:1 to 1:2. This was because more active sites and surface were produced by increasing the catalyst loading. Meanwhile, higher ratio of zeolites made an improved production of oil components, increasing from 16.33% to 26%. This was because the decomposition reaction controlled by NTP decreased because of the increased space filled by the catalyst. Consequently, the gas yield decreased. On the whole, the gas yield was greater than 70%, which was elevated. There are two reasons for this high gas yield. First, the HZSM-5 support possessed a broad intra-crystalline pore channel structure and a narrow pore diameter, which allowed heavy volatiles to further break into gaseous products. Secondly, as illustrated in Fig. 2, the Ga_2O_3 and GaO^+ species introduced by Ga loading may catalyze end-chain scission reaction and the dehydrogenation of volatiles to produce gas products (Biscardi and Iglesia, 1996; Iglesia and Baumgartner, 1993; Seo et al., 2003). The main components of the gaseous products were H2, CH4, C2H4, C2H6, C3H6, C3H8, C4H8, and C₄H₁₀, as discussed in our previous study (Song et al., 2021).

The compounds in the pyrolysis oil were classified into seven groups: benzene, toluene, ethylbenzene, xylene, other monocyclic aromatic hydrocarbons (MAHs), bicyclic aromatic hydrocarbons (BAHs) and alkane. As shown in Fig. 3(b), the highest selectivity of 77.04% for BTEX was obtained at a ratio of 2:1. Compared to the BTEX concentration of



Fig. 3. Effects of the PE/Ga-HZSM-5 ratio on (a) product yields, (b) oil components, (c) TG curves of coke deposition and (d) DTG curves of coke deposition.

PE pyrolysis oil (55.11%) reported by Lin et al., 2004 and the BTEX concentration (49.5%) reported by Zeng et al., 2022, the BTEX content in our study was significantly elevated. The relative contents of benzene and ethylbenzene were low, and the main components of the BTEX products were toluene and xylene. Increasing the dosage of Ga/HZSM-5 had negligible influence on the observed quantities of benzene and ethylbenzene, which was consistent with the results of Zeng et al., 2022. The toluene content first increased to 26.42% when the PE/(Ga/HZSM-5) ratio changed from 4:1 to 2:1. This increase in toluene selectivity may be due to the conversion of alkanes to toluene. Upon further increasing the dosage of Ga/HZSM-5, the relative toluene content decreased. The relative content of xylene decreased from 46.91% to 35.47% with an increase in catalyst proportion. The decline in the relative contents of toluene and xylene was due to the condensation of MAHs to BAHs. The BAHs contents increased with an increase in the catalyst loading.

The degree of unsaturated of the oil composition increased because the extra-framework Ga to HZSM-5 was an effective dehydrogenation active site (Meriaudeau et al., 1993). As shown in the XPS results for the fresh and used Ga/HZSM-5 catalysts, both Ga₂O₃ and GaO⁺ species participated in the dehydrogenation reaction. HZSM-5 possesses both Brønsted and Lewis acid sites. The Brønsted acid sites catalyzed cracking and isomerization reactions which resulted in the formation of alkanes and olefins. The Lewis acid sites promoted an aromatization reaction that included cyclization and dehydrogenation reactions. The introduction of Ga did not produce new Brønsted acid sites but formed a dual-site mechanism including Ga₂O₃ and H⁺ in Brønsted sites (Espindola et al., 2020). Moreover, Fig. 2 (a) and (b) show that the addition of Ga generated new weak Lewis acid sites and Ga₂O₃ active sites on the zeolite surface. Therefore, the Ga species affected the yield and selectivity of the products as a consequence of catalyst acidity and the density of the acid sites. There were no alkanes in the oil products when the PE/(Ga/HZSM-5) ratio was <4:1. This was because both the HZSM-5 support and Ga2O3 species showed a good ability to catalyze dehydrocyclization (Cerqueira et al., 2008; Song et al., 2021).

The thermogravimetry (TG) and differential thermogravimetry (DTG) profiles of carbon deposition are shown in Fig. 3(c) and (d), respectively. There were three stages in the weight loss course. The first stage at temperatures below 200 °C was a result of water and light coke release (Song et al., 2021). The second stage at temperatures between 200 °C and 600 °C was for the reaction of heavy carbon deposition. Finally, the last stage at temperatures greater than 600 °C was the stabilization course (Fan et al., 2020). As shown in Fig. 3(c), the unit weight loss of catalyst decreased from 2.91% to 1.4% when the PE/(Ga/HZSM-5) ratio changed from 4:1 to 1:2. The DTG curves are shown in Fig. 3(d). The mass loss peak between 450 °C and 600 °C was due to the burning of highly condensed coke (Karge, 1998). The greater the mass loss temperature at the peak, the greater is the C/H ratio of the carbon deposition process (Cerqueira et al., 2008; Elordi et al., 2011). Coke was oxidized at a lower temperature maintained higher activity (Sun et al., 2021). Accordingly, the carbon deposition was most easily removed at a PE/(Ga/HZSM-5) ratio of 1:1.

The TEM images of the fresh and spent catalysts are shown in Fig. S1. The aggregated morphology of HZSM-5 with micron dimensions exhibited a hexagonal sheet structure (Kostyniuk et al., 2019). Compared to fresh HZSM-5, no distinct metallic particles were observed on the Ga/HZSM-5, indicating an extensive dispersion of Ga (Hu et al., 2015). It was difficult to detect carbon deposition inside the pores using TEM. The coke was mainly distributed in filaments or flakes at the edge of the catalysts. The EDS results indicated that carbon deposition on the surface of the zeolites decreased with a higher catalyst/PE ratio. This was consistent with the TG conclusion. The Ga loading ratio obtained by EDS was less than 0.92% (ICP-EDS), illustrating that some Ga species were not loaded successfully on the zeolite surface.

3.3. BTEX enhancement by different discharge power

The oil components and product yields at distinct discharge powers are shown in Fig. 4. Fig. 4(a) compares the product yields at varying discharge powers. The coke yield decreased with enhancing discharge power, declining from 1.37% at 20 W to 1.11% at 60 W. Both the carbon deposition and BTEX content were minimal without discharge. The oil yield improved from 15% at 0 W to 22.67% at 40 W and marginally reduced to 19.3% at 60 W. The oil yield distribution with the discharge power was similar to that reported in our previous study. Song et al., 2021 found that when the discharge power increased from 0 W to 15 W, there was an enhancement in the oil yield and a further increase in the discharge power resulted the decline of oil yield. The particular low oil yield of 15% by Ga/HZSM-5 was a consequence of zeolite properties. The small-scale pore diameter and broad intra-crystalline pore channel framework of zeolite allowed large chemicals to decompose further into the gas phase composition (Seo et al., 2003). The synergistic effect between NTP and the catalyst affects the product distribution (Song et al., 2021). When the NTP energy density was low (0-40 W), the modified zeolite and NTP were helpful for the decomposition of PE into oil products. However, further enhancement of the discharge power promoted cracking of larger hydrocarbons into gas components.

As exhibited in Fig. 4(b), the selectivity of BTEX increased significantly with the introduction of NTP, indicating a synergistic effect between NTP and Ga/HZSM-5. When the catalyst is placed in the NTP discharge zone, a micro-discharge is generated on the surface and pore structure of the catalyst; thus, more active species are generated. Meanwhile, the catalyst properties also changed, such as a better distribution of the Ga species, higher acid site density and stronger acidity. The oil composition evolved under the combined action of NTP and catalyst. Specifically, the toluene content increased by 14.81% and the xylene selectivity increased by 4.34% with the introduction of NTP. Xylene accounted for the majority of the BTEX products, with the highest selectivity of 46.14% at 40 W. The maximum yields of benzene (2.21%), ethylbenzene (26.42%), and BTEX (77.04%) were obtained at 20 W. Increasing the discharge power enhanced MAHs content and a consequent decline in BAHs content. These results are consistent with those reported by Fan et al., 2018. They suggested that the application of NTP technology improved the MAHs products and reduced the content of polycyclic aromatic hydrocarbons in the pyrolysis oil of camphorwood sawdust catalyzed by HZSM-5. It was suggested that the increase in power generated more short-chain hydrocarbons during the scission reaction of PE or hindered the MAHs condensation reaction.

As displayed in Fig. 4(c), the weight loss of the spent Ga/HZSM-5 was minimum 1.48% without discharge. It is established that HZSM-5 can effectively resist coking according to its uniform pore size and geometrical structure. Increasing the discharge power from 20 W to 60 W resulted in a decrease of 0.47% in the weightlessness of the zeolites. This was likely due to the further reaction of the heavy chemicals to oil and gas products. The DTG profiles are shown in Fig. 4(d). The oxidative composition peak of highly condensed carbon deposition at temperatures between 450 °C and 600 °C shifted to higher temperature, and the weight loss rate increased with enhancing the discharge power, which indicated that coke at 60 W was the most difficult to remove (Chen et al., 1989; Karge, 1998).

The morphology of the spent zeolites at various discharge powers are displayed in Fig. S2. The TEM images showed the formation of filamentous and flake coke on spent Ga/HZSM-5. The typical EDS spectrum reconfirmed the carbon deposition on the spent catalysts.

3.4. Regeneration effect by thermal and NTP

Olefins are produced by cracking reactions at the Brønsted acid sites. Afterward, aromatization was performed over Lewis acid sites by olefin cyclization and dehydrogenation reactions. Aromatics were also generated by the Diels-Alder reaction. During the catalytic pyrolysis reaction,



Fig. 4. Effects of discharge power on (a) product yields, (b) oil components, (c) TG curves of coke deposition and (d) DTG curves of coke deposition.

from one perspective, the acid sites were covered by the coke; from a different perspective, the acid sites were consumed. For example, active Ga_2O_3 can be reduced to monomeric Ga^0 or Ga^{1+} compounds (Meitzner et al., 1993). Therefore, fresh catalysts could be deactivated after several uses.

The catalytic pyrolysis oil by fresh Ga/HZSM-5 (FGa/HZSM-5), Ga/ HZSM-5 by thermal regeneration (Ga/HZSM-5-TR) and Ga/HZSM-5 by NTP regeneration (Ga/HZSM-5-NTPR) were analyzed as shown in Fig. 5. Thermal regeneration is the most common method for coke removal via oxidation at high temperatures. However, the input energy is high, and active sites are easily lost (Lu et al., 2017; Sharma and Bakhshi, 1993). In comparison with the oil product obtained with FGa/HZSM-5, the oil product obtained with Ga/HZSM-5-TR contained a lower BTEX compound content and a higher content of other aromatics, illustrating that the catalyst regenerated by the thermal oxidation method was not conducive to BTEX production. During NTP regeneration conducted in an oxidative atmosphere, active substances, such as O_2^+ , O_-^- , O_2^- , O_3^- , and O₃, were generated, which could oxidize aliphatic hydrocarbons on the outer surface of the catalyst and aromatics (primary coke) into gaseous CO, CO₂, and H₂O. As a result, coke was removed. There were significant observed differences in the Ga/HZSM-5-NTPR oil composition. In contrast to the oil produced by FGa/HZSM-5, the proportion of toluene and BAHs increased significantly, whereas the relative content of xylene and other MAHs decreased. In other words, the MAHs further condensed to BAHs by catalysis with Ga/HZSM-5-NTPR.

As displayed in Fig. 5(b), the primary catalytic pyrolysis oil had carbon numbers between 7 and 12. The relative contents of oil compounds with different carbon atom numbers by Ga/HZSM-5-TR were similar to those over FGa/HZSM-5. However, compared to other

catalytic reactions, the reaction occurring over Ga/HZSM-5-NTPR produced fewer C_8-C_9 components but more $C_{11}-C_{12}$ compositions.

The TG and DTG curves of the various catalysts are shown in Fig. 5(c) and (d), respectively. It could be seen that all of the heavy coke was removed by both thermal and NTP regeneration. Besides, the total weight loss of Ga/HZSM-5-TR and Ga/HZSM-5-NTPR was 0.96%, suggesting that NTP regeneration at low temperature (150 °C) could achieve the same coke removal rate as the thermal regeneration at high temperatures (500 °C). Notably, most of the weight loss in the first stage was due to desorption of water.

3.5. Discussion of the reaction mechanism

The catalytic pyrolysis of PE over zeolite is known to occur according to the carbonium iron theory (Meriaudeau et al., 1993; Song et al., 2021). As analyzed above, the Ga species affect the yield and selectivity of the products owing to the acidity of the catalysts and the density of the acid sites. When Ga/HZSM-5 settled into the discharge region of NTP, synergetic interactions occurred between NTP and the catalyst. NTP changes the characteristics of the zeolites (surface, acidity, and the distribution of Ga species) by the reactive species, such as iron, electrons, radicals, and photons. The catalyst affects the discharge performance, such as the electric field, discharge type, and microdischarge formation (Puliyalil et al., 2018; Whitehead, 2016). A plausible reaction mechanism is illustrated in Fig. 6.

There are four types of acid sites on the catalyst: Brønsted and Al Lewis acid sites of HZSM-5, and two kinds of Lewis acid sites caused by Ga loading. In addition, there are metal-active sites on the zeolite. Brønsted acid sites are known to catalyze the cracking and isomerization



Fig. 5. The relative content of (a) BTEX, MAHs, BAHs and alkanes and (b) oil composition in various carbon number, (c) TG and (d) DTG curves of coke deposition on different catalysts.

reactions, while Lewis acid sites promote alkylation and aromatization reactions (Espindola et al., 2020). Metal sites can catalyze the dehydrogenation of volatiles (Biscardi and Iglesia, 1996; Iglesia and Baumgartner, 1993). Plasma may decompose reaction intermediates and activate ring-open reactions through collisions with active species (Liu et al., 2017; Mei et al., 2019). In the alkane and olefin formation process, all the initiation, β-scission, isomerization, hydrogenation, and decomposition reactions are catalyzed by acid sites. Both the plasma and Brønsted acid sites activate the decomposition reaction. As a result, a broad distribution of chain hydrocarbons is produced. In the aromatization process, chain hydrocarbons cyclize to cycloalkanes, which undergo dehydrogenation and aromatization reactions to produce aromatics. The Diels-Alder reaction also participates in the formation of aromatics. Aromatic compounds undergo secondary reactions by alkylation, dealkylation, disproportionation, transalkylation, hydrogen transfer, isomerization, and condensation reactions to produce BTEX and other aromatics.

Overall, acid sites participate in all catalytic reactions. Plasma mainly affects the aromatization and secondary reactions of aromatics, while metal active sites promote dehydrogenation reaction.

4. Conclusions

PE was pyrolyzed into BTEX-enriched oil by NTP synergistic catalytic pyrolysis. The results showed that the combination of NTP and catalytic pyrolysis over Ga/HZSM-5 exhibited good performance for plastic waste management and high-value oil production. The effects of the PE/(Ga/HZSM-5) ratio and discharge power on the BTEX enhancement and carbon deposition were investigated experimentally. In addition, the

coked catalysts were regenerated using NTP and thermal methods. The main conclusions are as follows: (1) XPS analysis indicated that Ga was loaded into HZSM-5 in the form of Ga_2O_3 and $Si-O(GaO^+)$ -. The Ga species affected the yield and selectivity of the products because of the presence of acid and metal active sites.

(2) The highest BTEX selectivity of 77.04% and relatively low coke yield of 1.37% were achieved when PE/(Ga/HZSM-5) ratio was 2:1, with an NTP discharge power of 20 W.

(3) To obtain the maximum oil yield (26%) and minimum gas yield (72.12%), the optimum PE/(Ga/HZSM-5) ratio and discharge power must be 1:2 and 20 W, respectively.

(4) Ga/HZSM-5-NTPR showed higher activity for BTEX formation compared to that exhibited by Ga/HZSM-5-TR, and the respective BTEX selectivities were 42.10% and 40.59%.

Credit author statement

Jiaxing Song: Writing - original draft. Jun Wang: Writing - review & editing. Yuhan Pan: Methodology. Xudong Du: Conceptualization. Jingyuan Sima: Data curation. Chenxi Zhu: Validation. Fangfang Lou: Investigation. Qunxing Huang: Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 6. The plausible reaction mechanism of plasma synergistic catalytic pyrolysis of PE over Ga/HZSM-5.

Data availability

Data will be made available on request.

Acknowledgments

The authors would like to gratefully acknowledge the National Natural Science Foundation of China (52076190), National Key Research and Development Program (2018YFC1901300), Key Research and Development Program of Zhejiang province (2020C03084) and Zhejiang University Ecological Civilization Plan.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.116096.

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