

Enhanced Production of High-Value BTEX Aromatic Hydrocarbons from the Pyrolysis/Nonthermal Plasma/Catalysis of Waste Plastics

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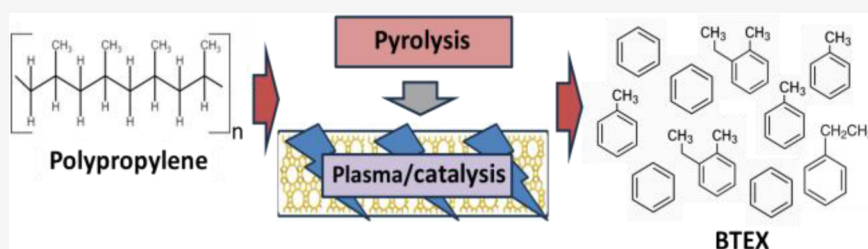


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ABSTRACT: The escalating accumulation of waste polypropylene poses a severe environmental challenge, necessitating advanced upcycling technologies to convert this carbon-rich resource into high-value chemical feedstocks. In this study, a two-stage pyrolysis/nonthermal plasma/catalysis reactor was investigated to maximize the production of single-ring aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene (BTEX)). The synergistic effects of plasma input power, catalyst temperature, and zeolite topology (Y-zeolite vs β -zeolite) on product distribution were systematically evaluated. Furthermore, to enhance aromatization efficiency, β -zeolite was modified with four distinct metal promoters (Ni, Ga, Mo, Zn). The results indicated that optimal conditions of 40 W plasma power and 500 °C catalyst temperature achieved high BTEX yields for both Y-zeolite (~32.5%) and β -zeolite (~40.0%), with the latter exhibiting superior shape-selectivity. Among the metal-modified catalysts, the Ga- β -zeolite achieved the highest BTEX yield of 45.6%. This enhanced performance is attributed to a triple synergy: the generation of reactive intermediates by nonthermal plasma, the shape-selective confinement of the β -zeolite pores, and the specific promotion of dehydrogenation-cyclization pathways by gallium species. This work demonstrates that integrating plasma with Ga-modified zeolites offers a highly efficient, sustainable route for upcycling waste plastics into essential petrochemical precursors.

1. INTRODUCTION

Greater than 410 million tonnes of plastic are manufactured each year, consisting mainly of polyethylene (26.2 wt %), polypropylene (19 wt %), polyvinyl chloride (12.8 wt %), polyethylene terephthalate (6.2 wt %), polyurethane (5.3 wt %), and polystyrene (5.2 wt %).¹ Such plastics are mainly used for consumer product packaging and end up in the municipal solid waste stream. The impact of waste plastics on human health and the environment is well documented.^{2,3} Consequently, there are investigations into the application of novel thermochemical technologies, such as pyrolysis and gasification, for the upcycling of waste plastics to produce higher-value products.^{4–9}

Pyrolysis is an upcycling process where the large polymer chain of waste plastic is thermally degraded in an inert atmosphere to produce low molecular weight hydrocarbon oils and gases. The oils and gases have the potential to be reprocessed at refineries to produce liquid fuels, chemicals, or even the production of new plastics.¹⁰ Pyrolysis of waste

plastics to produce an oil for use as liquid fuels and chemicals is attractive because high yields of oil can be produced, for example, pyrolysis of polystyrene produces ~95 wt % liquid oil, while polyethylene and polypropylene produce a wax/oil product of 80 wt % yield, depending on process conditions.¹¹

There is interest in improving the quality of the product oil by the use of catalysts, with the aim of producing a higher value chemical feedstock with a high single aromatic content, such as benzene, toluene, ethylbenzene, and xylenes.^{11–13} Zeolite catalysts are known for their unique pore architectures with accessible Brønsted/Lewis acid sites for promoting the

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formation of aromatic chemicals and have been widely used in plastic/catalysis processing of waste plastics.¹¹ Typical zeolite catalysts used in plastic pyrolysis/catalysis processes tend to be either microporous, such as ZSM-5 and Y-zeolite, or mesoporous, such as MCM-41 and SBA-15.¹⁴ HZSM-5 are aluminosilicate catalysts comprising a 10-ring microporous structural system with channels of 0.51–0.56 nm, resulting in shape-selectivity catalysis.¹⁵ Due to the channel-matching micropore size of the HZSM-5 zeolite and the aromatic molecular size for benzene, toluene, and *p*-xylene,^{16,17} zeolite catalysts have become widely used catalysts for the selective production of hydrocarbon liquid fuels and aromatic compounds.¹⁸ For example, Muhammad et al.¹¹ reported a marked increase in the production of benzene, toluene, ethylbenzene, and xylenes for the pyrolysis-catalysis of polyethylene and polypropylene using a HZSM-5 catalyst. Also, Zhang et al.¹⁹ processed low-density polyethylene into gasoline-range hydrocarbons, with a high mono-ring aromatic compound yield (84.34%) in the liquid product oil. The microporous HZSM-5 type zeolite catalysts are more conducive to cracking reactions of the plastics pyrolysis vapors, and tend to form C1–C4 gases and C6–C12 hydrocarbon range oil products.¹⁹

Other types of zeolite catalysts investigated for processing waste plastics through the pyrolysis/catalysis process include Y-zeolite (Y-zeolite or the protonated HY type), which has a larger, 12-member ring structure consisting of SiO₄ and AlO₄ tetrahedra, with micropores of 0.74 nm diameter. The Y-zeolite catalyst tends to produce C6–C12 hydrocarbons from the pyrolysis-catalysis of waste plastic.²⁰ For example, the Y-zeolite catalyst has been shown to greatly improve the yield of C₅–C₁₁ hydrocarbons (around 45 wt %) in liquid oil products during the pyrolysis-catalysis of HDPE.²¹ However, the Y-zeolite is prone to coke formation and, consequently, catalyst deactivation. Due to the pore structure of the Y-zeolite containing cavities, high molecular weight hydrocarbons block the active catalyst sites, and increased coke is formed.²² Whereas, ZSM-5 zeolite has no such cavities and its channels are interconnected, therefore the higher molecular weight hydrocarbons can easily exit the pores, leading to lower coke formation.²² Therefore, the pore structure, pore shapes, and sizes impact catalyst activity, coke formation, and product selectivity.^{22,23} BEA-type zeolites (i.e., β -zeolite) have also been used for the catalytic upgrading of plastic pyrolysis volatiles, but there are only a few studies. The β -zeolite catalyst has a three-dimensional structure consisting of a 12-membered ring with interconnected channels, which allow for high molecular diffusion. Therefore, β -zeolite catalysts are suitable for reactions involving the larger molecules generated from the pyrolysis of waste plastics. Elordi et al.²⁰ used a β -zeolite catalyst for the pyrolysis-spouted bed catalysis of waste plastic. They reported that lower yields of single-ring aromatic compounds and higher catalyst coke formation were produced using a β -zeolite catalyst compared to ZSM-5 zeolite catalyst.

In addition to the physical structure of zeolite catalysts, the surface acidity is an important characteristic that influences the composition of the product oil from the plastics pyrolysis-catalysis process. Zeolites are solid acid catalysts, with the acidity linked to the Si/Al ratio, lower ratios, that is, more alumina, are more acidic than at higher silica/alumina ratios.²⁴ This is because each Al atom introduces a negative charge in the framework, which is balanced by a proton (H⁺), forming Si–OH–Al groups. This results in stronger acidity and higher

catalytic activity for reactions requiring proton donation, such as cracking and isomerization.²⁵ Both Brønsted-acid and Lewis-acid sites are formed. Higher Si/Al ratios result in a zeolite with a reduced number of Brønsted acid sites and can lead to the formation of Lewis acid sites, which are useful in reactions like aromatization.

There have been further innovations in the pyrolysis-catalysis process for the upcycling of waste plastics to produce high-value oils, via the combination of nonthermal plasma with the catalyst environment.^{26–30} Dielectric barrier discharge (DBD) reactors have been commonly used.^{29,30} A radial electric field, applied by an alternating voltage, causes the electrical breakdown of the flowing gases through the reactor, including the carrier gas and the pyrolysis volatiles produced from the pyrolysis of the plastic. The nonthermal plasma represents a unique, highly reactive environment where the electrons are highly energetic, with a reported electron energy of up to 10 eV, which is equal to very localized, extremely high temperatures, but where the overall gas temperature remains low (<200 °C).³¹ The nonthermal plasma induces a highly reactive environment where very reactive molecular and atomic species are formed, which readily react with the hydrocarbons produced from the plastic pyrolysis.³² Introducing a zeolite catalyst to the highly reactive nonthermal plasma environment can enhance the catalyst activity, affecting the yield and selectivity of the target end-products.³³ For instance, micro-discharges on the surface and within the structure of catalysts promote the formation and uniform distribution of active sites. Also, high-energy electrons and radicals promote the formation of active sites, resulting in enhanced reaction activity and selectivity.^{34,35}

The combination of waste plastic pyrolysis and nonthermal plasma/catalysis has been shown to synergistically increase the production of aromatic hydrocarbons in the product oil during the processing of waste plastics. For example, Song et al.²⁶ used a dielectric barrier discharge (DBD) nonthermal plasma reactor to process polyethylene with an HZSM-5 zeolite catalyst. They reported that the selectivity for the production of aromatic compounds in the oil was ~98% using a polyethylene/zeolite catalyst ratio of 1:5, with a consequent marked decrease in the production of alkanes and alkenes. They also reported that the application of the nonthermal plasma reduced the formation of coke on the catalyst during the process. In a later report, Song et al.²⁷ investigated the use of a gallium-modified HZSM-5 (Ga-HZSM-5) catalyst to produce a product oil enriched in single-ring aromatic compounds, benzene, toluene, ethylbenzene, and xylene (BTEx) from the pyrolysis/nonthermal plasma/catalysis of polyethylene. They reported that a BTEx selectivity of 77% was achieved at a plastic:catalyst ratio of 2:1 with a nonthermal plasma discharge power of 20 W, and that coke formation on the catalyst was only 1.37%.

There is a need for further investigation into the pyrolysis/nonthermal plasma/catalysis process for the treatment of waste plastics. Particularly, the detailed composition of the product oils and gases in relation to the process parameters of the nonthermal plasma. In addition, while ZSM-5 zeolite and Y-zeolite have been investigated in the pyrolysis/catalysis of waste plastics, there are very few studies examining β -zeolite catalysts. The physical and chemical properties of different types of zeolites can markedly affect the product oil composition from the pyrolysis-catalysis of waste plastics. Here, we report on the pyrolysis/nonthermal plasma/catalysis

of polypropylene using different plasma input powers, and catalyst temperature, using Y-zeolite and β -zeolite catalysts, and also using different metal-based β -zeolite catalysts (Ni/ β , Ga/ β , Mo/ β , Zn/ β). The BTEX content of the product oil and the composition of the product gases are reported in relation to the process parameters, and catalyst type, and catalyst coke deposition. A reaction mechanism is also proposed. This work distinguishes itself by systematically exploring the synergistic effects between the nonthermal plasma field and the specific pore topology of metal-modified zeolites. Unlike conventional catalytic pyrolysis, we elucidate how plasma activation overcomes the diffusion limitations of larger zeolite pores while maintaining high selectivity through specific metal-acid site interactions.

2. MATERIALS AND METHODS

2.1. Materials

The polypropylene used in this study was a “real-world” recycled waste plastic, with an average particle size of 3–5 mm and a purity of >99%, and was supplied by Regain Polymers Limited, Castleford, UK. The polypropylene sample was characterized in terms of its thermal degradation profile using thermogravimetric analysis and the results are shown in Figure 1. The thermogravimetric (TG) and derivative

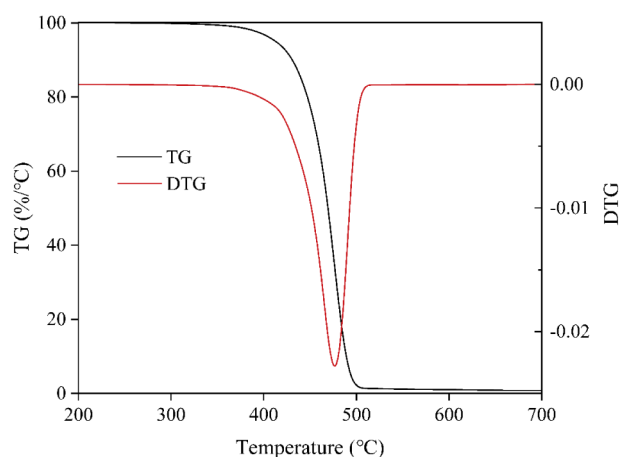


Figure 1. Thermal decomposition thermograms of the polypropylene waste plastic feedstock.

thermogravimetric (DTG) profiles of polypropylene exhibit a single, well-defined decomposition stage, indicating a uniform thermal degradation process. The onset of weight loss occurs at approximately 400 °C, with the most pronounced mass loss observed between 420 and 500 °C. The DTG curve displays a sharp peak centered around 470 °C, corresponding to the maximum degradation rate. Above 500 °C, the TG curve approaches a plateau, implying nearly complete volatilization of the polymer and minimal residual char formation, which is characteristic of the nonoxidative pyrolysis of polyolefins.

The catalyst supports, Y zeolite (FAU, Si/Al molar ratio of 5) from Nankai University Catalyst Plant, China, and β -zeolite (BEA, Si/Al molar ratio of 360) from Thermo Fisher Scientific, were both in H^+ -exchanged powder form. Metal precursors: gallium nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$, 99.9% metals purity), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, analytical grade, 99%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, analytical grade, 99.5%), and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, analytical grade, 99.5%) were all purchased from Scientific Laboratory Supplies Ltd., Nottingham, UK. These metals were selected to represent distinct catalytic functionalities: Ga and Zn are typical aromatization promoters functioning via dehydrogenation; Ni is a strong

cracking/hydrogenolysis metal; and Mo was chosen to investigate its potential for dehydro-aromatization in a plasma environment.

2.2. Catalyst Preparation

All metal-modified β -zeolite catalysts were prepared by the incipient wetness impregnation method, with a target metal loading of 5 wt %. Taking the preparation of the Ga/ β catalyst as an example, 9.5 g of β -zeolite powder was accurately weighed and predried in an oven at 110 °C for 2 h to remove physically adsorbed water. Concurrently, the required mass of gallium nitrate was calculated based on the target loading and completely dissolved in an appropriate amount of deionized water, with the water volume precisely matching the predetermined water absorption capacity of the zeolite. The mixture was stirred at a constant temperature of 40 °C using a magnetic stirrer, and the zeolite powder was slowly added to the metal salt solution. Stirring was continued at this constant temperature for several hours until the mixture formed a paste. After impregnation, the wet sample was oven-dried at 110 °C for 12 h, then calcined in a static air atmosphere by ramping the temperature to 500 °C at a rate of 5 °C min^{-1} and holding for 4 h to obtain the final Ga/ β catalyst. Other metal-modified catalysts (Mo/ β , Ni/ β , Zn/ β) were prepared using similar procedures.

2.3. Catalyst Characterization

The following catalyst characterization techniques were employed:

2.3.1. X-ray Diffraction (XRD). XRD was used to identify the crystalline structure of the catalysts, to confirm whether the zeolite framework remained intact after metal loading, and to observe the presence of any metal oxide crystalline phases. It was also used to observe changes in the structure and crystal phases of the used catalysts. The analysis was performed on a Bruker D8 instrument diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) with a tube voltage of 40 kV and a tube current of 40 mA. The scanning range was $2\theta = 5$ – 90° with a scan rate of $5^\circ/min$.

2.3.2. X-ray Photoelectron Spectroscopy (XPS). The produced catalysts were analyzed by XPS to determine the active metal chemical valence states on the surface of the metal-loaded catalysts. An Enviro ESCA NAP XPS was used with a monochromatic Al $K\alpha$ X-ray source. The C 1s peak (284.8 eV) was used as an internal standard for charge correction. Survey scans were used to determine the surface elements, and high-resolution scans of Ga 3d and Ga 2p were used for valence state analysis.

2.3.3. Temperature-Programmed Desorption of Ammonia (NH_3 -TPD). The acid strength and total acidity of the catalysts were evaluated using an automated chemisorption analyzer. Briefly, the catalyst samples were pretreated in a helium flow (30 sccm) at 300 °C for 90 min to remove physisorbed impurities and moisture. After cooling to 60 °C, the samples were saturated with a 10% NH_3/He gas mixture (30 sccm) for 60 min, followed by a pure helium purge for 15 min to remove weakly physisorbed NH_3 . The desorption profiles were then recorded using a thermal conductivity detector (TCD) from 60 to 550 °C at a heating rate of 10 °C/min.

2.3.4. Thermogravimetric Analysis of Basic Probe Molecules (Py/Lut-TGA). To differentiate and quantify Brønsted (B) and Lewis (L) acid sites, thermogravimetric analysis was performed using pyridine and 2,6-lutidine as basic probe molecules. Due to steric hindrance, 2,6-lutidine selectively adsorbs on B acid sites, whereas pyridine adsorbs on both B and L sites. Pretreated samples were saturated with the respective probe molecule vapors. Subsequently, TGA was conducted in an inert atmosphere, maintaining a temperature of 100 °C for 30 min to completely eliminate physisorbed species via capillary forces, and then heating to 800 °C at 10 °C/min. The L acid amount was calculated from the difference in chemical mass loss between pyridine and 2,6-lutidine absorptions.

2.3.5. Nitrogen Physisorption. To analyze the effect of metal loading on the textural properties of the catalysts, including specific surface area, pore volume, and pore size distribution, tests were conducted at -196 °C using an Anton Paar Nova 800 physisorption analyzer. Samples were vacuum-degassed at 150 °C for 6 h prior to analysis. The calculation of the specific surface area used the Brunauer–Emmett–Teller (BET) multipoint method at the relative

pressure range of $P/P_0 = 0.05\text{--}0.3$. Total pore volume was $P/P_0 = 0.99$. The pore size distribution was calculated using the DFT method.

2.3.6. Scanning Electron Microscopy (SEM)/Energy-Dispersive X-ray Spectroscopy (EDXS). SEM-EDXS was used for surface morphology and microstructure of the catalysts and to analyze the distribution of the loaded metals. A Hitachi SU3900 SEM instrument was used with an accelerating voltage of 15 kV. The EDX spectrometer was used for point element analysis and surface element mapping to confirm the uniformity of the metal loading.

2.3.7. Thermogravimetric Analysis (TGA). To quantitatively and qualitatively analyze the coke deposited on the deactivated catalysts. The analysis was performed using a Mettler Toledo thermogravimetric analyzer. In an air atmosphere, the temperature was increased from room temperature to 800 °C at a rate of 10 °C/min, while the mass change (TGA) and the rate of mass loss (DTG) signals were recorded.

2.4. Experimental Reactor System and Procedure

The two-stage pyrolysis and plasma-assisted catalytic experimental system used in this study is shown in Figure 2. The reactor consisted

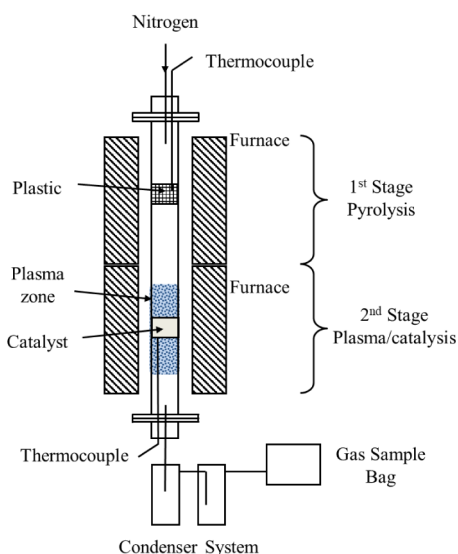


Figure 2. Schematic diagram of the two-stage pyrolysis and plasma-assisted catalytic reactor system.

of a corundum ceramic tube of 890 mm length and 20 mm internal diameter with stainless steel flanges at each end. The temperatures of the first-stage pyrolysis and second-stage catalysis reaction zones were heated by two separate furnaces and independently controlled by two temperature controllers. The nonthermal plasma reactor was a coaxial dielectric barrier discharge (DBD) plasma reactor. The nonthermal plasma was generated by a copper mesh external electrode and an internal stainless steel electrode in the second stage, producing a discharge gap of 2 mm. The corundum tube acted as the dielectric material, separating the inner and outer electrodes. The plasma input power was regulated by a plasma generator controller. Input high-voltage power to the DBD, with an AC frequency of 1500 Hz, and a maximum peak-to-peak voltage of 20 kV, was delivered to the internal stainless steel electrode, and the external copper mesh electrode was grounded. The discharge process was monitored by using a Tektronix MDO3024 digital oscilloscope. Nitrogen was used as the carrier gas.

The calculation of the average power consumption of the plasma system was based on the synchronized voltage and current measurements shown in the oscilloscope trace. The instantaneous power, $p(t)$, consumed by the plasma is determined by the product of the voltage, $V(t)$, applied across the electrodes, and the current, $I(t)$, flowing through the circuit:

$$p(t) = V(t) \cdot I(t)$$

The average power, P_{avg} , is subsequently calculated by integrating the instantaneous power over one full period, T :

$$P_{\text{avg}} = \frac{1}{T} \int_{t_0}^{t_0+T} V(t) \cdot I(t) dt$$

In this measurement, the digital oscilloscope's built-in math function was used to calculate the instantaneous power curve, $p(t)$ (Trace M, red), where P_{avg} is represented by the DC offset (mean value) of this curve. Accurate power calculation required precise calibration of the voltage and current probes; The Tektronix MDO3024 oscilloscope was used for voltage measurement, along with a Tektronix P6015A high-voltage probe was used. For current measurement, a Fluke 1000S AC Current Probe was used, operating on the 20 A range, which has a sensitivity of 50 mV/A.

Exactly 2.0 g of polypropylene plastic was loaded into a stainless steel crucible, held within the middle of the first-stage pyrolysis zone. Subsequently, 1.0 g of the prepared catalyst was uniformly packed in the middle of the second-stage reactor, secured at both ends with quartz wool to form a fixed bed. Before the reaction, the system was purged with N_2 at a flow rate of 100 mL/min for 30 min to completely remove air from the reactor. Under the applied voltage (20 kV) and atmospheric pressure, a uniform and stable discharge was maintained. Due to the high bond energy of $N \equiv N$ (945 kJ/mol), nitrogen dissociation is negligible under these conditions, serving primarily as a carrier gas and heat transfer medium. First, the temperature of the second stage was raised to and maintained at 500 °C. Then, the temperature controller for the first stage was switched on, raising the pyrolysis temperature to 500 °C at 10 min⁻¹ heating rate and holding it for 20 min. The plasma was kept on throughout the experiment and adjusted to the power level required for the specific operating conditions. Product gas collection and timing commenced when the first-stage temperature reached 200 °C, and the experiment lasted for 60 min. The gaseous products passed through a three-stage condenser system and into a Tedlar gas sample bag. Dry ice was used as the cooling medium to enhance condensation efficiency. Liquid products were collected in the condenser system, while all noncondensable gases were collected in the gas sample bag. After the reaction, the power and heating were turned off, and the system was cooled to room temperature under a N_2 atmosphere.

2.5. Product Oil and Gas Analysis

The products from the thermal treatment of waste plastics consist of char (pyrolysis residue left behind in the sample holder), liquid oil (condenser product), and gases collected in the sample gas bag. The gases were analyzed offline using three separate Varian CP-3380 packed-column gas chromatographs (GC): (i) C1–C4 hydrocarbons (methane, ethene, ethane, propene, propane, butane, butene, and butadiene) by GC-flame ionization detector (GC/FID), (ii) H_2 , O_2 , N_2 , and CO by GC-thermal conductivity detector (GC/TCD), and (iii) CO_2 separately, also using GC/TCD. Details of the GC columns and operating conditions of the GC have been reported previously.²⁹ Gas standards with known concentrations were used to calculate the response factors (RFs) and enable quantitation for each gas. Each gas sample was injected three times, and the average was used to calculate the gas yield. The results from the GCs were obtained in volume percent and were converted to moles of each gas by using the ideal gas equation.

The oil products were analyzed using a Varian 430 GC/FID using a Zebron ZB-SMS capillary column (30 m length, 0.25 mm internal diameter, 0.25 μ m film thickness). The identification and quantification of compounds in the oil were carried out using a range of analytical aromatic and aliphatic standards and relative retention time data. Compound identifications were confirmed with a Varian 3800-GC/Varian Saturn 2200 tandem mass spectrometer. The composition and yields of the oil products were determined using a gas chromatograph equipped with a flame ionization detector (GC-FID). To ensure analytical rigor, the quantification was based on weight percentages (wt %) derived from multipoint external standard

calibration curves rather than a simplified area-percentage assumption. Prior to analysis, the liquid oil samples were accurately diluted in dichloromethane (DCM) to a concentration of 5000 ppm (w/w) to maintain the detector response within its linear range. Identification of the individual components was performed by comparing their retention times with high-purity analytical standards, including aliphatics (cyclohexane, *n*-decane, *n*-undecane, *n*-tridecane, and *n*-tetradecane) and aromatics (benzene, toluene, ethylbenzene, *p*-o-xylene, *m*-xylene, cumene, and naphthalene), with further validation provided by GC-MS NIST library matching. For each identified compound, a calibration curve was established ($R^2 > 0.99$); for minor components where a direct standard was unavailable, the response factor of the most chemically analogous standard within the same functional group was applied. The final yield of each specific compound was calculated by multiplying its determined weight fraction by the total mass of the liquid oil obtained through gravimetric measurement of the condensers, thereby providing a precise mass balance of the products.

The product distribution was calculated based on the mass balance of the polypropylene feed. The total yield includes gas, liquid oil, and coke deposited on the catalyst. The gas yield was calculated by the results from gas GC, and the liquid oil yield was determined by weighing the condensers before and after the experiment, coupled with detailed compound analysis using GC/FID for individual compound analysis. The catalyst coke deposits were determined by the TPO test of the used catalysts.

3. RESULTS AND DISCUSSION

To understand the product characteristics of the pyrolysis of polypropylene without a catalyst or the influence of nonthermal plasma, initial experiments were carried out involving only the pyrolysis of polypropylene. Pyrolysis of polypropylene at a final temperature of 500 °C and in the absence of the zeolite catalyst and the nonthermal plasma, produce a gas product yield of 15%, while the oil/wax product yield was 80%.

Analysis of the pyrolysis product oil (Table 1) reveals that it contains a large quantity of high-molecular-weight compounds

Table 1. Composition of the Product Oil/Wax from the Pyrolysis of Polypropylene

Compounds	Wt.% of Total
C ₁₅ H ₃₂	25.42%
C ₉ H ₁₈	17.53%
C ₂₀ H ₄₀ /C ₂₀ H ₄₂	15.54%
C ₁₂ H ₂₄	11.67%
C ₁₃ H ₂₆ /C ₁₃ H ₂₄	9.39%
C ₇ H ₁₄	9.09%
C ₁₈ H ₃₆	6.25%
C ₇ H ₁₂	3.05%
C ₁₄ H ₂₈	2.85%
C ₁₀ H ₂₀	2.47%
C ₈ H ₁₆	1.69%
Others	1.88%

with carbon numbers ranging from C12 to C20 and beyond. It is a mixture of many linear, cyclic, saturated, and unsaturated hydrocarbons. These long-chain, heavy components are the primary constituents of wax. This complex chemistry and oil/wax consistency prevent the product from being directly used as either a high-quality fuel or specific chemical feedstocks, and the subsequent separation and purification processes would be extremely difficult and costly. Therefore, this research primarily focuses on the beneficial impacts of the synergistic use of nonthermal plasma and the zeolite catalyst on the hydrocarbon

pyrolysis products generated from the pyrolysis of polypropylene to produce a higher-value chemical feedstock.

3.1. Yield and Composition of Gases and Oil from the Pyrolysis/Nonthermal Plasma/Catalysis of Polypropylene

The influence of input plasma power from 0 W to 60 W and catalyst temperature from 400 to 500 °C was investigated in relation to the Y-zeolite and β -type zeolite catalysts, focusing on the composition of the product oils and gases.

3.1.1. Effect of Plasma Input Power. The results for the gas and liquid oil product compositions from the catalytic pyrolysis of polypropylene using commercial Y-type and β -type zeolite catalysts operated at 500 °C catalyst temperature are shown in Figure 3. As can be seen from the Figure 3, the

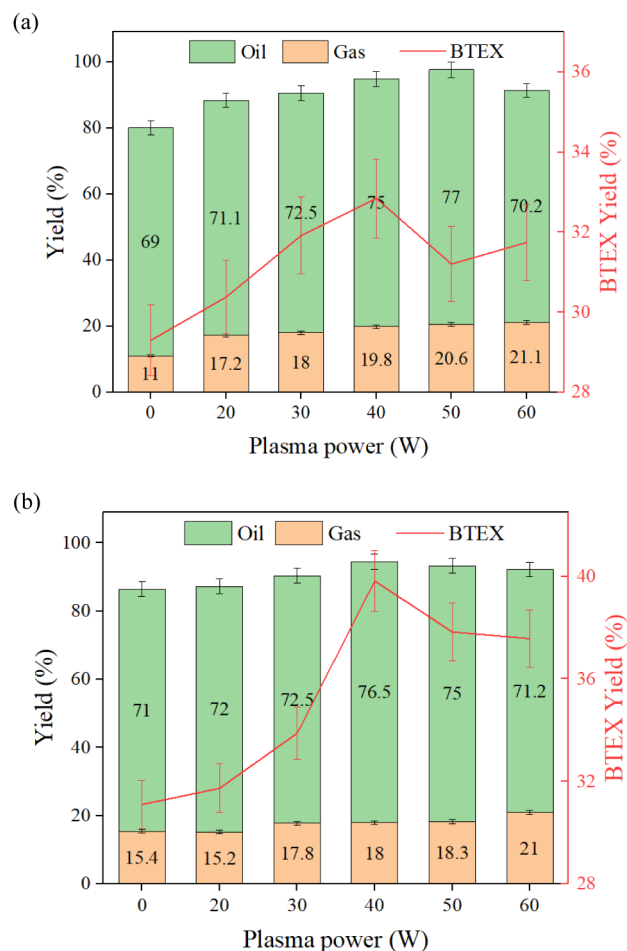


Figure 3. Product yields from the pyrolysis-catalysis of polypropylene over (a) Y-zeolite and (b) β -zeolite as a function of input plasma power.

introduction of plasma has a significant impact on the product distribution from the pyrolysis of polypropylene catalyzed by both Y-zeolite and β -zeolite. Figure 3 shows that for both Y-zeolite and β -zeolite catalysts, as the input plasma power was increased from 0 W (i.e., pyrolysis-catalysis without the presence of nonthermal plasma) to 60 W input plasma power, the yield of gaseous products continuously increased. For example, for the pyrolysis/nonthermal plasma/catalysis of polypropylene using β -zeolite, the gas yield steadily increased from 15.4% at 0 W to 21.0% at 60 W input plasma power. As a consequence, the oil yield increased from 71% at 0 W to a peak of 76.5% at 40 W for the β -zeolite catalyst. However, as the

power was further increased to 60 W, the yield decreased to 71.2%. This indicates that a moderate input plasma energy (40 W) can effectively activate the pyrolysis vapors, promoting their aromatization conversion on the catalyst and thus enhancing the oil yield. However, when the power is too high (>40 W), the cracking effect of the plasma becomes dominant. This leads to the excessive decomposition of key intermediates, such as C6–C8 olefins, into light C1–C3 gases instead of into liquid aromatic hydrocarbons, thereby causing a decrease in the oil yield.³⁶ The reason for the increase in gas yield with the application of the nonthermal plasma lies in the generation of many high-energy electrons (e^-) and active species (N_2^*) within the plasma discharge region. Through inelastic collisions, these high-energy particles can easily break the high-energy-barrier C–C (~ 3.6 eV) and C–H (~ 4.3 eV) bonds in the initial plastic pyrolysis products (mainly C_4^+ long-chain alkanes and olefins).³⁷ This triggers more cracking and secondary cracking reactions, thereby breaking down longer hydrocarbon chains into smaller molecule gas products like methane and ethene.³⁸

The main objective of this study was to maximize the yield of high-value single-ring aromatic compounds, BTEX (benzene, toluene, ethylbenzene, xylene). Figure 3 shows (red line) that the trend for BTEX yield is highly consistent with that of the oil yield, also reaching its maximum value at a power of 40 W, representing a yield of $\sim 40\%$ in the presence of the β -zeolite catalyst. This suggests that the presence of the nonthermal plasma generates active species that synergistically interact with the catalyst to significantly accelerate the rate-limiting steps in the aromatization pathway, such as dehydrogenation and cyclization, to enhance the formation of single-ring aromatic hydrocarbons, as also suggested by Loenders et al.³⁹ Comparison of the two zeolite catalysts shows that the catalytic performance of β -zeolite (BEA crystal structure) was superior to that of Y-zeolite (FAU crystal structure) for the production of BTEX. At the optimal input power of 40 W, the BTEX yield in the β -zeolite system ($\sim 40\%$) was significantly higher than in the Y-zeolite system ($\sim 32.5\%$). The advantage of β -zeolite primarily stems from its unique microstructure and acidity. It possesses a three-dimensional intersecting pore system ($0.66\text{ nm} \times 0.67\text{ nm}$ and $0.56\text{ nm} \times 0.56\text{ nm}$).⁴⁰ This pore size is highly compatible with the kinetic diameter of BTEX molecules ($\sim 0.6\text{ nm}$), which facilitates the formation and rapid desorption of the target products, thereby inhibiting secondary reactions and coke formation. In contrast, the Y-zeolite catalyst has a larger supercage structure ($\sim 1.2\text{ nm}$).⁴¹ While this provides more reaction space, it also tends to lead to the formation of large molecular intermediates (especially polycyclic aromatic hydrocarbons, PAHs) and coke, which can block the pores and deactivate the catalyst.

Figure 4 shows the gas composition produced from the pyrolysis-catalysis of polypropylene for the Y-zeolite (Figure 4a) and the β -zeolite (Figure 4b) in relation to input plasma power. The main gases produced were hydrogen, methane, ethane, ethene, propane, propene, butane, and butene. The main gas produced for both the Y-zeolite and β -zeolite catalysts was propene, derived from the thermal cracking of the polypropylene polymer chain. The impact of increasing plasma power was not particularly significant for the Y-zeolite, but there was a distinct reduction in the production of propene as the input plasma power was increased, with a resultant increase in the production of methane.

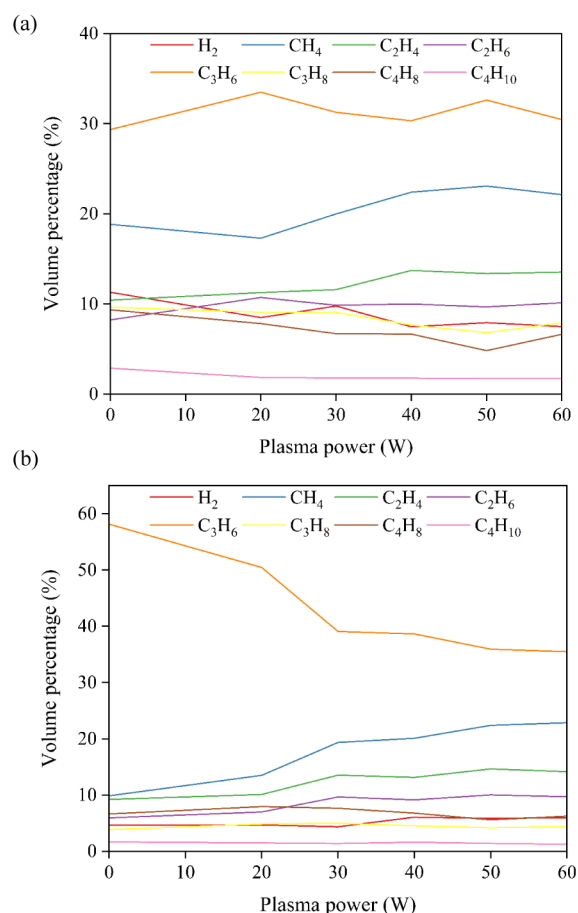


Figure 4. Gas composition (vol %) from the pyrolysis-catalysis of polypropylene over (a) Y-zeolite and (b) β -zeolite as a function of input plasma power.

3.1.2. Effect of Catalyst Temperature. The optimal nonthermal plasma input power that produced the highest BTEX yield was 40 W, therefore, the influence of catalyst temperature at an input power of 40 W was investigated in relation to the β -zeolite and Y-zeolite catalysts. The results, in terms of oil, gas, and BTEX yield, are presented in Figure 5. The results show that as the reaction temperature was raised

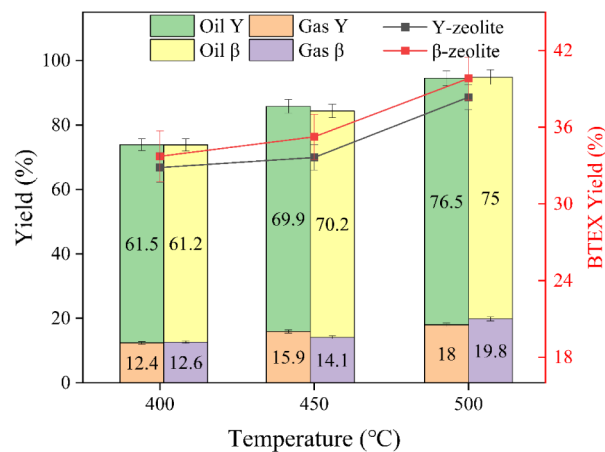


Figure 5. Effect of the second-stage catalyst-nonthermal plasma reaction temperature on the oil, gas, and BTEX yield in relation to the Y-zeolite and β -zeolite catalysts (40 W input power).

from 400 to 500 °C, the gas yield significantly increased from 12.6% to 19.8%, with a consequent increase in oil from 61.5% to 76.5%. The increase in catalyst temperature intensifies endothermic cracking reactions, shifting the product distribution toward thermodynamically more stable, small-molecule gaseous products.⁴²

This study focuses on the effect of temperature on the aromatization reaction pathway and the production of single-ring aromatic compounds: benzene, toluene, ethylbenzene, and xylenes. Figure 5 shows the production of BTEX in relation to catalyst temperature for the Y-zeolite and β -zeolite catalysts in relation to pyrolysis/nonthermal plasma/catalysis of polypropylene (40 W input plasma power). Aromatization is a complex, multistep tandem reaction network involving: (1) the initial cracking of aliphatic hydrocarbons derived from the pyrolysis of the polypropylene plastic; (2) the oligomerization of small-molecule olefins (e.g., propene, butene) produced from cracking; (3) the cyclization of the resulting C6+ chain olefins; and (4) the dehydrogenation of cycloparaffins to form aromatic hydrocarbons.^{43,44} Among these, the cyclization and dehydrogenation steps typically have higher activation energies and are the rate-determining steps for the overall reaction. At lower temperatures of 400 °C and 450 °C, the thermal energy supplied by the system is insufficient to effectively overcome the energy barriers of these steps. Although initial cracking occurs, the subsequent cyclization-dehydrogenation processes proceed very slowly. This leads to a large quantity of C6+ aliphatic intermediates (olefins and alkanes) failing to convert completely, resulting in low concentrations and yields of aromatic hydrocarbons in the oil product. When the temperature is raised to 500 °C, the reaction system gains sufficient activation energy to greatly accelerate the rates of cyclization and dehydrogenation, enabling the efficient conversion of aliphatic intermediates into thermodynamically more stable aromatic hydrocarbons. This allows the selectivity and yield of single-ring aromatic hydrocarbons to reach their peak.

Although higher temperatures (e.g., >550 °C) could theoretically increase reaction rates further, extensive literature reports indicate this often triggers negative effects.⁴⁵ On one hand, excessive cracking produces a large amount of undesirable dry gas (methane, ethane), reducing carbon atom economy. On the other hand, high temperatures dramatically accelerate the rate of coke deposition on the catalyst surface, leading to rapid catalyst deactivation during a short period of performance evaluations.⁴⁶

Figure 6 shows the influence of catalyst temperature on the gas composition in relation to the Y-zeolite and β -zeolite catalysts at 40 W input plasma power. For the Y-zeolite catalyst, the increase in catalyst temperature showed a small reduction in the yield of propene and an increase in methane. For the β -zeolite catalyst, the maximum cracking of propene occurred at 450 °C.

3.1.3. Comparison of Y-Zeolite and β -Zeolite Catalysts. Under the operating conditions of 40 W input plasma power and a catalytic temperature of 500 °C, the gas and oil product compositions from the pyrolysis with nonthermal plasma/catalysis of polypropylene with the Y-zeolite and β -zeolite catalysts were compared. The results, in terms of the detailed oil and gas composition, are shown in Figure 7. The composition of the product gases (Figure 7a) shows that the yields of the C1–C4 gases were relatively similar for both catalysts. However, the propene yield from β -zeolite was

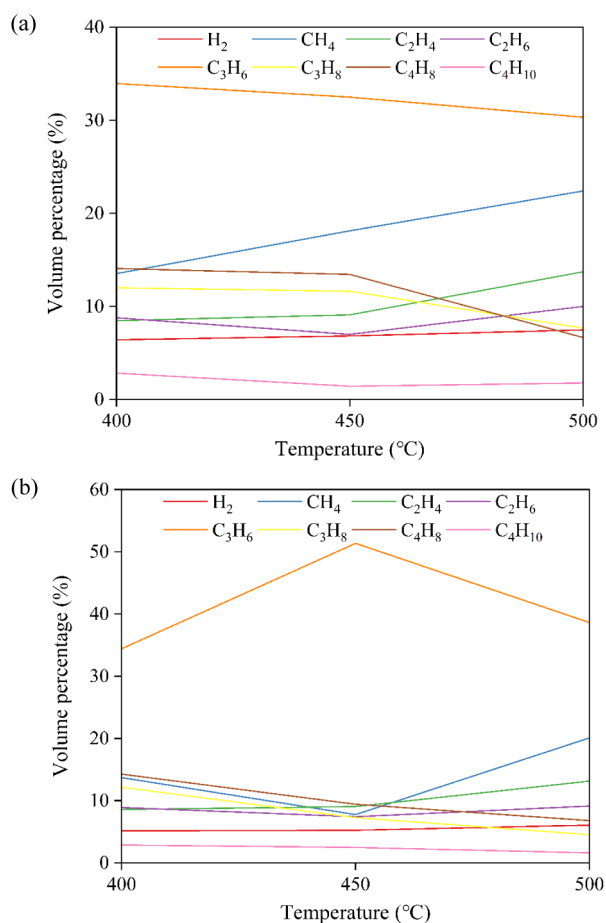


Figure 6. Effect of the second-stage catalyst temperature on the gas composition in relation to the (a) Y-zeolite and (b) β -zeolite catalysts (40 W input power).

~49%, compared to 41% for Y-zeolite, indicating its stronger cracking capability for the derived pyrolysis gases from polypropylene pyrolysis. In conjunction with literature reports, low-carbon-number olefins like propene are often important intermediates for aromatization, suggesting that β -zeolite facilitates an efficient pathway for the formation of alkyl aromatic hydrocarbons.⁴⁷

From the specific BTEX component content shown in Figure 7b, it is evident that β -zeolite demonstrates a quantitative advantage over the Y-zeolite catalyst in relation to the formation of all the BTEX components (benzene, toluene, ethylbenzene, xylene), indicating its stronger promotional effect. This was particularly evident for toluene and xylene yield, for example, the yields of toluene at 15.5% and xylene at 15.7% β -zeolite were significantly higher than those produced using Y-zeolite at 13% and 12%, respectively. This preferential formation of single aromatic hydrocarbons can be attributed to the stronger acidity of the β -zeolite catalyst and its relatively narrow pore structure, which favor dehydrogenation, cyclization, and alkylation reactions of olefin intermediates to form monocyclic aromatic hydrocarbons.⁴⁸ Figure 7c shows that the total BTEX content of the oil obtained using the β -zeolite was approximately 40%, whereas the BTEX content was only 32.5% for the Y-zeolite catalyst. However, the Y-zeolite shows a greater tendency to produce heavy aromatic compounds (Figure 7c), β -zeolite exhibits stronger selectivity toward single-ring lower-carbon-number aromatics, which is

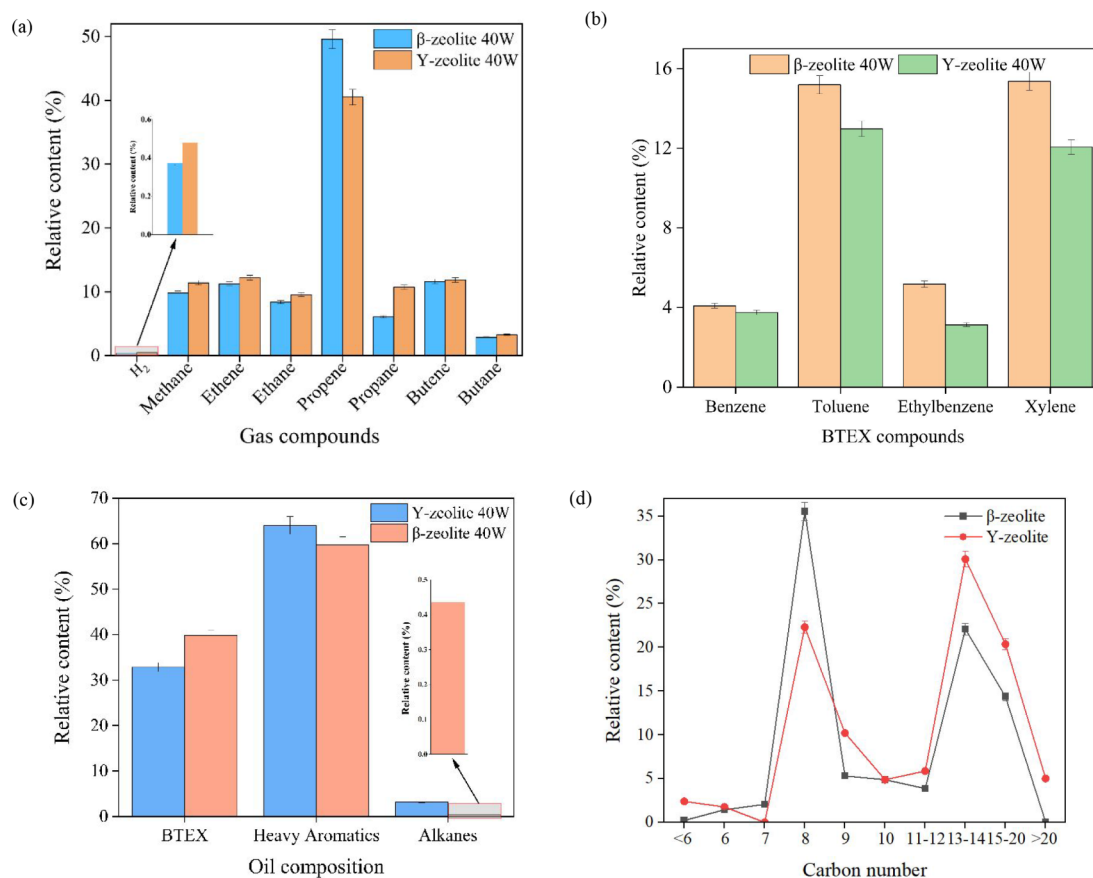


Figure 7. Comparison of Y-zeolite and β -zeolite catalysts for the pyrolysis with nonthermal plasma catalysis of polypropylene in relation to (a) product gas composition, (b) single-ring aromatic compounds (BTEX), (c) total oil composition, and (d) product oil carbon number distribution.

more advantageous for the targeted production of high-value-added chemicals.⁴⁹ The very different Si/Al ratios of the two zeolites will result in different surface acidities, with the low Si/Al ratio of 5 for the Y-zeolite being more acidic (mostly Brønsted acid sites). However, the high Si/Al ratio (360) of the β -zeolite reduces the acidity (reduced Brønsted acid sites), but can lead to higher Lewis acid sites, which are associated with promoting aromatization reactions.^{25,50}

Additionally, the analysis of the oil-phase carbon number distribution shown in Figure 7d also shows that the C8 carbon fraction in the β -zeolite sample reached about 35%, significantly higher than the 22% in relation to the Y-zeolite. The C8 products are primarily xylenes, further verifying strong selectivity for specific carbon-number aromatics in the aromatization reaction exhibited by the β -zeolite catalyst. This characteristic can be attributed to the three-dimensional, intersecting 12-membered ring pore structure of the β -zeolite, which effectively promotes the diffusion and conversion of reaction intermediates, making it particularly suitable for the localized, highly active reaction environment created by the plasma.⁵¹

The β -zeolite catalyst demonstrates very good performance in the selective catalytic cracking for BTEX production. Its strong acidity and specific pore structure characteristics make it more favorable for forming monocyclic aromatic hydrocarbons with high selectivity and yield in polyolefin cracking. Therefore, in the next stage of developing metal-loaded catalysts, β -zeolite was used as the support material to further enhance BTEX yield and selectivity from the processing of

polypropylene using pyrolysis coupled with a nonthermal plasma/catalytic process.

3.2. Influence of Metal-Modified β -Zeolite Catalysts on the Pyrolysis-Catalysis of Polypropylene

3.2.1. Physicochemical Properties of Fresh Metal-Modified β -Zeolite Catalysts. To further optimize catalytic performance in relation to the production of BTEX production from polypropylene, especially the efficiency of the aromatization step, various active metal components (Ga, Mo, Ni, Zn) were introduced onto the β -zeolite catalyst support via the impregnation catalyst preparation method. From previous sections, the catalyst temperature of 500 °C and nonthermal plasma input power of 40 W were identified as the optimum reaction conditions for the investigation of metal- β -zeolite on the yield and composition of the product oils and gases.

The metal- β -zeolite catalysts were characterized using XRD and SEM-EDXS, and their surface area and porosities were also determined. The X-ray diffraction (XRD) spectra of the different metal-based catalysts are shown in Figure 8a and illustrate the crystal structure of the catalysts. All metal-modified samples, including Ga- β , Mo- β , Ni- β , and Zn- β , retained all the characteristic diffraction peaks of the parent β -zeolite (BEA-type structure), such as peaks at 2θ of 22.4° and 29.5°. The peaks remained sharp, with no peak position shift or significant decrease in intensity. This indicates that the metal introduction and subsequent calcination process were mild and did not destroy the delicate framework structure of the zeolite. More importantly, no independent crystalline phase diffraction peaks corresponding to elemental metals or

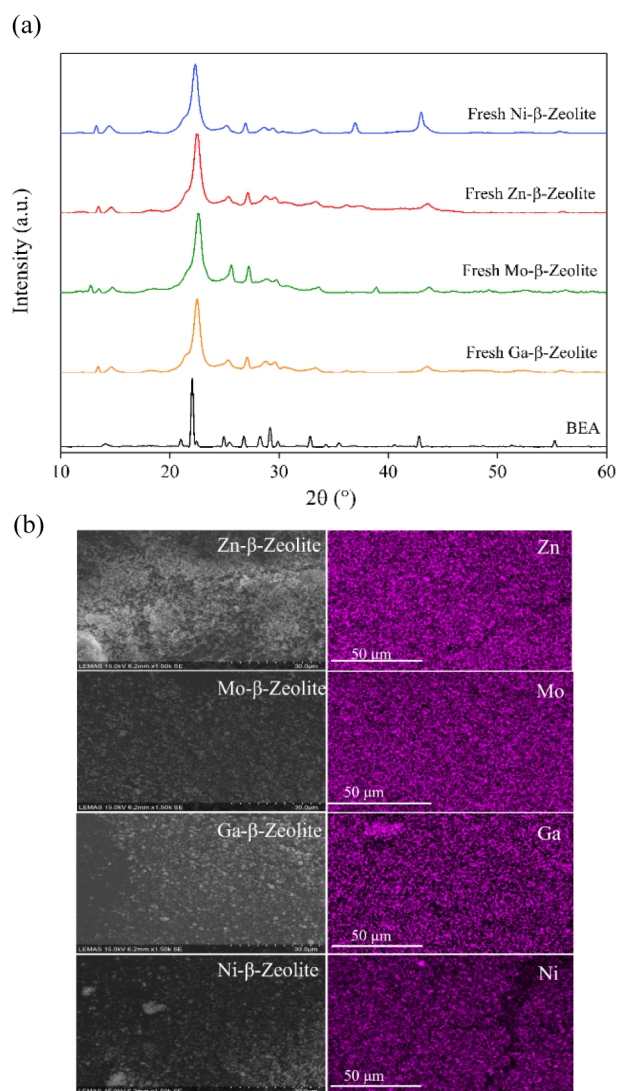


Figure 8. Physicochemical characterization of the fresh catalysts: (a) XRD spectra, (b) representative SEM images, and EDXS metal mapping.

their oxides (e.g., Ga_2O_3 , ZnO , NiO) were observed in the patterns. This provides strong evidence that the metal species exist in a highly dispersed form, as atoms, ions, or nanoclusters, on the zeolite surface or within its pores, with sizes below the lower detection limit of XRD. Such high dispersion is crucial for maximizing the utilization of precious or active metals and providing a greater number of active sites.

The SEM-EDXS elemental mapping in Figure 8b also visually demonstrates that all metal elements (Ga, Mo, Ni, and Zn) are uniformly distributed on the micrometer-sized zeolite particles. This result is highly consistent with the XRD findings and confirms the effectiveness of the preparation methods.

The surface area and porosity of the β -zeolite metal-based catalysts were determined by the N_2 adsorption–desorption data, and the results are shown in Table 2. Also shown is the surface area and porosity data for the Y-zeolite catalyst. The β -zeolite shows superior catalytic potential compared to Y-zeolite in the nonthermal plasma/catalytic pyrolysis of polypropylene. The results also show that Y-zeolite possesses a larger pore volume and pore size, making it more suitable for the diffusion and reaction of large molecules.⁵² Yet, its specific surface area,

Table 2. Textural Properties of the Prepared Catalysts

Zeolite	Pore Volume (cm^3/kg)	Pore Width (nm)	Surface Area (m^2/g)
β -Zeolite	0.2932	1.868	770
Ga- β -Zeolite	0.316	1.868	834
Mo- β -Zeolite	0.2472	1.868	597
Ni- β -Zeolite	0.3183	1.868	857
Zn- β -Zeolite	0.3101	1.868	810
Y-Zeolite	0.4941	2.583	395

at $395 \text{ m}^2 \text{ g}^{-1}$ is much lower than that of pure β -zeolite, at $770 \text{ m}^2 \text{ g}^{-1}$. The β -zeolite catalysts loaded with Ga, Ni, and Zn all maintained very high specific surface areas at, 834, 857, and $810 \text{ m}^2 \text{ g}^{-1}$, respectively, and their pore volumes also increased slightly compared to the fresh β -zeolite. This suggests that these metal species successfully entered the zeolite's pore system without causing significant blockage. However, the Mo- β -zeolite exhibited a significant decrease in both specific surface area ($597 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.247 \text{ cm}^3 \text{ g}^{-1}$). The primary reason for this phenomenon is that the precursor used, ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$), forms large $[\text{Mo}_7\text{O}_{24}]^{6-}$ polyanions in aqueous solution. During impregnation and drying, these large polyanions struggle to enter the smaller pores of β -zeolite and tend to accumulate and decompose at the pore entrance.⁵³ This leads to the blockage of some pore entrances, preventing N_2 molecules from entering these pores for detection.⁵⁴ This indicates that Mo is not a suitable metal to be loaded onto a β -zeolite support using this method.

3.2.2. Acidic Properties of the Metal-Modified β -Zeolite Catalysts. The surface acidity of the catalysts, which plays a pivotal role in the cascade aromatization reactions, was systematically investigated using NH_3 -TPD and Py/Lut-TGA (Figures 9 and 10). The NH_3 -TPD profiles revealed two main desorption regions for the samples: a low-temperature peak (150 – 250°C) corresponding to weak acid sites and a high-temperature peak (350 – 500°C) attributed to strong acid sites. The incorporation of different metals significantly altered the acid strength distribution. Mo- β -zeolite exhibited an overwhelmingly large weak acid peak with a near disappearance of strong acid sites, correlating with the aforementioned pore blockage and the potential neutralization of intrinsic strong acid sites by large molybdate polyanions. Conversely, Ni- β -zeolite showed a broadened and intensified high-temperature peak, indicating an increase in strong acid sites. Ga- and Zn-modified β -zeolites displayed moderate acid strength distributions, which are highly favorable for preventing overcracking while providing sufficient energy for intermediate activation.

To quantitatively decouple the Brønsted (B) and Lewis (L) acid sites, Py/Lut-TGA was employed. As shown in Table 3, the parent β -zeolite possessed a total acidity of 0.869 mmol/g , dominated by Brønsted acid sites (0.798 mmol/g) derived from its framework Al-OH-Si groups. The addition of Ni further increased the B acid density to 0.945 mmol/g . This hyperabundant Brønsted acidity explains its excessively strong hydrogenolysis and cracking capability, which subsequently converts intermediates into light gases rather than aromatics. In stark contrast, the incorporation of Ga and Zn dramatically enhanced the Lewis acidity, increasing from 0.071 mmol/g to 0.226 and 0.290 mmol/g , respectively. These newly generated Lewis acid sites, originating from highly dispersed metal oxides

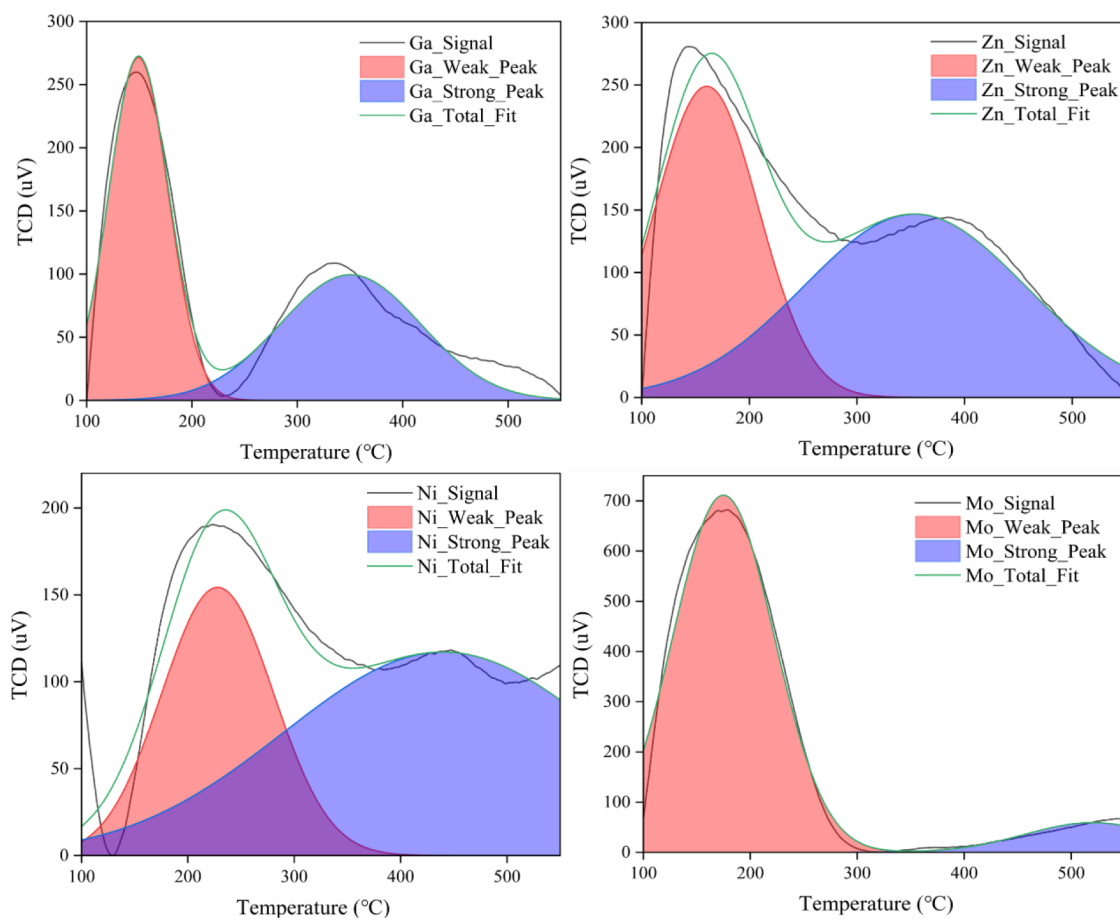


Figure 9. NH₃-TPD results of four different metal-modified catalysts.

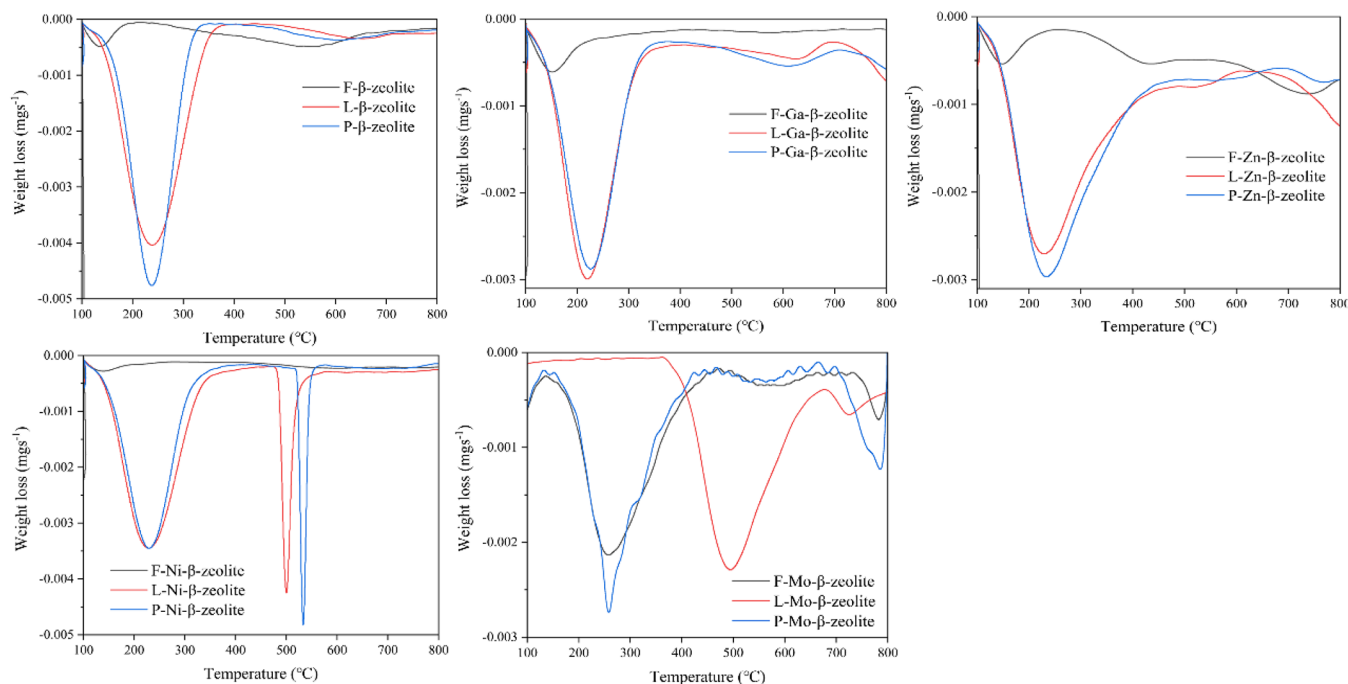


Figure 10. Py/Lut-TGA results of four different metal-modified catalysts.

(e.g., Ga₂O₃ and ZnO nanoclusters), act as potent electron acceptors that selectively catalyze the critical dehydrogenation step. This optimal bifunctional combination—intrinsic

Brønsted acid sites for cracking/cyclization and newly introduced Lewis acid sites for targeted dehydrogenation—perfectly bridges the structural mechanism with the catalytic

Table 3. Total Acidity of Different Catalysts

Zeolite	L+B (mmol/g)	B (mmol/g)	L (mmol/g)
β -Zeolite	0.8689	0.7981	0.0708
Ga- β -Zeolite	0.9410	0.7145	0.2265
Ni- β -Zeolite	1.0332	0.9454	0.0878
Zn- β -Zeolite	1.1200	0.8298	0.2903
Mo- β -Zeolite	0.6839	0.6692	0.0147

performance, explaining why the Ga- β and Zn- β catalysts exhibited the highest BTEX selectivity and yields in the subsequent evaluations.

3.2.3. Pyrolysis-Catalysis of Polypropylene with the Metal- β -Zeolite Catalysts. Initial experiments were carried out using only pyrolysis-catalysis of the polypropylene, i.e., in the absence of the nonthermal plasma environment, to determine the influence of metal addition to the β -zeolite catalyst in relation to oil and gas composition. Experiments were conducted with the four different metal-loaded β -zeolite catalysts, under conditions without any input of the non-thermal plasma (0 W) and at 500 °C catalyst temperature. The results are shown in Figure 11 in relation to the oil, gas, and BTEX yield, as well as gas composition, in relation to the pyrolysis-catalysis of polypropylene. The results show clear differences in the yield and composition of gases and BTEX components, illustrating the controlling role of the introduced metal components on the catalytic pathway. As seen in Figure

11, the Ni- β -zeolite catalyst exhibited the highest gas yield at 21.4% and the lowest BTEX yield at 33.8%. This is because Ni metal is a traditional and extremely active hydrogenation/hydrogenolysis catalyst. During the reaction, it effectively cleaves C–C bonds, cracking large molecules.⁵⁵ In an environment lacking external hydrogen but with hydrogen produced by the pyrolysis and catalytic reaction itself, its powerful hydrogenolysis capability leads to the excessive conversion of aliphatic intermediates into light gases like methane and ethane, severely compromising the selectivity for oil products, especially the target aromatic compounds.⁵⁶ In contrast, the Ga- β -zeolite and Zn- β -zeolite catalysts exhibited superior overall performance, achieving the highest BTEX conversions (with yields reaching 44.4% and 43.4%, respectively) while simultaneously maintaining a substantial yield of gaseous products.

In comparison, the BTEX yield for the β -zeolite without any metal loading was 32.4%. The catalytic metals, Ga and Zn, are recognized as excellent dehydrogenation metals, wherein the aromatization reaction, they form a “bifunctional catalytic” mechanism with the zeolite’s acid sites.⁵⁷ The zeolite Brønsted acid sites are responsible for protonating, isomerizing, and oligomerizing olefins, while the Ga/Zn species (such as Ga⁺ or ZnO) act as Lewis acid sites, greatly accelerating the dehydrogenation step by promoting hydride (H[−]) abstraction. This synergistic effect significantly enhances the overall rate of aromatization.⁵⁸ Figure 11a shows that the performance of the Mo- β -zeolite catalyst produced a BTEX yield of 35.8%. Although Mo also has dehydrogenation capabilities, its performance in terms of BTEX yield was inferior to that of Ga and Zn. This is partly attributed to its potential transformation into molybdenum carbide species under reaction conditions, thereby altering its catalytic properties. The Mo- β -zeolite catalyst may also be negatively affected by metal pore blockage.⁵⁹

Figure 11b shows the composition of the gases produced from the pyrolysis/catalysis of polypropylene (in the absence of plasma) in relation to the metal-modified β -zeolite catalysts. Propene is the main gas produced with the β -zeolite catalyst without any metal addition and is also the main gas produced using the Ga- β -zeolite and Mo- β -zeolite catalysts, suggesting that the catalytic process is less effective at cracking the polypropylene-derived propene. In contrast, the Zn- β -zeolite and Ni- β -zeolite catalysts produced much smaller amounts of propene but increased concentrations of ethane and propane.

Figure 12 provides a detailed breakdown of the oil compositions for each of the β -zeolite metal-modified catalysts for the pyrolysis-catalysis of polypropylene at a catalyst temperature of 500 °C (in the absence of nonthermal plasma). Figure 12a displays the composition of the oil products in relation to the total BTEX, heavy aromatic compounds, and alkanes in the product oil from the pyrolysis-catalysis of polypropylene in relation to the metal- β -zeolite catalysts. The influence of all four metals addition to the β -zeolite results in only a small amount of alkanes. In terms of BTEX selectivity, Ga produced the highest BTEX yield, while also having a relatively low selectivity for heavy aromatics (PAHs). This indicates that Ga- β -zeolite catalyst not only efficiently generates the target BTEX products but also effectively inhibits the further conversion of BTEX into larger-molecule PAHs. The primary reason is that, while Ga metal has high dehydrogenation activity, its activity for catalyzing intermolecular polymerization is much weaker. The reaction is

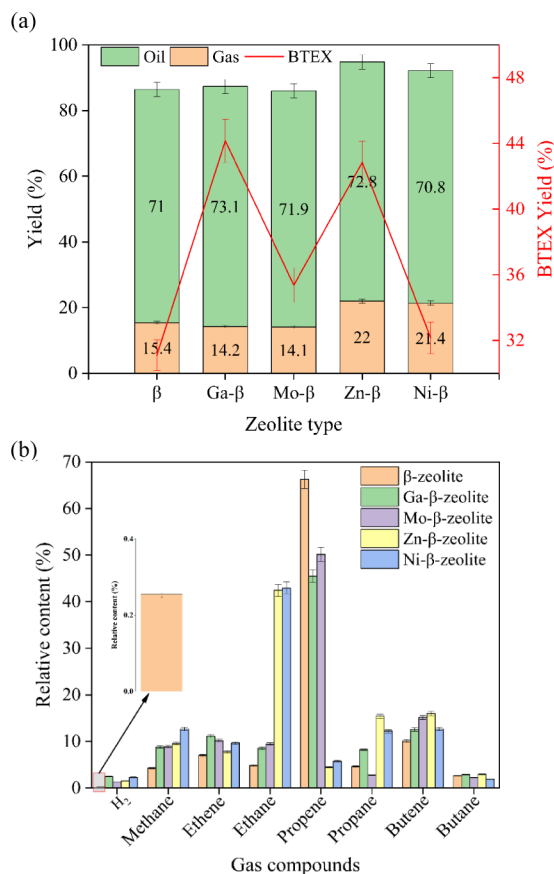


Figure 11. Influence of metal-based β -zeolite catalysts on (a) the oil and gas yield and BTEX yield and (b) gas composition in relation to the pyrolysis-catalysis of polypropylene (in the absence of nonthermal plasma).

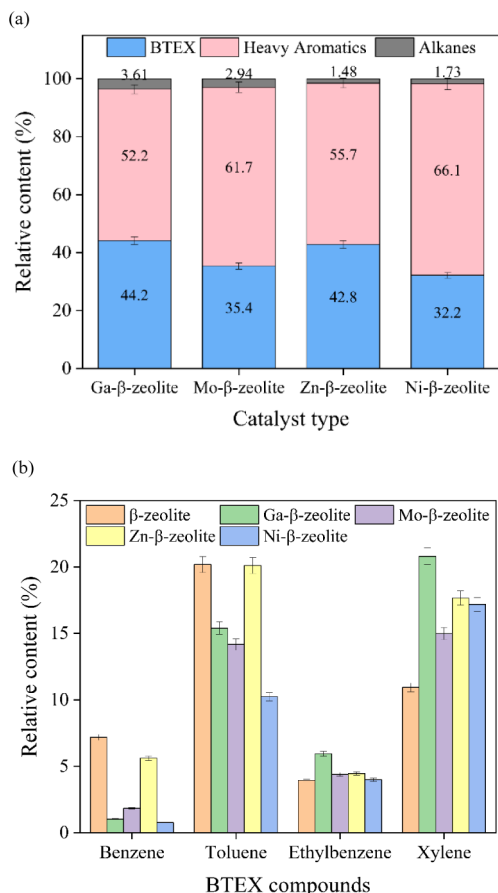


Figure 12. Composition of the product oil in terms of (a) total BTEX, heavy aromatic compounds, and alkanes, and (b) BTEX compound yields, in relation to the different metal-modified β -zeolite catalysts for the pyrolysis-catalysis of polypropylene.

primarily confined within the zeolite pores and is strictly controlled by the shape-selectivity effect. Once appropriately sized molecules like xylenes are formed, they can readily diffuse out, and the narrow space within the pores effectively inhibits their continued polymerization into larger molecules.⁶⁰ This modification by Ga allows the reaction to stop at the monocyclic aromatic stage.

Figure 12b shows the changes in benzene, toluene, ethylbenzene, and xylene component yields in relation to the metal- β -zeolite type. The results show that, compared to unmodified β -zeolite, Ga, Ni, and Mo all effectively suppressed the formation of benzene and toluene and increased the selectivity toward xylene. The performance of Zn- β -zeolite was relatively close to the unmodified catalyst in most aspects, only increasing the xylene conversion rate. Among the four metals, only Ga could both suppress benzene and toluene formation while also effectively increasing the selectivity for ethylbenzene and xylene, highlighting the superiority of Ga- β -zeolite in enhancing the selectivity for high-value products. The main reason is that the introduction of Ga greatly increases the conversion rate of light alkanes to aromatics and the aromatic selectivity, with its core function being the promotion of the dehydrogenation step.⁶¹

Figure 13 shows the carbon number distribution of the oil produced from the pyrolysis-catalysis of polypropylene (in the absence of plasma) in relation to the metal-modified β -zeolite catalysts. The β -zeolite catalysts produced peak C8–C9 carbon

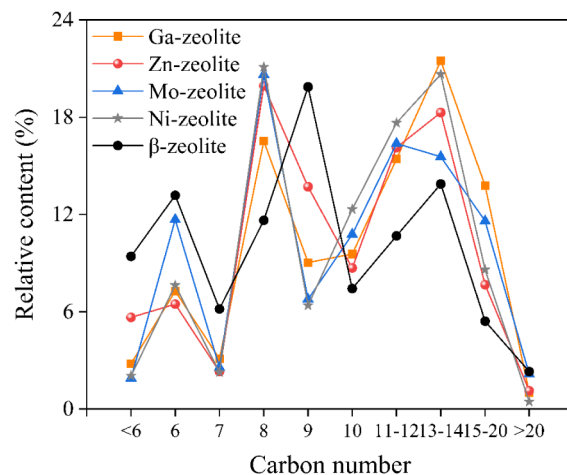


Figure 13. Carbon number distribution in the oil produced from the pyrolysis-catalysis of polypropylene (in the absence of plasma) in relation to the metal-modified β -zeolite catalysts.

fractions, representing the single-ring aromatic compounds found in the product oil. In addition, higher-range carbon numbers in the range of C11–C20 were also present.

3.3. Pyrolysis/Nonthermal Plasma Catalysis of Polypropylene with the Metal- β -Zeolite Catalysts

3.3.1. Product Yield, Oil and Gas Composition. To investigate the impact of adding nonthermal plasma to the catalytic pyrolysis of polypropylene, the product changes for the four different metal-modified catalysts at 0 W (purely catalytic pyrolysis) and 40 W plasma power, with both the pyrolysis and catalytic temperatures set at 500 °C. The product and BTEX yield results are shown in Figure 14. As can be seen

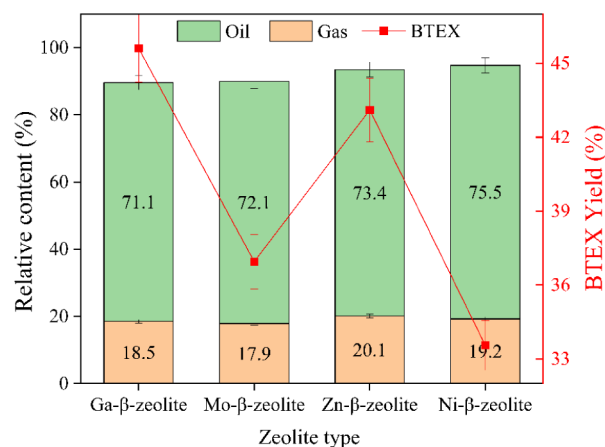


Figure 14. Oil, gas, and BTEX yield from the pyrolysis/nonthermal plasma/catalysis of polypropylene in relation to the metal-modified catalysts.

from Figure 14, under both conventional heating and nonthermal plasma-assisted pyrolysis conditions, the oil product yield and BTEX yield followed the same order: Ga- β -zeolite > Zn- β -zeolite > Mo- β -zeolite > Ni- β -zeolite. Furthermore, under plasma-assisted pyrolysis, Ga- β -zeolite achieved the highest BTEX yield of 45.6%. It can also be observed that, with the introduction of plasma assistance, the BTEX selectivity of all four metal-modified catalysts improved to some extent. This indicates the existence of a synergistic

effect between the plasma and the catalysts, which helps to enhance the product selectivity toward BTEX.

By comparing the gas component content for each metal-modified catalyst without plasma assistance (Figure 11b) and in the presence of the nonthermal plasma (Figure 15), it is

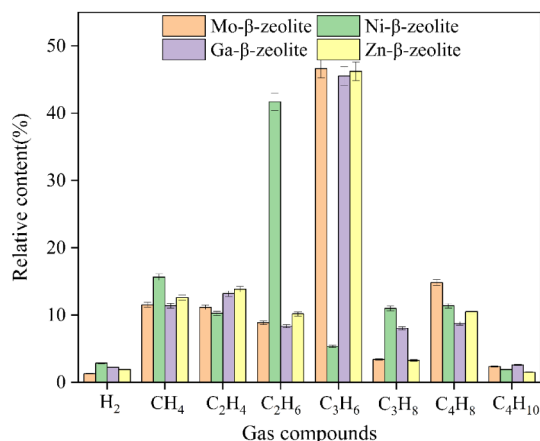


Figure 15. Gas composition from the pyrolysis/nonthermal plasma/catalysis of polypropylene in relation to the metal-modified catalysts (40 W input plasma power and 500 °C catalyst temperature).

evident that the content of smaller molecules like methane and ethene increased slightly after the introduction of plasma. Although this came at the expense of a small portion of propene production, it further demonstrates that nonthermal plasma can indeed crack the feedstock into smaller, active fragments.

The most unique case among them is Zn- β -zeolite. With the introduction of plasma, its product distribution shifted from a very high ethane yield (42.4%) to an extremely high propylene yield (46.2%). This suggests that the influence of plasma on Zn- β -zeolite causes a fundamental shift in the reaction pathway. The interaction between the plasma and the active sites of Zn- β -zeolite guides the reaction toward the formation of propylene, a more favorable intermediate for BTEX synthesis. This illustrates the potential of nonthermal plasma in controlling product selectivity.

Figure 16a displays a comparison of the oil component compositions and specific BTEX content for the different metal-modified catalysts, for BTEX, heavy aromatic compounds, alkanes, and the individual BTEX compounds from the pyrolysis nonthermal plasma/catalysis of polypropylene in relation to the metal-modified β -zeolite catalysts. From Figure 16a, it is evident that for all four catalysts, the relative content of BTEX increased after the introduction of nonthermal plasma: Ga- β -zeolite increased from 44.2% to 45.6%, Mo- β -zeolite from 35.4% to 37.0%, Zn- β -zeolite from 42.8% to 43.1%, and Ni- β -zeolite from 32.2% to 33.6%. This serves as strong evidence that the synergistic effect of the nonthermal plasma favors the reaction pathway toward generating more BTEX. Concurrently, for the Ga, Mo, and Zn catalysts, the introduction of plasma also effectively suppressed the production of long-chain alkanes. This effect was particularly significant for Ga, with alkane content decreasing from 3.61% to 1.26%, signifying that a purer product can be obtained with higher selectivity for the aromatization reaction. In contrast, the Ni catalyst produced more long-chain alkanes, suggesting that in the Ni catalytic system, the addition of plasma might

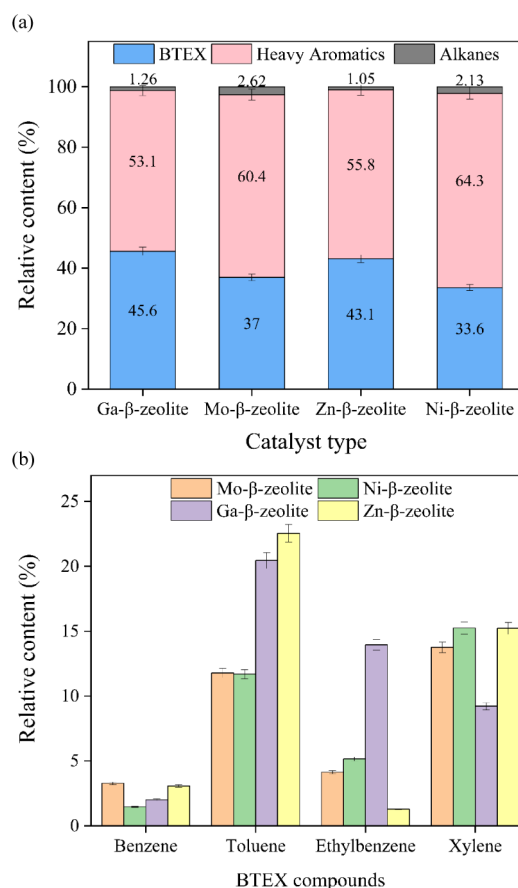


Figure 16. Composition of the product oil in terms of (a) BTEX, heavy aromatic compounds, and alkanes, and (b) individual BTEX compounds from the pyrolysis nonthermal plasma/catalysis of polypropylene in relation to the metal-modified β -zeolite catalysts (40 W input plasma power and 500 °C catalyst temperature).

simultaneously promote side reactions such as hydrogenation, which forms alkanes.⁶²

Figure 16b shows a comparison of the specific BTEX component content in the products obtained in the presence of the nonthermal plasma. The results for Ga and Zn show that although the introduction of nonthermal plasma increased the total amount of BTEX, it was compared to the pyrolysis-catalysis experiments without the nonthermal plasma. For both, the xylene content decreased while the toluene content increased, which suggests that the high-energy particles in the nonthermal plasma can break the methyl side chains on the benzene ring, causing a dealkylation reaction.⁶³ In the results for Ni and Mo, both xylene and toluene contents decreased, accompanied by an increase in benzene content. This also indicates that the energy from the nonthermal plasma shifts the reaction toward aromatics with lower carbon numbers and simpler structures.

Observing from the perspective of heavy aromatics, the Ga catalyst generated a significantly lower content in its products compared to the other three catalysts. Furthermore, as seen in the carbon number distribution results for the oil products from the four catalysts shown in Figure 17, the carbon numbers are primarily distributed in the C6–C8 and C13–C20 ranges. After introducing the nonthermal plasma, the content in the higher carbon number range noticeably decreased, while the proportion in the C6–C8 range increased

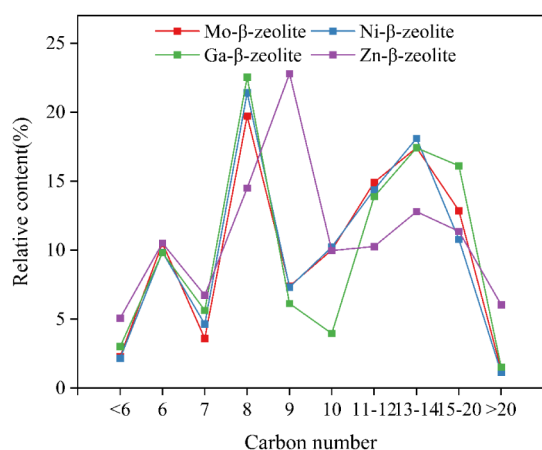


Figure 17. Carbon number distribution of the product oils produced from the pyrolysis nonthermal plasma/catalysis of polypropylene in relation to the metal-modified β -zeolite catalysts (40 W input plasma power and 500 °C catalyst temperature).

to varying degrees for all catalysts, with the effect being particularly pronounced for Ga and Zn. In general, the introduction of nonthermal plasma can, in most cases, reduce the production of heavy aromatics and alkanes, shifting the reaction to generate more BTEX.

3.3.2. Coke Deposition Analysis. Coke deactivation of the catalyst is a core challenge in the catalytic aromatization process. In this study, the postreaction catalysts were characterized using thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG), with the results shown in Figure 18a and 18b, respectively.

The weight loss in the TGA curves of Figure 18a directly reflects the amount of coke deposited on the catalyst surface. By comparing the residual weight percentage at 800 °C, the amount of coke can be ranked as follows: Y-zeolite (20.3 wt.% coke) > β -zeolite (12.9 wt.% coke) > Ni- β -zeolite (12.2 wt.% coke) > Ga- β -zeolite (9.4 wt.% coke) > Zn- β -zeolite (8.2 wt.% coke) > Mo- β -zeolite (5.8 wt.% coke). This sequence clearly indicates that coking is most severe on Y-zeolite, which is related to its large-pore structure that readily facilitates the formation and storage of large-molecule coke precursors. Within the β -zeolite series, the amount of coke shows a strong negative correlation with catalytic performance. The Ga- β and Zn- β catalysts, which showed the best aromatization performance in the previous results, had the least amount of coke, whereas the poorer-performing pure β -zeolite and Ni- β -zeolite had significantly more coke. The case of Mo is rather special; the most likely reason for it having the least coke is the presence of agglomeration during its loading, which may allow the coke to be removed in whole chunks during combustion.

The DTG curves in Figure 18b reveal the combustion characteristics of the deposited coke. The DTG curves for all β -based catalysts show a primary combustion peak below 600 °C, which is typically attributed to the relatively easy-to-combust amorphous-type carbon located within the zeolite pores. This type of coke has a higher H/C ratio and is well-defined. In contrast, Y-zeolite exhibits a very broad and strong peak around 550 °C, indicating that the coke species are more complex and likely contain more highly graphitized carbon, which requires higher temperatures for oxidation.⁶⁴

By combining the coke analysis with the catalytic performance evaluation from the previous section, a core conclusion

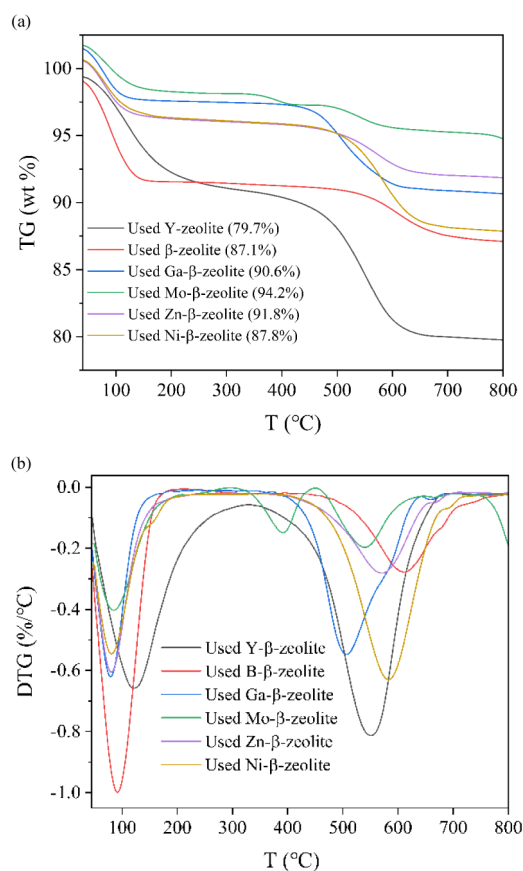


Figure 18. Temperature-programmed oxidation analysis of the used catalysts from the pyrolysis nonthermal plasma/catalysis of polypropylene in relation to the metal-modified β -zeolite catalysts (40 W input plasma power and 500 °C catalyst temperature). 18(a) TGA, 18(b) DTG thermograms.

can be drawn: high aromatization efficiency is the key to suppressing coke formation. In the catalytic reaction, coke mainly originates from the deep polymerization and cyclization of unsaturated intermediates such as olefins.⁶⁵ On the Ga- β and Zn- β catalysts, due to their excellent dehydrogenation-cyclization functionality, these highly active olefin intermediates are rapidly converted into thermodynamically stable aromatic products, which then desorb. This efficient target reaction pathway creates a competitive relationship with the side reaction pathway of coke formation. The faster the rate of the former, the lower the concentration of precursors available for coking, thereby inhibiting coke formation at its source.

3.3.3. XRD and XPS Analysis of the Catalysts. To investigate whether the catalyst structure remained stable before and after the reaction, the XRD patterns of each catalyst from before and after the experiment were compared, the results shown in Figure 19a. As can be seen from the results, all postreaction catalysts successfully retained the complete set of characteristic diffraction peaks of β -zeolite, without any shift in their positions. This is a positive result, indicating that the framework structure of the metal-loaded catalysts did not collapse during the reaction and that they possess good structural stability.

In terms of diffraction peak intensity, only the Ni- β catalyst showed a significant loss in crystallinity, while the other metals maintained a relatively stable state. The reason for the loss of crystallinity in the Ni catalyst is likely related to the numerous

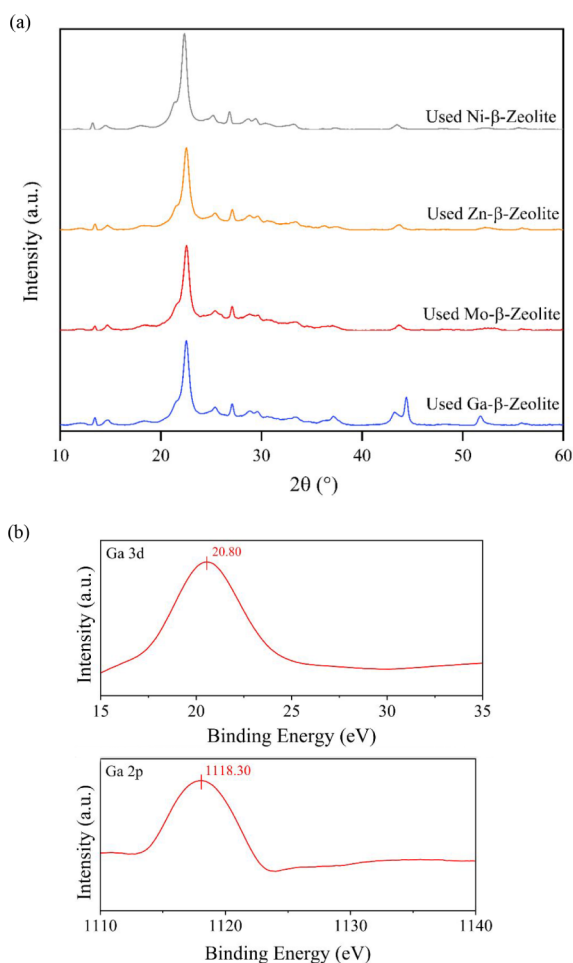


Figure 19. (a) X-ray diffraction analysis of the used catalysts from the pyrolysis non thermal plasma/catalysis of polypropylene in relation to the metal-modified β -zeolite catalysts, and (b) XPS analysis of the unused Ga- β -zeolite.

side reactions mentioned earlier, which lead to a more vigorous overall reaction. This exerted a greater physical and chemical impact on the catalyst framework.⁶⁶ The XRD analysis results provide structural-level support for the preceding performance evaluation.

With its excellent performance, good coke resistance, and outstanding structural stability, Ga- β -zeolite has emerged as the most promising catalyst for the synergistic pyrolysis of polypropylene in the presence of nonthermal plasma. To investigate the potential reaction mechanism behind this result, an XPS analysis was performed on the unused Ga- β -zeolite, with the results shown in Figure 19b. From the Ga 3d and 2p spectra, it can be clearly seen that the binding energies are 20.8 eV and 1118.3 eV, respectively. These values differ significantly from the binding energies of metallic Ga (Ga^0), which are 18.5 eV (3d) and 1116.6 eV (2p), but they are in perfect agreement with the binding energies for Ga_2O_3 (Ga^{3+}) in these respective spectra. This indicates that the Ga element exists on the catalyst in the form of gallium oxide with a +3-oxidation state.

Furthermore, combining this with the previous EDXS results, it is confirmed that gallium oxide is uniformly distributed as nanoclusters on the zeolite surface. The absence of metallic Ga^0 also confirms that no reduction reactions occurred during the preparation. Well-dispersed gallium oxide is an important indicator of a successfully prepared catalyst.

Although Ga^{3+} itself is not the most reactive state, it serves as the perfect precursor to the truly active species (such as Ga^+). In industrial catalysis, having a stable precursor that is easy to store and transport is of great importance. After the catalyst is loaded into the reactor, it is under the specific reaction atmosphere (in situ activation) that these well-dispersed Ga^{3+} precursors are transformed into the active sites that perform the actual catalytic function.⁶⁷

The acidity characteristics of β -zeolite with a high Si/Al ratio (ca. 360) have been reported in the literature. It is well established that such a high Si/Al ratio results in a very low concentration of framework aluminum atoms, thereby significantly reducing the number of bridging hydroxyl groups responsible for Brønsted acidity.⁵⁰ Therefore, the surface acidity is predominantly derived from coordinatively unsaturated framework or extraframework aluminum species, which behave as Lewis acid sites. In addition, the introduction of metal species can further contribute to the formation of Lewis acid sites, since the metal cations or their oxides can act as electron pair acceptors on the zeolite surface.⁶⁸ Additionally, it has been reported that zeolite Ga-Lewis acid sites strongly favor aromatization reactions.⁶⁹ Therefore, based on the known structural features of high-silica β -zeolite and the influence of metal loading, the catalyst used in this study can be reasonably regarded as possessing mainly Lewis acid sites with limited Brønsted acidity, which is consistent with previously reported observations.⁷⁰

3.4. Proposed Reaction Pathway

In the nonthermal plasma-assisted catalytic pyrolysis of polypropylene over Ga-loaded β -zeolite, a strong synergistic effect is observed among plasma activation, acid catalysis, and Ga-related chemical functions. As illustrated in Figure 20, polypropylene is first thermally degraded at a temperature of ~ 500 °C into long-chain alkenes and alkanes. These primary intermediates are further activated by plasma-generated reactive species—such as electrons, radicals, and photons—which initiate C–C bond cleavage, β -scission, isomerization, and decomposition reactions, thereby enhancing the formation of reactive hydrocarbon fragments.⁷¹ The introduction of Ga significantly modifies the acid properties and the active site distribution of β -zeolite. Four types of acid sites are present: Brønsted acid sites, framework Al-based Lewis acid sites, and two types of Ga-related Lewis acid sites.⁷² In addition, Ga species provide mild metal-like activity that facilitates the dehydrogenation of intermediates, which is essential for aromatization. Brønsted acid sites mainly catalyze cracking, isomerization, and cyclization, while Lewis acid sites promote alkylation, dealkylation, and aromatization reactions.⁶⁷ In the aromatization stage, chain hydrocarbons are cyclized into cycloalkanes and subsequently dehydrogenated to form monocyclic aromatics. The presence of Ga improves this transformation by stabilizing intermediate species and lowering the energy barrier. The formed aromatic compounds undergo secondary reactions such as alkylation, transalkylation, isomerization, hydrogen transfer, condensation, and dealkylation, ultimately yielding single-ring BTEX compounds (benzene, toluene, ethylbenzene, and xylenes).⁷³

Meanwhile, the nonthermal plasma continues to play a critical role by generating energetic species that can activate ring-opening reactions, promote hydrogen abstraction, and decompose intermediates that may otherwise lead to coke formation. The interaction between plasma and catalyst is

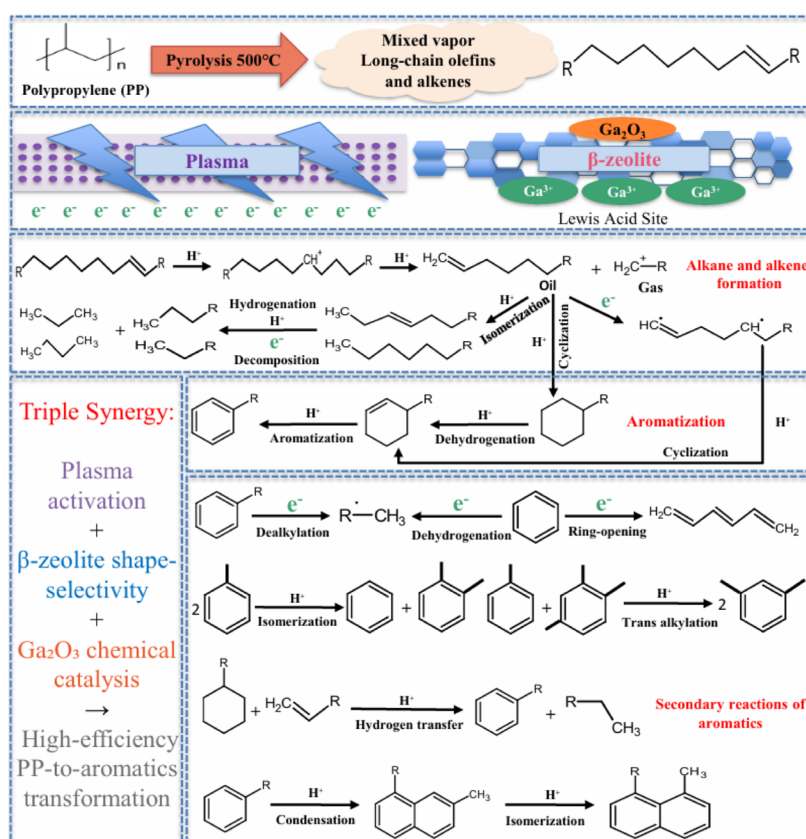


Figure 20. Proposed reaction pathway for the two-stage pyrolysis and plasma-assisted catalytic upgrading of polypropylene.

mutual: while plasma alters the surface properties, acidity, and Ga distribution of the zeolite, the catalyst also influences plasma behavior by modifying the local electric field, discharge mode, and microdischarge characteristics.⁷⁴ Compared with other metal-loaded $\beta\text{-zeolites}$ (e.g., Mo, Ni, Zn), the Ga-loaded catalyst shows superior BTEX selectivity. This is attributed to the properties of gallium in terms of moderate Lewis acidity, effective dehydrogenation ability, and strong compatibility with the shape-selective pore structure of $\beta\text{-zeolite}$.⁷⁵ Together, these factors suppress polyaromatic and coke formation while enhancing the formation of light aromatic compounds. In summary, the enhanced BTEX production observed with the Ga/ $\beta\text{-zeolite}$ system arises from a triple synergy: nonthermal plasma activation, shape-selective acid catalysis, and Ga-induced chemical promotion. Each component plays a unique but complementary role in facilitating the efficient transformation of polypropylene into the high-value single aromatic compounds, benzene, toluene, ethylbenzene, and xylenes.

Overall, this work has shown that the pyrolysis/nonthermal plasma/catalysis process for the processing of waste polypropylene plastic can produce a product oil with high concentrations of benzene, toluene, ethylbenzene, and xylenes. The BTEX chemicals are higher-value industrial chemicals, accounting for almost 25% of the global chemical market.⁷⁶ They are used as intermediates to make a wide range of secondary valuable feedstock chemicals and eventually end-use products, such as plastics, solvents, pharmaceuticals, paints, insecticides, and dyes. The current production of BTEX chemicals on an industrial basis is by the catalytic refining of naphtha produced from fossil fuel petroleum crude oil via the petrochemical industry. Since almost all plastics are also produced from petroleum crude oil, producing BTEX from

waste plastics would offset the use of new petroleum crude oil resources for the production of these chemicals, while also mitigating the problematic environmental impact of waste plastics.

4. CONCLUSIONS

This work has investigated the application of nonthermal plasma/catalysis for the upgrading of pyrolysis volatiles derived from the pyrolysis of waste polypropylene plastic to produce a product oil enriched with higher-value single-ring aromatic compounds. The main aromatic compounds produced were benzene, toluene, ethylbenzene, and xylenes (BTEX). The influence of different nonthermal plasma/catalysis revealed that a plasma input power of 40 W and catalyst temperature of 500 °C were optimal for BTEX production. Pyrolysis/nonthermal plasma/catalysis experiments compared Y-zeolite and $\beta\text{-zeolite}$ catalysts and showed that the $\beta\text{-zeolite}$ produced higher yields of BTEX at 40% compared to the Y-zeolite, which produced a 32.5% yield. Addition of metal promoters (Ni, Ga, Zn, Mo) to the $\beta\text{-zeolite}$ catalyst resulted in an increase in BTEX yield for the pyrolysis/nonthermal plasma/catalysis process. The highest yield of BTEX was 45.6%, produced with the Ga- $\beta\text{-zeolite}$ catalyst, and was attributed to the synergy between the pyrolysis volatiles produced from the pyrolysis of polypropylene interacting with the acidic properties and crystalline structure of the $\beta\text{-zeolite}$ catalyst, promoted by the gallium and enhanced by the nonthermal plasma reaction environment.

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