

Article

Effects of Metal–Acid Proximity on Aromatics Production in CO₂-Assisted Catalytic Pyrolysis of Polypropylene over Fe-Modified ZSM-5

Yao He ¹, Jie Zhang ¹, Renhua Huang ¹, Nanxin Li ¹ and Yunwu Zheng ^{2,*}

¹ Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China

² Key Laboratory of National Forestry and Grassland Administration on Highly-Efficient Utilization of Forestry Biomass Resources in Southwest China, College of Materials and Chemical Engineering, Southwest Forestry University, Kunming 650224, China

* Correspondence: zyw85114@swfu.edu.cn

Abstract

CO₂-assisted catalytic pyrolysis presents a viable and promising approach to addressing plastic waste pollution and mitigating climate change. However, the effects of the metal–catalyst combination mode and the spatial distance between metal–acid sites on catalytic performance remain unclear. In this study, the reaction behaviors of the configurations, Fe₃O₄ and ZSM-5 in tandem catalysis (Fe₃O₄&HZ), their physical mixture (Fe₃O₄-HZ), and Fe-loaded ZSM-5 (Fe/HZ), were compared in polypropylene pyrolysis under a CO₂ atmosphere. The aromatic contents followed this order: Fe/HZ > Fe₃O₄-HZ > Fe₃O₄&HZ > ZSM-5 > Fe₃O₄. Specifically, Fe/HZ with the highest degree of metal–zeolite proximity achieved an aromatic content of 66.1%, significantly higher than the 34.2% obtained with Fe₃O₄&HZ, demonstrating that closer metal–acid proximity promoted aromatic formation. Moreover, Fe/HZ significantly reduced coke deposition. Based on characterization results from XRD, SEM, TEM, XPS, and NH₃-TPD, the enhanced spatial proximity between metal and acid sites strengthened the functional synergy between iron-based redox sites and zeolitic Brønsted acid sites. This synergy facilitated the reverse water–gas shift reaction of CO₂, which consumed hydrogen generated during aromatization and shifted the reaction equilibrium toward enhanced aromatic production. These findings would offer theoretical and strategic insights into the optimization of CO₂-assisted catalytic pyrolysis systems for the sustainable upcycling of plastic waste.

Keywords: catalytic pyrolysis; aromatics production; metal–acid proximity; CO₂-assisted; Fe-modified ZSM-5



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1. Introduction

Plastics dominated by polyolefin are widely used in many industries such as packaging, transportation, and clothing due to their light weight, durability, high plasticity, and cost-effectiveness [1,2]. According to data from the United Nations Environment Programmer, more than 430 million tons of plastics are produced globally every year, with continued annual growth observed [3]. Correspondingly, the escalating accumulation of plastic waste has emerged as a critical global challenge. Only 9% of plastic waste has been recycled, while the overwhelming majority of the remainder is disposed of through landfilling and incineration [4,5]. This not only exacerbates greenhouse gas emissions and environmental degradation but also leads to significant resource wastage. Consequently, it

is of great significance to explore technologies that can recycle plastic waste and transform it into valuable chemicals.

Compared with other recycling technologies, thermal chemical recycling demonstrates greater capability for large-scale waste processing and represents an effective approach to the resource recovery of plastic waste [6–8]. Among these methods, pyrolysis has recently garnered increased attention due to its potential to convert plastic waste into high-value chemicals in an environmentally sustainable manner, such as benzene, toluene, ethylbenzene, and xylene (BTEX) [9–11]. Pyrolysis primarily includes the traditional thermal cracking and catalytic pyrolysis. Thermal cracking of plastics typically requires high temperatures in the range of 600–1000 °C and tends to produce a significant number of waxy byproducts [12,13]. To overcome these limitations, the incorporation of catalysts has been demonstrated to effectively lower the required reaction temperature (450–600 °C) and reduce energy consumption, while enabling selective control over product distribution [14,15]. Hence, this catalytic pyrolysis has the potential to significantly enhance the yield of high-value products.

The selection of catalysts plays a crucial role in determining the product distribution from plastic pyrolysis. Among various catalysts, ZSM-5 zeolite exhibits exceptional performance in the reaction of preparing aromatics from plastic pyrolysis, owing to its distinctive acidity and shape selectivity [16–19]. The modification of ZSM-5 through the introduction of specific metals (e.g., Fe, Ga, and Zn) enables precise regulation of acidity and dehydrogenation activity, thereby significantly enhancing aromatic yield as well as improving resistance to carbon deposition [10,20,21]. Metallic iron exhibits potential as a modifier for ZSM-5 zeolite owing to its abundance, low cost, and low toxicity [22,23].

On the other hand, the substantial rise in atmospheric CO₂ emissions has intensified the greenhouse effect, thereby accelerating global warming [24–26]. In response to this pressing environmental challenge, the development of effective CO₂ mitigation strategies has become a widely shared priority across scientific and policy communities. Consequently, catalytic utilization of CO₂ as a reactant or co-reactant for the synthesis of value-added chemicals has emerged as a rapidly growing research frontier [27–34]. Among emerging carbon utilization pathways, CO₂-assisted catalytic pyrolysis of plastics represents a particularly promising dual-benefit approach, which is attributed to the fact that it enables chemical recycling of waste plastics into high-value aromatic hydrocarbons while simultaneously consuming CO₂ [35–37]. Recent studies have demonstrated notable improvements in aromatic yield using metal–zeolite bifunctional catalyst systems. For instance, Chen et al. [38] employed a physically mixed Cu-Fe₃O₄/Zn-ZSM-5 catalyst under CO₂ co-feeding conditions, achieving an increase in aromatic hydrocarbon yield from 30.7 wt.% (under Ar) to 39.5 wt.% during polyethylene (PE) upgrading. Similarly, Zhang et al. [39] reported that ZSM-5 loaded with metallic Ga exhibited strong synergistic effects when coupled with CO₂, elevating the selectivity of BTEX to over 60% in low-density polyethylene (LDPE) pyrolysis. Although both catalyst systems with different degrees of proximity between metals and zeolites have enhanced the performance of producing aromatic hydrocarbons in CO₂-assisted plastic pyrolysis, their comparative performance under the rapid pyrolysis of plastics in a continuous-flow tubular furnace remains unexplored. Mechanistically, CO₂ primarily acts as an in situ hydrogen acceptor to participate in the reverse water–gas shift (RWGS) reaction in the plastic pyrolysis process [40]. However, the effects of the metal–catalyst combination mode and the spatial distance between metal–acid sites on catalytic performance remain unclear in CO₂-assisted plastic pyrolysis.

In this study, proton-form ZSM-5 (HZ) is synthesized via the method of hydrothermal synthesis. On this basis, Fe/HZ with the closest metal–zeolite components is prepared by incipient wet impregnation. Subsequently, comprehensive physicochemical characteri-

zations are performed to systematically evaluate structural and acidic property changes induced by Fe loading. Furthermore, physical composites of HZ and Fe_3O_4 are fabricated through varied methods of combination to achieve controlled degrees of metal–acid spatial proximity. The influence mechanism of the proximity of the dual-component system on the performance of plastic pyrolysis to produce aromatics under a CO_2 atmosphere was systematically investigated. This work will provide mechanistic insight into the application of bifunctional catalysts in plastic pyrolysis to promote circular economy strategies for plastic waste valorization.

2. Results and Discussion

2.1. Characterization

The XRD patterns of Fe-free HZ and Fe/HZ samples are shown in Figure 1. The five labeled characteristic diffraction peaks in the range of $7\text{--}9^\circ$ and $22\text{--}25^\circ$ display the typical diffraction patterns of MFI topological structure. The characteristic peak positions of the Fe-modified zeolite and the unmodified HZ zeolite are not significantly different, which indicates that the introduction of iron does not cause any damage to the MFI structure of ZSM-5 [36,41]. Conversely, compared with HZ, the decrease in characteristic peak intensities of Fe/HZ is attributed to the dilution effect caused by the addition of Fe species [20,42]. It can be observed that almost no difference in the XRD patterns of the HZ and Fe/HZ samples and no additional peaks of Fe oxides appear, indicating that the Fe species are uniformly distributed in the Fe/HZ due to the low content of metal (1 wt.%) [43].

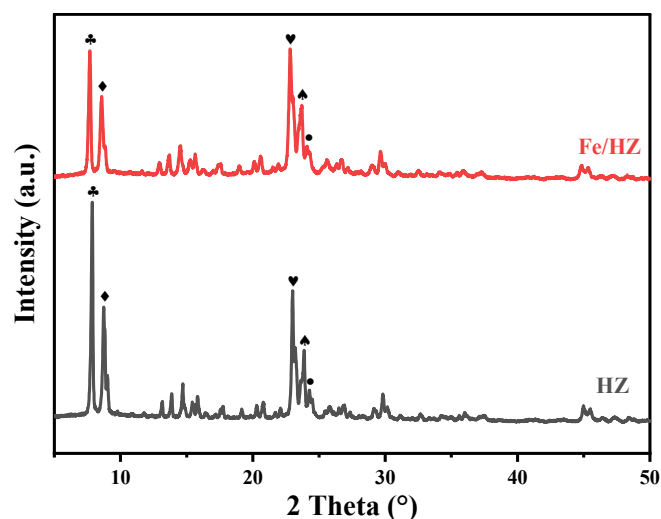


Figure 1. XRD patterns of HZ and Fe/HZ catalysts ($2\theta = 5\text{--}50^\circ$).

The SEM images in Figure 2 clearly show the morphology structure of zeolites. Specifically, HZ is composed of small, square crystal particles with a size of approximately 95 nm, which are stacked together to form a spherical structure with a diameter of about 3 μm . After iron modification, the spherical stacking structure of Fe/HZ remained unchanged, but the small crystal particles that constitute the structure elongated to approximately 120 nanometers.

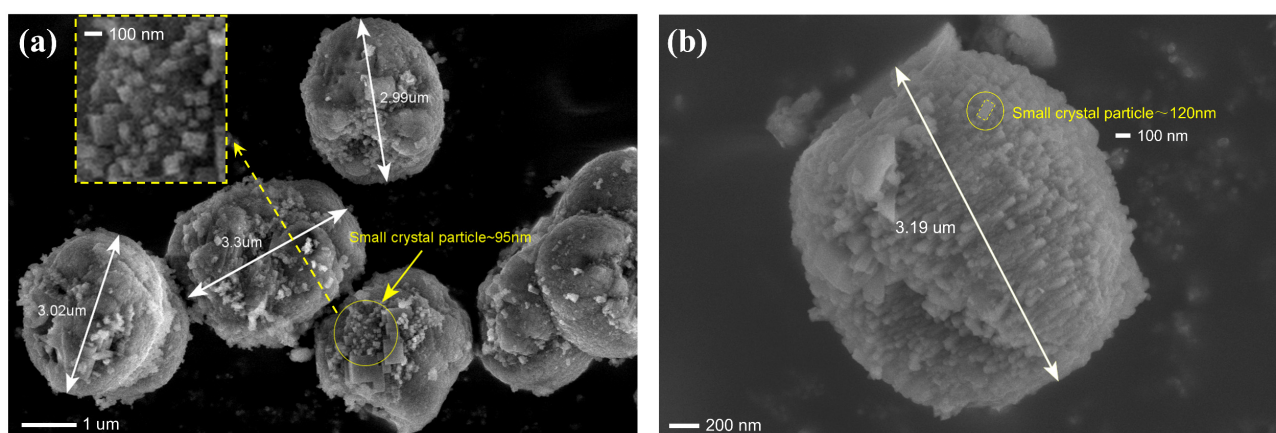


Figure 2. SEM images of (a) HZ, and (b) Fe/HZ catalysts.

By comparing the TEM images and EDS mappings in Figure 3, it can be found that all elements of Fe-free HZ are uniformly dispersed on the zeolites. Furthermore, for the Fe/HZ sample, although there is a slight localized concentration of aluminum and iron elements, the overall distribution of all elements remains largely uniform. This is consistent with the results of XRD analysis. Furthermore, elemental composition analysis reveals that the actual iron loading of the Fe/HZ catalyst is 0.83 wt.%, in close agreement with the theoretical value of 1 wt.% (Figure 3c).

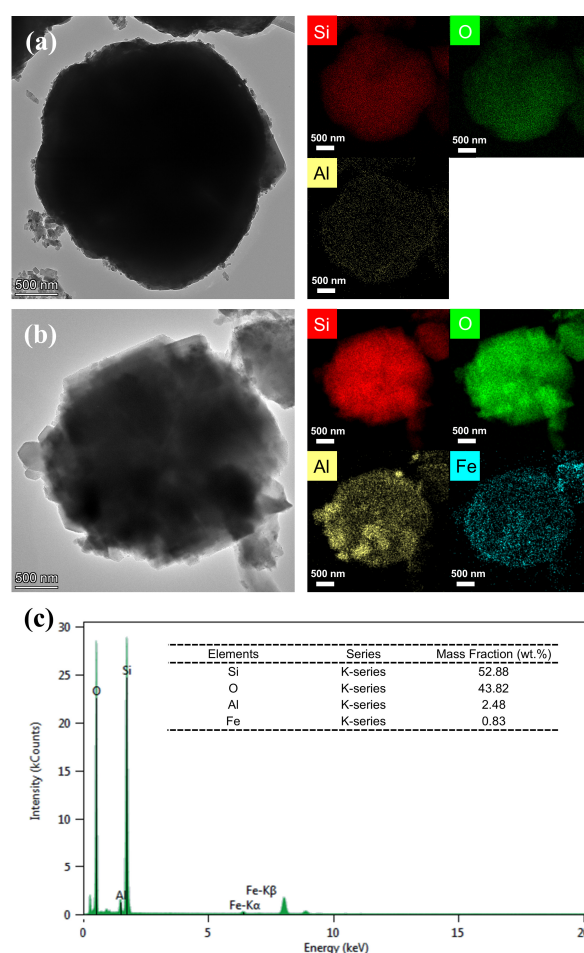


Figure 3. TEM and EDS mapping images of (a) HZ and (b) Fe/HZ catalysts; (c) elemental composition analysis of Fe/HZ catalyst.

X-ray photoelectron spectroscopy (XPS) serves as an effective analytical technique for determining the chemical states of transition metal ions supported on impregnated zeolites. As illustrated in Figure 4, the core-level spectra of Fe 2p_{3/2} and Fe 2p_{1/2} exhibit binding energies at 711.0 eV and 724.5 eV, respectively, and two distinct satellite peaks appear approximately 8 eV higher in binding energy than their corresponding main Fe 2p peaks, which is a spectral signature characteristic of Fe₂O₃, arising from spin–orbit coupling and final-state effects in high-spin Fe³⁺ species [44,45]. These observations collectively indicate that Fe species on the Fe/HZ catalyst is predominantly present as iron oxide (Fe₂O₃).

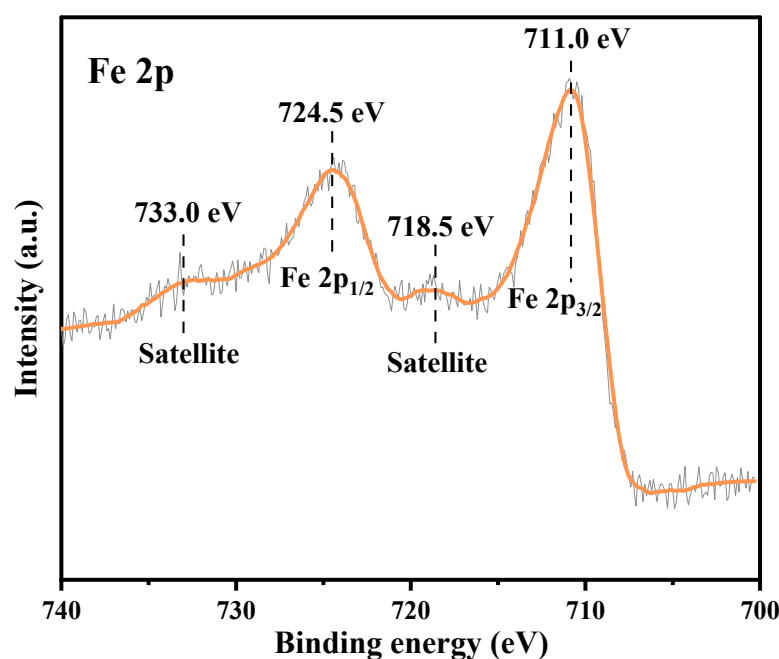


Figure 4. Fe 2p XPS spectra of Fe/HZ catalyst.

The acidity of HZ and Fe/HZ catalysts is evaluated by using ammonia temperature-programmed desorption (NH₃-TPD) tests (Figure 5), and the corresponding amount of acidity is presented in Table 1. All samples exhibit two distinct NH₃ desorption peaks in NH₃-TPD profiles. The low-temperature peak centered at approximately 250 °C corresponds to weak acid sites, and the high-temperature peak located at approximately 430 °C is associated with strong acid sites [46–48]. The low-temperature desorption peak positions for Fe/HZ and HZ are nearly identical, suggesting that loading Fe onto the ZSM-5 catalyst via incipient wetness impregnation exerts negligible influence on the strength of weak acid sites. In contrast, the high-temperature desorption peak position for Fe/HZ was shifted to a higher temperature relative to that of HZ, indicating an increase in the strength of strong acid sites upon iron loading, likely due to electronic or structural modifications induced by Fe species. Similarly, Lima and Perez-Lopez [49] impregnated HZ with iron and observed a shift in the strong acid peak to a higher temperature (685 °C), indicating enhanced acid strength of these corresponding acid sites. In addition, the numbers of total acid sites and weak acid sites of HZ are considerably higher than those of Fe/HZ, whereas the amount of strong acid sites remains relatively similar between the two catalysts, suggesting that HZ exhibits stronger overall acidity. With regard to acid site distribution, notable differences are observed between HZ and Fe/HZ. Specifically, Fe/HZ possesses a higher content of strong acid sites, while the contents of strong and weak acid sites are more balanced in HZ.

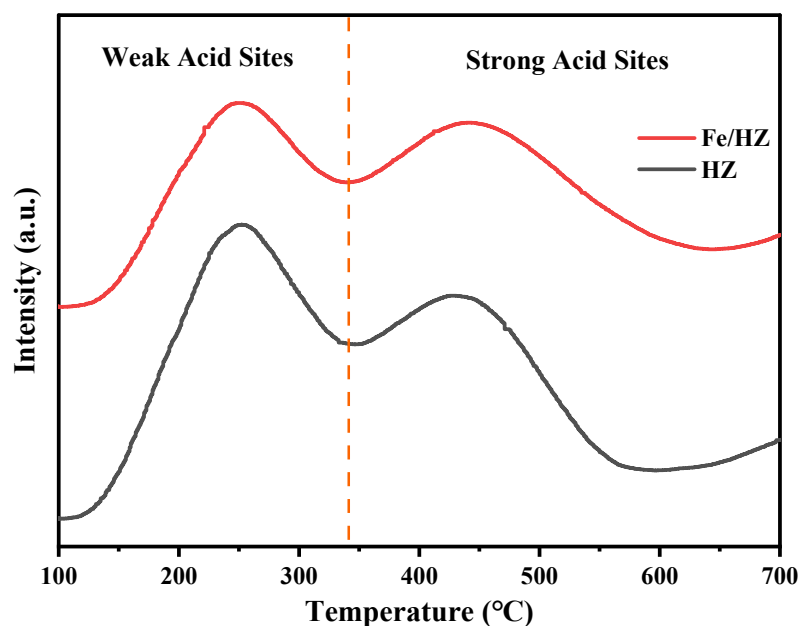


Figure 5. NH_3 -TPD profiles of HZ and Fe/HZ catalysts.

Table 1. Acidities of HZ and Fe/HZ catalysts.

Zeolite	Acidity Amount (mmol/g)				Total Amount
	Weak Acid Sites	Content (%)	Strong Acid Sites	Content (%)	
HZ	0.116	46.96	0.131	53.04	0.247
Fe/HZ	0.080	39.41	0.123	60.59	0.203

2.2. Catalytic Performance

Catalytic pyrolysis of PP was conducted under a CO_2 atmosphere using Fe_3O_4 , HZ, and their dual-component catalysts of various proximity. The corresponding three-phase product distributions are presented in Figure 6. Pyrolysis over single-component catalysts yielded predominantly liquid products, accounting for over 60 wt.%. In contrast, the incorporation of metal–zeolite combinations markedly altered the yields of gases and liquids. To be specific, physical mixed catalysts (Fe_3O_4 &HZ and Fe_3O_4 -HZ) led to reduced liquid yields, while wax and coke formation remained comparable to that observed with mono-component systems. Notably, the impregnated dual-component catalyst Fe/HZ achieved the highest liquid yield of 69.4 wt.%, concomitant with decreased wax and coke formation. These results suggest that the enhancement of liquid production is highly dependent on intimate chemical integration (e.g., impregnation) of Fe species with the ZSM-5 framework, thereby enabling strong interfacial synergy and high dispersion of active Fe sites.

The catalytic performance of various catalysts is evaluated by analyzing the composition of gaseous and liquid products. In this study, CO serves as an indicator of the RWGS reaction, and its content correlates directly with the extent of RWGS conversion. As illustrated in Figure 7a, except for HZ, other Fe-contained catalysts exhibit detectable CO formation, indicating that the RWGS reaction is thermodynamically and kinetically favored at metal-active sites [50,51]. Introduction of metal oxides markedly enhances dehydrogenation activity of catalysts and the performance of the RWGS reaction. Notably, Fe/HZ achieves the highest contents of H_2 and CO of 5.3 vol.% and 5.5 vol.% among all tested catalysts, attributed to the highly dispersed Fe sites effectively enhancing the accessibility of the reactants. C_2 – C_5 alkene constitutes the predominant gaseous product of the cracking of polyolefin plastics. Among mono-component catalysts, HZ delivered

a C₂–C₅ alkene content 10 vol.% higher than that obtained over Fe₃O₄, underscoring the superior efficacy of Brønsted acid sites in zeolites for C–C bond cracking relative to metal oxide. Compared to the pure HZ, the combination of metal and zeolite reduces the content of C₂–C₅ alkene to varying degrees. This trend is further supported by the observation that the increase of proximity between the metal–zeolite components correlates with a progressive decline in C₂–C₅ alkene content, implying that further reactions consume these primary cracking intermediates. Furthermore, the experimental results indicate that the generation of gases, such as hydrogen, remains unchanged after the addition of Fe species when compared to using HZ alone. This suggests that the addition of Fe does not notably impact the diffusion of pyrolysis vapor and the production of gases. This observation is in line with the findings of Li et al. [52], who showed that a low content of Fe loading on ZSM-5 does not significantly change its specific surface area or pore volume.

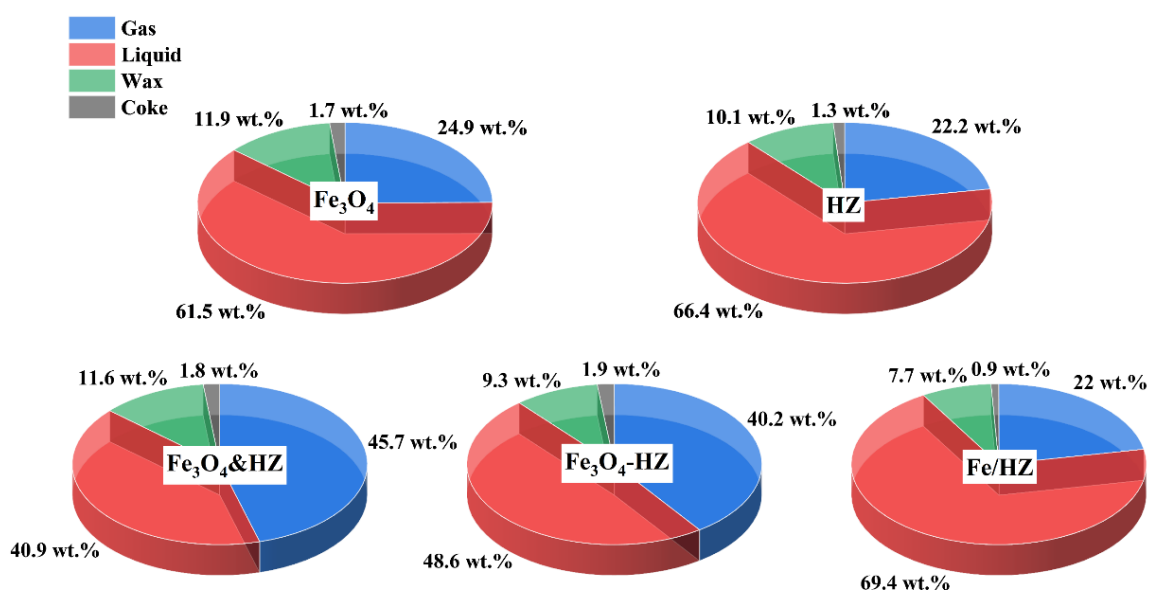


Figure 6. Three-phase product distributions of PP catalytic pyrolysis over different catalysts under CO₂ atmosphere.

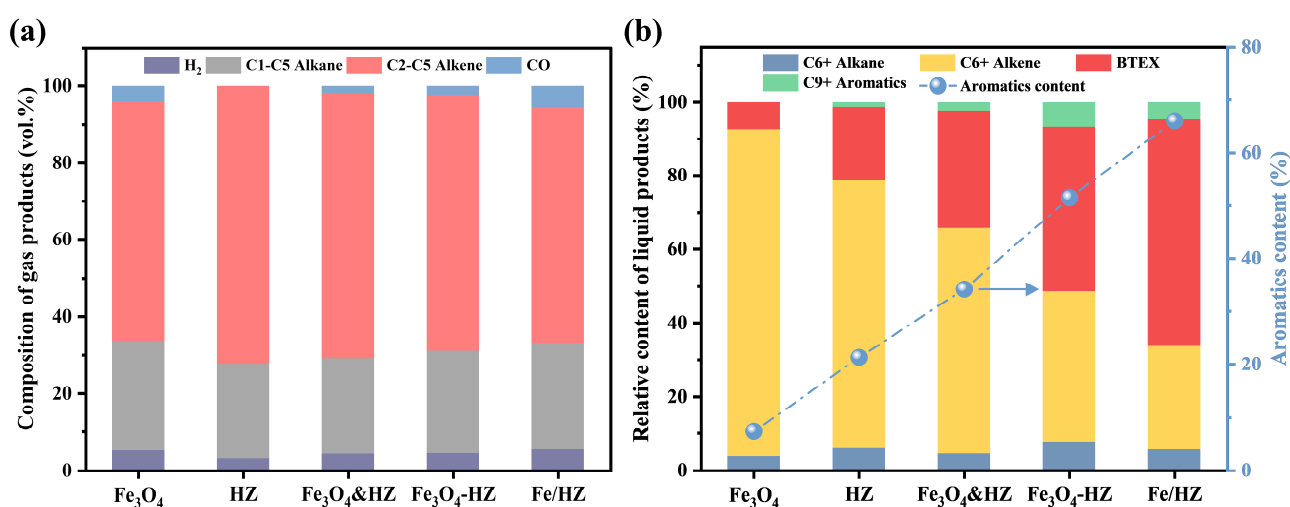


Figure 7. Catalytic performance of PP pyrolysis over different catalysts under CO₂ atmosphere: compositions of (a) gas product and (b) liquid product.

Figure 7b presents the relative content of liquid-phase components during the catalytic pyrolysis of polypropylene (PP) over various catalysts. From a product distribution

standpoint, the catalytic products consist predominantly of C_{6+} alkene and aromatic hydrocarbons. The aromatic fraction is primarily composed of BTEX (benzene, toluene, ethylbenzene, and xylenes), with trace amounts of C_{9+} aromatics produced by over-alkylation of benzene rings. The Fe_3O_4 catalyst markedly suppresses aromatic formation, with its relative content (7.4%) being much lower than the 21.3% obtained over unmodified HZ. This contrast underscores that the Brønsted acidity and well-defined microporous architecture of HZ are pivotal for promoting aromatization during plastic pyrolysis [53,54], whereas Fe_3O_4 primarily facilitates dehydrogenation without enabling efficient cyclization or aromatization. Therefore, the effective combination of Fe species with zeolite can synergistically promote the generation of aromatics. Indeed, the dual-component catalysts demonstrate a significantly higher aromatic yield compared to either mono-component catalyst, with aromatic content increasing progressively to 66.1% in Fe/HZ as the distance between Fe species and acidic zeolitic sites decreases. Concurrently, combined with the reduction in the content of C_2 – C_5 alkene in the gas products mentioned earlier, the increase in aromatic content can be attributed to these light alkenes further undergoing sequential reactions of oligomerization, cyclization, and dehydrogenative aromatization to generate aromatics, which is efficiently catalyzed by the dual-component system of metal–zeolite. Notably, physical combined catalysts (Fe_3O_4 &HZ and Fe_3O_4 -HZ) exhibit markedly lower aromatic contents than Fe/HZ due to insufficient local concentration and residence time of reactive intermediates (e.g., C_2 – C_5 alkenes) at active site interfaces. In contrast, by integrating iron species highly dispersedly into the zeolite surface, Fe/HZ enables synergistic cooperation between metal sites and acid sites, thereby significantly enhancing aromatic content. Collectively, these findings demonstrate that intimate structural integration of Fe species within HZ is critical to synergistic catalysis and achieving high aromatic content in PP pyrolysis, which is not achievable by physical combined catalysts.

2.3. Coke Analysis

As shown in Figure 8, the amount of coke deposited on the catalysts during PP pyrolysis reaction under a CO_2 atmosphere is determined by the TGA method. In this paper, the coke amount calculated decreases significantly from 2.53% in HZ to 1.71% in Fe/HZ, indicating that the coke formation is significantly suppressed with the presence of CO_2 , which is attributed to the fact that the presence of metal sites promotes the occurrence of the reverse Boudouard reaction ($CO_2 + C \rightarrow 2CO$) [27,39]. According to the literature, low-temperature thermal treatment primarily removes oligomers (soft coke), whereas highly condensed, graphitic carbonaceous species (hard coke) require elevated temperatures for removal [55,56]. The accumulation of hard coke is widely recognized as the predominant reason for catalyst deactivation. For the tested spent catalysts, soft coke is identified by the region of peaks below 500 °C, while hard coke corresponds to the region at higher temperatures. Obviously, the coke of HZ and Fe/HZ predominantly consists of soft coke, along with a minor amount of hard coke (Figure 8b). Compared with HZ, Fe/HZ exhibits a significantly broader and more dispersed peak distribution in DTG profiles. Although both catalysts display a small peak region above 500 °C, Fe/HZ shows a pronounced peak shift toward lower temperatures, with a dominant peak centered at approximately 333 °C. This lower-temperature coke combustion behavior suggests that the carbonaceous deposits formed over Fe/HZ are structurally less condensed and more readily oxidizable, which is consistent with a reduction in acidity following Fe modification [57]. Experimental data confirm decreased hard coke with condensed polyaromatics as the main component and enhanced BTEX selectivity. Consequently, we deduce that CO_2 contributes to the suppression of coke formation through two complementary mechanistic pathways for the Fe/HZ catalyst. CO_2 modulates acid strength via competitive adsorption and partial

neutralization (carboxylation) to reduce dehydrogenation cyclization. In addition, CO₂ may alter aromatic pool dynamics by suppressing hydride transfer, which limits the formation of polyaromatics (key coke precursors) and favors the formation of light aromatics (BTEx).

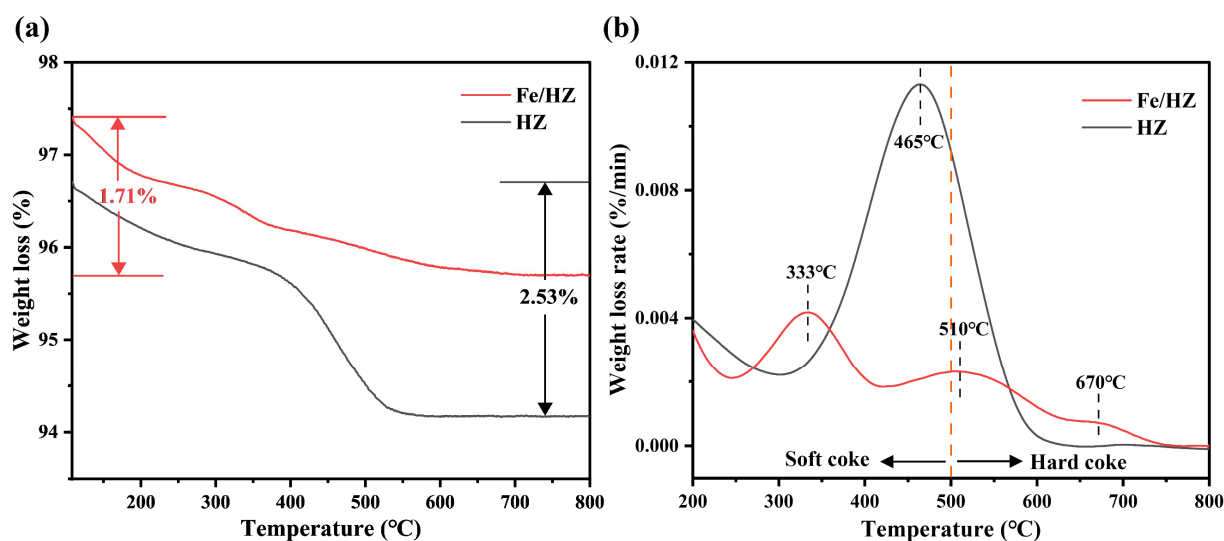


Figure 8. (a) TGA and (b) DTG curves of spent HZ and Fe/HZ catalysts after PP pyrolysis reaction under CO₂ atmosphere.

2.4. Possible Mechanism

Based on the above analysis, taking Fe/HZ as an example, we propose a plausible reaction pathway for the co-conversion of polypropylene and CO₂ (Figure 9). At 600 °C, polypropylene undergoes thermal cracking to generate long-chain alkenes. These intermediates are subsequently activated by Brønsted acid sites in the ZSM-5 framework, undergoing sequential cracking to yield C₂–C₅ alkenes, followed by oligomerization, cyclization, and dehydrogenative aromatization to form aromatic hydrocarbons. Concurrently, H₂ liberated during aromatization is immediately consumed via the RWGS reaction over highly dispersed Fe species, thereby thermodynamically driving the aromatization equilibrium toward higher aromatic selectivity. The spatial proximity and functional synergy between the iron-based redox sites and the zeolitic Brønsted acid sites enables efficient coupling of the above reaction steps, ultimately enhancing aromatic yield.

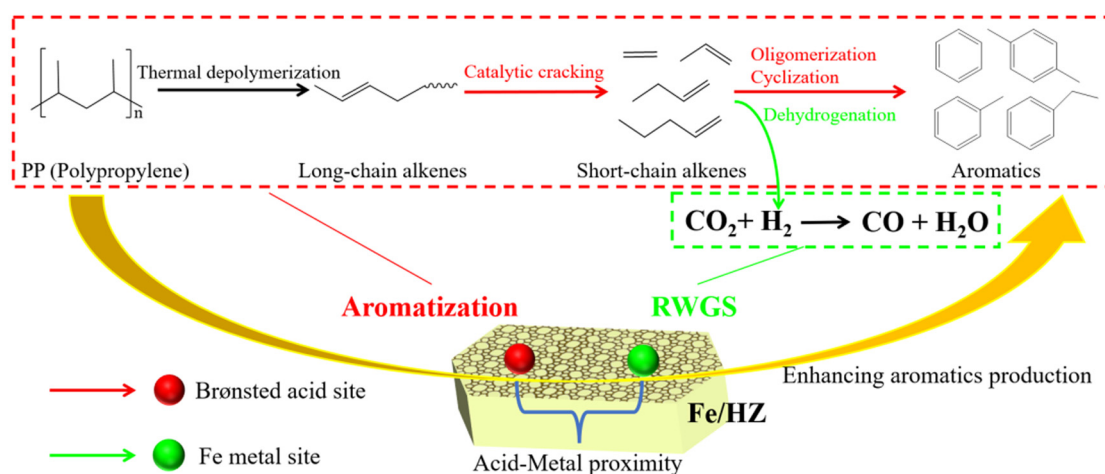


Figure 9. Possible reaction mechanism of PP catalytic pyrolysis over Fe/HZ catalyst under CO₂ atmosphere.

3. Materials and Methods

3.1. Materials

Tetraethoxysilane (TEOS, $C_8H_{20}O_4Si$, 99.99%) and tetrapropylammonium bromide (TPABr, $C_{12}H_{28}NBr$, 98%) were purchased from Aladdin Inc., Shanghai, China. $Al[OCH(CH_3)_2]_3$ (99.8%), NaOH (95%), $Fe(NO_3)_3 \cdot 9H_2O$ (99.99%), NH_4Cl (99.5%), and Fe_3O_4 (99.5%) were obtained from Macklin Inc., Shanghai, China. Gases including CO_2 (99.9%) and N_2 (99.9%) were supplied by Guangzhou Dan'outong Trading Co., Ltd., Guangzhou, China. Other reagents were sourced from certified commercial vendors and utilized directly.

3.2. Catalyst Preparation

The synthesis of Fe-free HZSM-5 (HZ) followed this procedure. Originally, $Al[OCH(CH_3)_2]_3$ and NaOH were successively added into a TPABr solution under stirring at 600 rpm for 3 h. Afterwards, TEOS was slowly added dropwise to the mixture under vigorous stirring, yielding a clear sol-gel with a molar composition of $60SiO_2: 1Al_2O_3: 21.4TPABr: 21.4NaOH: 2300H_2O$. After aging for 24 h, the homogeneous solution was heated at 80 °C in an oil bath for 5 h. Hydrothermal crystallization occurred in a Teflon-lined autoclave at 170 °C under tumbling (50 rpm) for 1 d. After crystallization, the solid product was centrifuged, washed, dried at 105 °C overnight, and subsequently calcined at 550 °C for 6 h with a heating rate of 2 °C/min to eliminate organic templates. Lastly, the Na-forms zeolite was twice ion-exchanged with 1 mol/L NH_4Cl solution at 80 °C for 4 h, followed by drying and calcination at 550 °C for 6 h to obtain HZ.

To compare the influence of the proximity of metal and zeolite components on catalytic reactions, the dual-bed structure of Fe_3O_4 and HZ ($Fe_3O_4\&HZ$), powder mixtures of Fe_3O_4 and HZ (Fe_3O_4-HZ) and Fe-loaded zeolites (Fe/HZ) were synthesized. Previous studies by Xie et al. [27] and Wei et al. [58] have demonstrated that a 1:1 mixing ratio of metal oxide and ZSM-5 is an optimized catalytic system. As a result, we used the $Fe_3O_4\&HZ$ (dual-bed) and Fe_3O_4-HZ (powder mixing) with a mixing ratio of 1:1 to investigate the catalytic effect of metal–acid proximity. $Fe_3O_4\&HZ$ was formed by dividing sieved Fe_3O_4 and HZ of the same mass into two beds, with quartz cotton placed in between, as shown in Figure 10. Fe_3O_4-HZ was obtained by grinding the powder mixture of Fe_3O_4 and HZ at a mass ratio of 1:1. Fe/HZ was prepared by a conventional impregnation method. To be specific, an appropriate amount of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in water (30 mL) and then added to HZ ensure Fe loading of 1%. After stirring into a paste at 60 °C in an oil bath, the mixture was dried at 105 °C for 12 h and then calcined at 550 °C for 6 h. The obtained material was labeled as Fe/HZ.

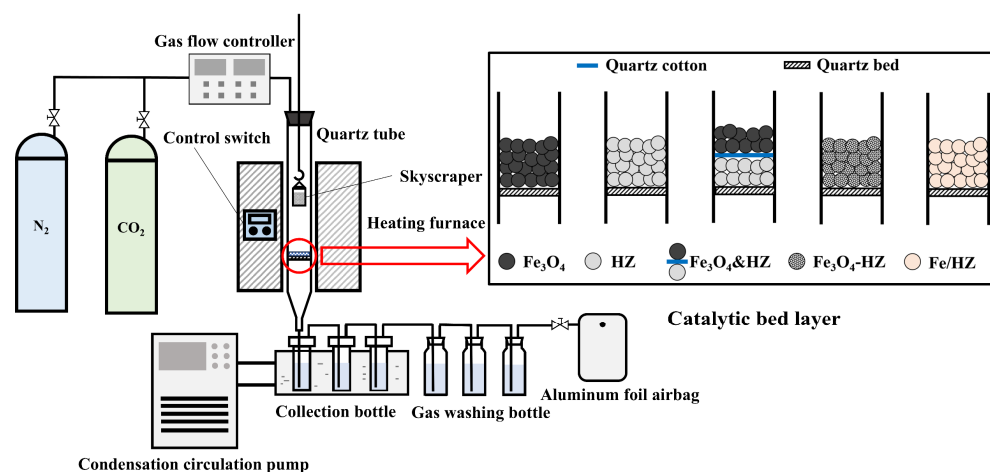


Figure 10. Schematic diagram of the plastic catalytic pyrolysis reaction system.

3.3. Catalyst Characterization

X-ray diffraction (XRD) was characterized using a Malvern Panalytical Empyrean instrument (Almelo, The Netherlands). The 2θ scanning angle range was set to $5\text{--}80^\circ$ with a step size of 0.01° . SEM images of zeolites were obtained on a scanning electron microscope (Taloz L120C). TEM and EDS mapping images were recorded on a Talos F200X microscope (Thermo Fisher Scientific, Waltham, MA, USA) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo (Waltham, MA, USA) ESCALAB K-Alpha instrument equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6\text{ eV}$). NH_3 -TPD tests were conducted on a chemical adsorption instrument, model TP-5080 (Xian Quan, Tianjin, China), to determine the acid content and acid strength of the catalyst, and the amount of acidity was calculated from the peak areas.

3.4. Catalytic Pyrolysis Experiment and Product Analysis

As shown in Figure 10, the catalytic pyrolysis experiments of PP were carried out at 600°C for 30 min in a fixed-bed reactor with an inner diameter of 20 mm and a 200 mm heating zone. Prior to reaction, the quartz reactor was purged with mixed $20\%\text{CO}_2/80\%\text{N}_2$ gas at a flow rate of 100 mL/min for 30 min to ensure an air-free environment. Generally, 0.5 g of catalyst (30–60 mesh) was packed in a quartz sand fixed bed in the reactor tube, while 1.0 g of PP powder was loaded into a suspended quartz basket located above the heating zone. Lowering the quartz basket to the heating zone indicated the start of the reaction, which was allowed to proceed for 30 min. Pyrolysis products passed through cold traps (-20°C) charged with dichloromethane (99.9%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), where pyrolysis liquids were collected. Non-condensable gases were subsequently directed to a gas bag.

The gaseous products were quantified by external standards using a gas chromatography instrument (Agilent-GC9800, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The liquid products were characterized by gas chromatography–mass spectrometry (GC-MS, Agilent 7890B-5977B) with an HP-5ms column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The coke contents and properties of spent catalyst samples were quantified and qualified by a thermogravimetric (TG) analyzer (DSC1 METTLER TOLEDO).

The calculation formulas for the yields of wax, gas, coke, and liquid are Equations (1)–(4). The relative content of the compounds in the liquid product is determined by Equation (5).

$$\text{Yield}_{\text{Wax}}(\text{wt.}\%) = \frac{M_{\text{Wax}}}{M_{\text{PP}}} \times 100\% \quad (1)$$

$$\text{Yield}_{\text{Gas}}(\text{wt.}\%) = \frac{M_{\text{Gas}}}{M_{\text{PP}}} \times 100\% \quad (2)$$

$$\text{Yield}_{\text{Coke}}(\text{wt.}\%) = \frac{M_{\text{coke}}}{M_{\text{PP}}} \times 100\% \quad (3)$$

$$\text{Yield}_{\text{Liquid}}(\text{wt.}\%) = \frac{M_{\text{PP}} - M_{\text{Wax}} - M_{\text{Gas}} - M_{\text{coke}}}{M_{\text{PP}}} \times 100\% \quad (4)$$

$$R_i(\text{wt.}\%) = \frac{A_i}{A_{\text{total}}} \times 100\% \quad (5)$$

where M_{Wax} , M_{Gas} , and M_{Liquid} are the mass of wax, gas, and liquid products, respectively; M_{PP} is the mass of the reactant PP; M_{coke} is the mass of coke in the spent catalyst samples; R_i is the relative content of each component in the liquid product; A_i is the peak area of each component in the liquid product; and A_{total} is the total peak area of all components in the liquid product.

4. Conclusions

In this study, the reaction scenarios over $\text{Fe}_3\text{O}_4\&\text{HZ}$, $\text{Fe}_3\text{O}_4\text{-HZ}$, and Fe/HZ were compared under a CO_2 atmosphere to elucidate the effect of metal–acid proximity on aromatic production in CO_2 -assisted catalytic pyrolysis of polypropylene. The yields of aromatics followed this order: $\text{Fe/HZ} > \text{Fe}_3\text{O}_4\text{-HZ} > \text{Fe}_3\text{O}_4\&\text{HZ} > \text{HZ} > \text{Fe}_3\text{O}_4$. Aromatic yields ranked as follows: $\text{Fe/HZ} > \text{Fe}_3\text{O}_4\text{-HZ} > \text{Fe}_3\text{O}_4\&\text{HZ} > \text{HZ} > \text{Fe}_3\text{O}_4$. Notably, Fe/HZ , with the closest metal–zeolite integration, delivered an aromatic content of 66.1%, markedly surpassing the 34.2% content achieved by $\text{Fe}_3\text{O}_4\&\text{HZ}$, clearly indicating that shortening the distance between metal and acid sites enhanced aromatization. In addition, Fe/HZ significantly reduced coke deposition. Based on comprehensive characterization (XRD, SEM, TEM, XPS, and $\text{NH}_3\text{-TPD}$), the superior performance of Fe/HZ was ascribed to the tight spatial coupling between iron-based redox sites and Brønsted acid sites within the zeolite framework. This intimate proximity promoted synergistic interactions that drove the RWGS reaction of CO_2 , effectively consuming hydrogen produced during aromatization and shifting the reaction equilibrium toward higher aromatic yields. Together, these insights advance the design of efficient catalysts for CO_2 -assisted valorization of plastic waste, supporting the dual objectives of converting waste plastics and utilizing CO_2 .

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