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Catalytic co-pyrolysis of rubber waste and polyacrylonitrile for producing BTEX enriched oil via heterogeneous Diels-Alder reaction

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ABSTRACT

Monocyclic aromatic hydrocarbons are important chemicals with huge market demands. Recycling valuable hydrocarbons such as BTEX from rubber wastes is a sustainable and promising way, which can reduce the dependence on petroleum. Catalytic co-pyrolysis of rubber waste and polyacrylonitrile were conducted in this study, aiming to produce BTEX enriched light oil by enhancing the Diels-Alder reaction. The effects of catalytic mode, catalyst type, and mass ratio of the feedstocks were investigated to optimize the catalytic conditions for increasing BTEX yield. Meanwhile, quantitative analysis was performed with regard to BTEX by external standard methods. It was found that the primary pyrolytic products of rubber waste and polyacrylonitrile were rich in isoprene and dienophiles, respectively, which suggested it was feasible to enhance Diels-Alder reaction through the strategy of catalytic co-pyrolysis of rubber waste and polyacrylonitrile. The optimal result was obtained under the condition of ex-situ catalysis, Zn/HZSM-5 as catalyst, and Rubber-to-PAN ratio of 1:3, at which case the BTEX yield reached 22.01 wt%, much higher than those in previous literatures. This work provides a new strategy for recovering high value-added products (BTEX) from rubber wastes, which has the potential to be an alternative fuel in the future.

1. Introduction

Monocyclic aromatic hydrocarbons, especially benzene, toluene, ethylbenzene, and xylene are valuable industrial chemicals with huge market demands. According to statistics, the annual consumption of monocyclic aromatic hydrocarbons exceeds 140 million tons, and the number continues to grow at a rate of 2–6% annually [1]. As BTEX are mainly made from petroleum by catalytic cracking or reforming traditionally [2], the tightness of oil supply has led to the high cost of BTEX. Thus, in recent years, interests have been increased in exploring sustainable and low-cost alternatives to recover BTEX from wastes by pyrolysis [2–5], aiming to reduce the dependence on petroleum.

Among the many wastes, rubber wastes are potentially good feedstocks to recover BTEX for two reasons. On the one hand, with the rapid development of automobile industry, the annual production of waste tires has increased drastically accordingly, which are urgent to be handled reasonably [6]. On the other hand, polymerized from hydrocarbon monomers, rubber wastes themself are suitable to be recycled for

the production of valuable chemicals [7]. In the past decades, numerous researches have been conducted in catalytic pyrolysis of waste tires for generating aromatic hydrocarbons. Shen et al. [8] studied the effects of USY and ZSM-5 zeolites on the pyrolytic products of waste tires. They found that the content of single ring aromatic compounds increased dramatically after catalysis, and the highest content of benzene, toluene, and xylene reached 1.6%, 11.62%, and 16.69%, respectively. Miguel et al. [9] tested the aromatization performance of five catalysts on Py-GC/MS and the target products of benzene, toluene, and xylene reached up to 10.28%, 19.82%, and 16.91%, respectively.

According to previous researches, the formation mechanism of aromatic products in the pyrolysis process can be attributed to a series of reactions, including cyclization, dehydrogenation, aromatization, isomerization, and Diels-Alder reactions [10–12]. Among them, Diels-Alder reaction has received increasing attention in recent years due to its controllable and efficient characteristics in the process of generating aromatic compounds [5,13]. Diels-Alder reaction is a classic organic synthesis reaction for producing six-membered ring by coupling of a

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conjugated diene and a dienophile [1]. Researchers have found that the reaction is very suitable for the pyrolysis of biomass to produce monocyclic aromatic hydrocarbons, because the primary products of biomass contain plenty of dienes (e.g., furan and its derivatives), which can be easily converted into aromatics by Diels-Alder reaction [5,14]. Similarly, the primary volatile products of rubber waste also contain quite a lot conjugated dienes (e.g., isoprene and butadiene) [15,16], which means more potential can be tapped in generating aromatics from pyrolysis of rubber wastes, and the yield of BTEX could be further increased if Diels-Alder reaction could be enhanced during pyrolysis.

In order to promote the Diels-Alder reaction, dienophile is another crucial factor that must be met. Compared with ethylene and propylene, dienophiles with electron-withdrawing group, such as acraldehyde, acrylonitrile, and methyl acrylate, are more conducive to Diels-Alder reaction [1]. It was reported that acrylonitrile and its derivatives were main pyrolytic products of polyacrylonitrile [17], for which polyacrylonitrile could serve as ideal feedstock to co-pyrolyze with rubber wastes for the purpose of enhancing Diels-Alder reaction. Another advantage of using polyacrylonitrile as addend is cost-effectiveness. Polyacrylonitrile is known to produce clothing, for which it can be easily obtained from discarded clothes. Hence, the strategy of co-pyrolysis of rubber wastes and polyacrylonitrile is theoretically practicable as well as sustainable.

Catalysts also play an essential role in the enhancement of Diels-Alder reaction. It has been proved that acid catalysts can promote the Diels-Alder reaction by decreasing the HOMO-LUMO energy gap of diene and dienophile [1,18]. Pascal et al. [18] studied the Diels-Alder cycloaddition between 1,3-butadiene and methyl acrylate catalyzed by a series of Lewis acid catalysts, and discovered that the reaction barrier was lowered after using Lewis acid catalysts. Gao et al. [19] found high Lewis/Brønsted ratio was beneficial for the selectivity of BTEX as well as inhibiting the formation of by-products. In addition, Wang et al. [20] investigated the solid acid catalysts for the production of BTX by the reaction of ethylene and furans, and found that catalysts containing both Lewis and Brønsted acids were much more active than those containing predominantly Lewis acids, which indicated that Brønsted acids were also very important in the production of BTEX. These researches demonstrated that both Lewis and Brønsted acids are indispensable in promoting the Diels-Alder reaction. Thus, solid catalyst containing both Lewis and Brønsted acids such as HZSM-5 zeolite was chosen as catalyst in this research for its efficient heterogeneous catalytic activities in facilitating Diels-Alder reaction [21,22].

In general, Diels-Alder requires three factors, which are conjugated diene, dienophile and acid catalysts. The purpose of this study is to increase the BTEX yield by promoting the Diels-Alder reaction during the catalytic co-pyrolysis of rubber waste and polyacrylonitrile. HZSM-5 zeolite was selected as the catalyst in this study for its abundance of Lewis and Brønsted acids, and metal modified HZSM-5 zeolites (Fe, Zn, Co, Cu) were also studied for their activities in promoting Diels-Alder reaction. Moreover, the effects of catalytic mode and Rubber-to-PAN ratio were also investigated to optimize the catalytic condition for increasing BTEX yield.

2. Material and methods

2.1. Materials

The rubber waste used in this research was waste tire, provided by the Zhongce Rubber Group Company Limited, China. The raw material contained about 32% natural rubber (mainly isoprene rubber) and 23% synthetic rubber (mainly styrene–butadiene rubber and butyl rubber) [16]. Fibers and steel were separated from feedstock in advance. The feedstock was then ground to particles with a size less than 0.075 mm for uniformly sampling. The reagents used in this study, including polyacrylonitrile, dichloromethane, benzene, toluene, ethylbenzene, and xylene were provided by Shanghai Macklin Biochemical Co., Ltd. The

commercial HZSM-5 zeolite (Si/Al = 25) was purchased from Tianjin Yuanli Chemical Co., Ltd.

2.2. Catalyst preparation and characterization

The metal modified HZSM-5 catalysts were prepared by conventional incipient wet impregnation method [23,24]. First, 2.0 g of precisely weighed HZSM-5 zeolite was slowly added into 100 ml of $Fe(NO_3)_3$, $Zn(NO_3)_2$, $Co(NO_3)_2$, and $Cu(NO_3)_2$ hydrate solution, respectively. The amounts of nitrates were determined according to the metal-to-zeolite ratio, which was controlled at 5% in this study. The heterogeneous mixture was then stirred at 80 °C for 4 h on a magnetic stirrer, and successively dried at 105 °C for 24 h in an oven. The obtained metal modified HZSM-5 samples were further calcined at 550 °C for 5 h in air atmosphere. Finally, the catalysts were ground to powers with a size less than 0.075 mm and named as Fe/HZSM-5, Zn/HZSM-5, Co/HZSM-5, and Cu/HZSM-5, respectively. The specific area and pore structure of the prepared catalysts were characterized by a total micropore tester (Micromeritics 3Flex). The metal content of the catalyst was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 720ES). Ammonia temperature-programmed desorption (NH3-TPD) was used to test the acid strength of the catalysts on Auto Chem II 2920 (Micromeritics). The Lewis and Brønsted acidity were determined by pyridine adsorption infrared spectroscopy (Py-IR, Thermo fisher Nicolet iS50).

2.3. Catalytic experimental setups

The catalytic co-pyrolysis experiments were carried out on a tandem micro pyrolyzer (Rx-3050 TR, Frontier laboratories, Japan) coupled with Gas Chromatograph/Mass Spectrometer (GC/MSQP2010SE, Shimadzu, Japan), whose schematic diagram is shown in Fig. S1. The tandem micro pyrolyzer consists of two reactors, and the second reactor is switchable. Both of the reactors can be controlled independently with a temperature range of 40–900 °C. The sizes of the two reactors are identical (76 × 125 × 260 mm), while the functions are different. The first reactor is coupled with a sample cup, which is designed for pyrolysis. The second reactor has a quartz tube (φ = 3 mm, Φ = 4 mm, h = 78 mm) embedded in it, which is designed for catalysis. For in-situ catalytic co-pyrolysis, feedstock and catalyst were uniformly mixed and placed in the sample cup for catalytic process, while for ex-situ catalytic co-pyrolysis, only feedstock was pyrolyzed in the first reactor and the produced volatiles were transported by carrier gas to the secondary reactor for catalytic treatment. The products were then directly introduced into GC/MS for detailed compositional analysis. The volatiles were separated by a capillary column (SH-Rxi-5Sil MS, 30 m × 0.25 mm × 0.25 μm) and the GC oven was programmed as follows: (1) held at 30 °C for 2 min; (2) rose to 200 °C at a heating rate of 5 °C/min and held for 1 min; (3) rose to 300 °C at a heating rate of 10 °C/min and held for 1 min. The pyrolytic products were identified by comparing mass spectra with the NIST 17 mass spectral database, and only the compounds with similarities higher than 80% were identified for analysis in this study [25].

In each experiment, the amount of sample and catalyst were precisely controlled at 0.50 mg and 10.0 mg [26], respectively. The pyrolytic temperature and catalytic temperature were constant in each run, kept at 500 °C. The effect of in-situ and ex-situ catalytic co-pyrolysis was investigated first to determine the better catalyst placement mode. The catalytic activities of four types of metal modified catalysts were tested by ex-situ catalytic mode. The effect of Rubber-to-PAN ratio (1:0, 3:1, 2:1, 1:1, 1:2, and 1:3) was studied by keeping the total sample amount at 0.50 mg and changing the amount of waste tire and polyacrylonitrile. The detailed experimental conditions are presented in Table S1. Duplicate tests were conducted and average values were discussed.

2.4. Data processing method

The selectivity of volatile products was represented by the relative peak area and calculated as follows:

$$S_i = \frac{P_i}{\sum_{i=1}^{n} P_i} \times 100 \tag{1}$$

where S_i is the relative content of a specific component; P_i is the peak area of a specific component; $\sum_{i=1}^{n} P_i$ represents the cumulative peak area of all detected peaks.

As target products, benzene, toluene, ethylbenzene, and xylene were further analyzed quantitatively in this study. The calibration curves of BTEX were created by external standard method and the BTEX yield was calculated according to these calibration curves [27]. First, a series of standard solutions of different concentrations containing all target compounds were prepared. The concentrations of these solutions were determined according to the estimated catalytic yield of BTEX. Next, 1.0 μl of standard solution was injected into GC/MS for analysis, whose parameter settings were identical with those during catalytic co-pyrolysis. Then a series of data on BTEX concentration and peak area could be obtained, based on which calibration curves were created. The obtained calibration curves are shown in Fig. S2, and Table S2 lists more detailed information of the calibration curves.

3. Results and discussion

3.1. Primary products of waste tire and polyacrylonitrile under thermal pyrolysis

Before catalytic experiments, the distribution of primary products of waste tire and polyacrylonitrile were studied under thermal pyrolysis at 500 °C, whose chromatograms are shown in Fig. 1. Five primary products were emphasized because they were predominant compounds in

the pyrolytic products as well as important precursors of Diels-Alder reaction. For waste tire, it can be observed that isoprene and limonene were predominant compounds in the pyrolytic products, accounting for 31.98% and 40.77% of the peak area, respectively. The results were kind of different from the previous literature [28,29], in which isoprene was almost undetected. The reason is that isoprene, with boiling point of 34 °C, is easy to volatilize during the pretreatment process such as condensation, dissolution, and filtration before GC/MS detection. However, the Py-GC/MS used in this study allows online detection of the pyrolysis products, because the generated volatiles are directly introduced into GC/MS for detection. Therefore, those undetectable compounds were observed in this research as well as in the previous studies using Py-GC/MS [15,16]. It was reported that limonene was unstable at high temperature and easily underwent secondary reactions to form monocyclic aromatics and isoprene [30,31], which further increased the content of isoprene. If these large amounts of isoprene could be converted into monocyclic aromatics via Diels-Alder reaction, the yield of BTEX could be further improved on the original basis. For PAN, it can be found from the chromatogram that its primary pyrolytic products were rich in dienophile. Three significant peaks of dienophile accounted for 58.90% in total of the peak area. The results were consistent with the results obtained by Minagawa et al. [17], except that the compound e was not identified in the literature. The reason may be that the compound e was not stable at high temperature and was prone to secondary cracking to form smaller molecules.

In addition, the weight loss characteristics of waste tire and polyacrylonitrile were independently studied by thermogravimetric analysis. The TG/DTG curves of the samples are presented in Fig. 2. As can be seen from the figure, the weight loss temperature range of waste tire and polyacrylonitrile were almost coincident, starting from around 300 °C and ending at 500 °C. Thus, the pyrolytic temperature and catalytic temperature were set at 500 °C in this research. Since the experiments in this study were conducted under rapid pyrolysis, the volatiles of waste
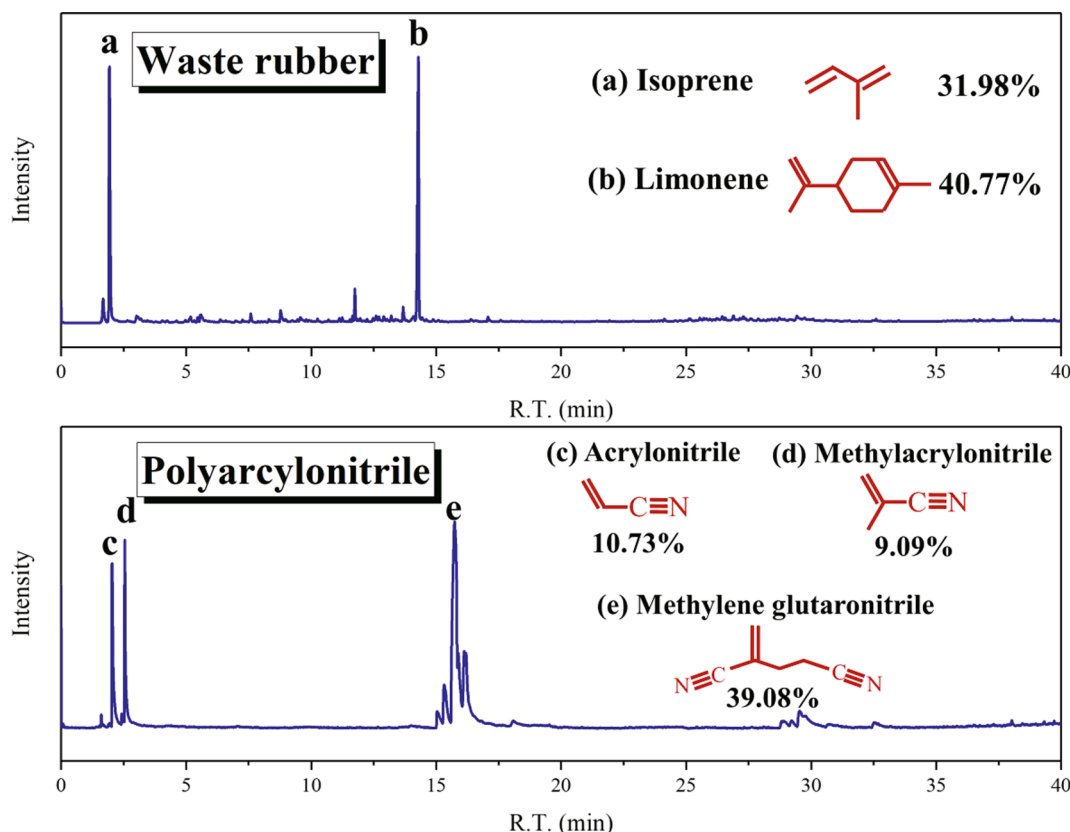

Fig. 1. Chromatograms of primary products of waste tire and polyacrylonitrile under thermal pyrolysis.
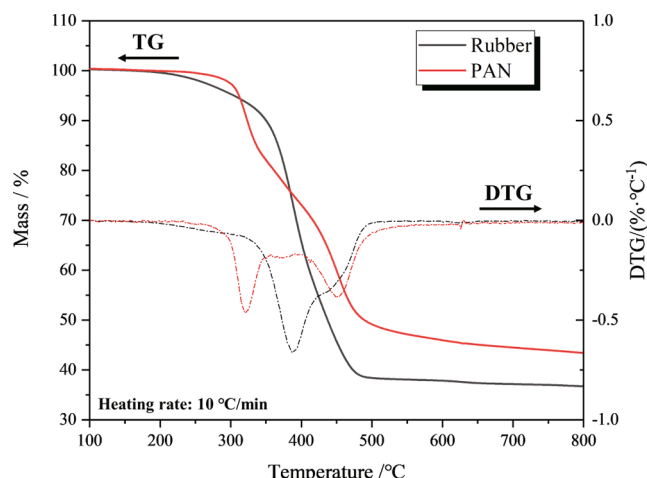
Fig. 2. TG/DTG curves of waste tire and polyacrylonitrile.

tire and polyacrylonitrile were generated almost simultaneously and passed through the catalytic section with carrier gas. The results of primary products analysis and thermogravimetric analysis demonstrated that it was theoretically feasible to produce BTEX through the strategy of catalytic co-pyrolysis of rubber wastes and polyacrylonitrile.

3.2. Effects of catalytic mode on the pyrolytic products

The effects of catalytic mode on the catalytic products were investigated using parent HZSM-5 as catalyst with Rubber-to-PAN ratio of 1:1. Three catalytic modes, non-catalysis, in-situ catalysis, and ex-situ catalysis were performed on Py-GC/MS, and the distribution of pyrolytic products is shown in Fig. 3. The histograms clearly express the distribution of overall pyrolysis products and the key pyrolysis products. As can be seen from the figure, alkenes and nitrogenous compounds dominated in the products under the condition of non-catalysts, which originated from waste tire and polyacrylonitrile, respectively. The low content of monocyclic aromatics in the non-catalysts group indicated that Diels-Alder reaction between conjugated diene and dienophile could hardly occur without catalysts. With the addition of HZSM-5 catalyst, the distribution of pyrolytic products changed significantly. As seen in Fig. 3(b), in-situ catalysis increased the BTEX content to 35.50% at the cost of conjugated diene and dienophile. Moreover, ex-situ catalysis further increased the BTEX content by 50.96% compared

with non-catalytic pyrolysis, reaching up to 54.93%, indicating ex-situ catalysis was more conducive to producing BTEX than in-situ catalysis. The variation trend of distribution of the pyrolytic products under different catalytic modes was obvious in Fig. 3. As reactants, conjugated diene and dienophile showed a downward trend, while the BTEX, as target products, increased continuously, which proved that Diels-Alder reaction was promoted with the use of catalyst.

Only analyzing the relative content of pyrolytic products is one-sided. To make the results more intuitive and persuasive, the yields of BTEX were calculated quantificationally and the results are presented in Fig. 4. As illustrated, each dash line represents one compound, and the solid line represents the cumulative yield of benzene, toluene, ethylbenzene, and xylene. As can be seen from the figure, compared to non-catalytic pyrolysis, the yields of four target compounds were all improved in in-situ and ex-situ catalysis. Thereinto, ex-situ catalysis increased the cumulative BTEX yield up to 16.72 wt%, which was almost eight times that non-catalytic pyrolysis. In-situ catalysis also promoted the formation of BTEX, but its effect was slightly inferior to that of ex-situ catalysis. The reason is that ex-situ catalysis occurred at a constant set point temperature, and had larger contact surface between volatiles and catalysts [26]. Among the four target products, it can be
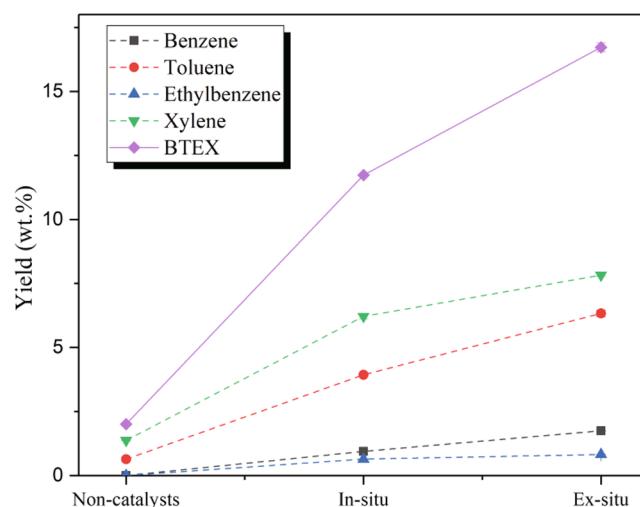

Fig. 4. BTEX yield under different catalytic mode (HZSM-5 as catalyst, Rubber-to-PAN ratio of 1:1).
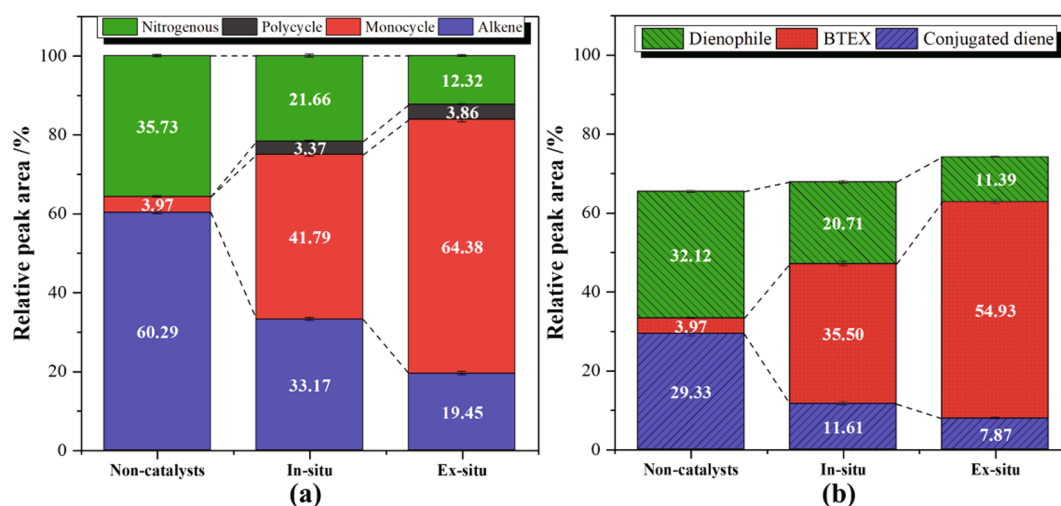

Fig. 3. Products distribution of pyrolytic oil under different catalytic mode (HZSM-5 as catalyst, Rubber-to-PAN ratio of 1:1). (a) Distribution of all products, (b) Distribution of some focused products.

clearly found that toluene and xylene accounted for the majority, while benzene and ethylbenzene accounted for only a small portion. The distribution of these four products may be due to the characteristics of the feedstock and the catalytic reaction mechanism, which will be analyzed and discussed in detail in the following paragraphs. All the results proved that ex-situ catalysis had better catalytic performance in promoting Diels-Alder reaction and increasing BTEX yield, which is in line with the results of Zheng et al. [32]. However, it should also be noted that there was still a small part of conjugated diene (7.87%) and dienophile (11.39%) remaining in the products that had not been completely converted into aromatics, which means the BTEX yield could be further improved if the catalyst could be optimized.

3.3. Effects of metal modified catalysts on the pyrolytic products

3.3.1. Characterization of the catalysts

Considerable literatures have demonstrated that Lewis and Brønsted acids on the catalysts were key factors to promote Diels-Alder reaction [18,22]. In order to optimize the distribution of the acid sites on the catalysts to further enhance the catalytic effect, four transition metals were loaded onto the parent HZSM-5 zeolite, respectively. The characterization results of the prepared catalysts are presented below.

The nitrogen adsorption-desorption isotherms of the parent and modified zeolites are shown in Fig. 5, and the physicochemical properties of the catalysts are summarized in Table 1. It can be found that the specific surface area of the catalyst was reduced to varying degrees after metal loading. Thereinto, the loss of the specific surface area of Co/HZSM-5 and Cu/HZSM-5 is more serious, suggesting their worse sintering states during calcination process than Fe/HZSM-5 and Zn/HZSM-5. A similar trend was observed in terms of pore volume, which also decreased with the loading of metals. The results of pore properties indicated that the modification of HZSM-5 zeolite with transition metals would cause blockage of a small part of pores, which had also been found in many studies, and the phenomenon was inevitable [5,24,33]. The blockage of pores may slightly weaken the adsorption effect of the catalyst in the catalytic process, but the catalytic activity of the catalyst will not be greatly affected because pores were not decisive factors in this reaction.

The acid sites on the prepared catalysts were paid high attention in this study. The NH$_3$-TPD profiles of the series catalysts are shown in Fig. 6. The broad desorption signal could be divided into three peaks located at ~150 °C, 200–300 °C, and 400–450 °C, which represents weak, medium, and strong acid sites, respectively [34]. Fig. 7 shows the Py-IR spectra of the catalysts degassed at 200 °C and 300 °C,
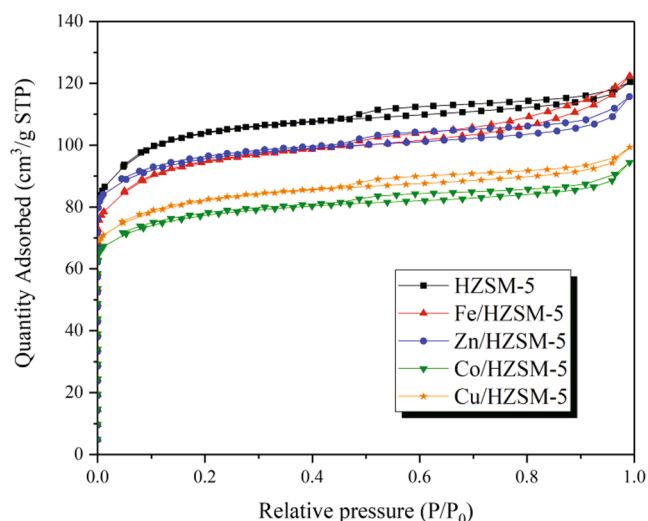
Table 1
Physicochemical properties of the catalysts.

Sample	Metal content (wt.%)	S_{BET}① (m²/g)	S_{mic}② (m²/g)	V_{total}③ (cm³/g)	V_{mic}④ (cm³/g)	D_{avg}⑤ (nm)
HZSM-5	/	337.34	252.43	0.1863	0.1230	3.695
Fe/HZSM-5	5.02	313.93	225.62	0.1892	0.1071	4.808
Zn/HZSM-5	5.05	317.20	246.62	0.1790	0.1167	4.385
Co/HZSM-5	4.91	256.53	193.65	0.1460	0.0918	4.343
Cu/HZSM-5	5.08	267.11	197.66	0.1536	0.0962	4.075

① Total specific surface area, by BET method; ② Micropore area, by t-plot method; ③ Total pore volume, by t-Plot method, calculated at $p/p_0 = 0.99$; ④ Micropore volume, by t-Plot method; ⑤ Average pore diameter, by BJH method.
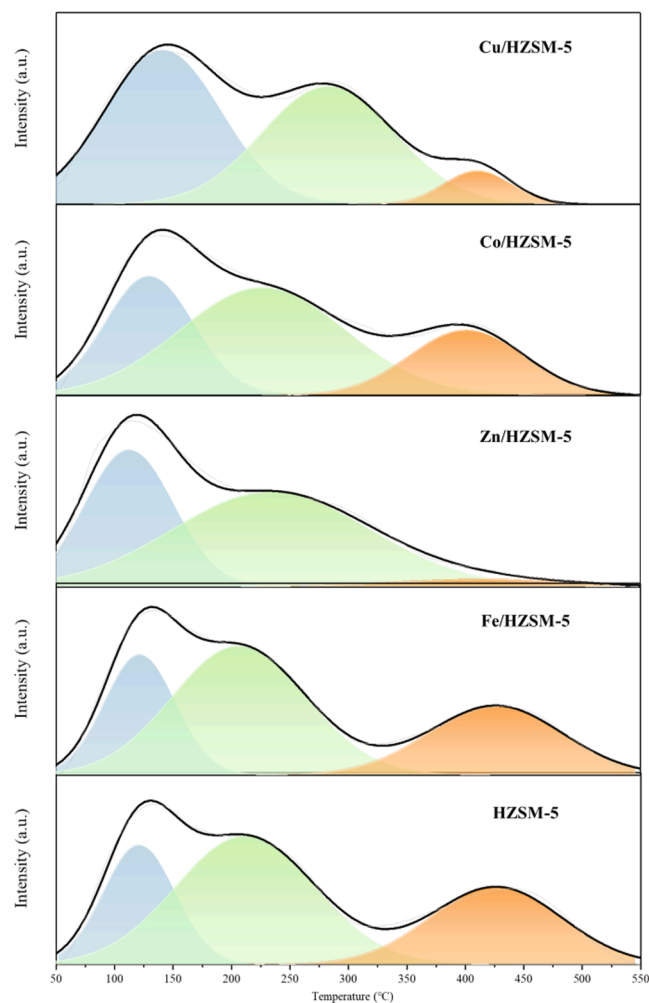

Fig. 6. NH$_3$-TPD profiles of the prepared catalysts.

representing the distribution of Lewis and Brønsted acid sites. According to the reported literature [35,36], the peak signals at around 1450, 1580, and 1620 cm^{-1} are assigned to pyridine adsorbed at Lewis acid sites, while the signals at around 1545 and 1640 cm^{-1} are attributed to Brønsted acids. Furthermore, the peak at 1485 cm^{-1} indicates the presence of both Lewis and Brønsted acid sites.

The overall acidic properties of the series catalysts are summarized in Table 2. As can be seen from the table, parent HZSM-5 catalyst and metal modified catalysts were all dominated by medium acids. After loading with Zn and Cu, the fraction of weak acid sites increased significantly at
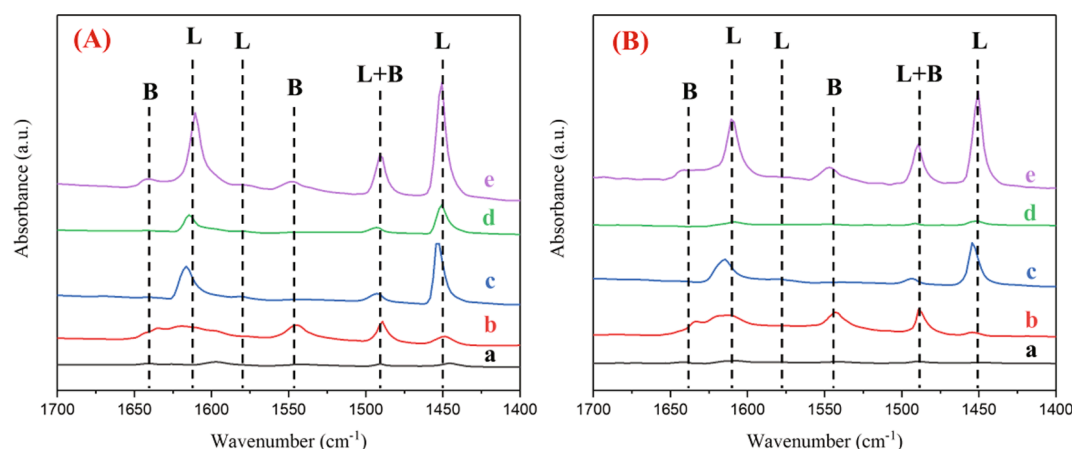

Fig. 5. N$_2$ adsorption-desorption isotherms of the catalysts.

Fig. 7. Pyridine IR spectra of the prepared catalysts after degassing at (A) 200 °C and (B) 350 °C: (a) HZSM-5; (b) Fe/HZSM-5; (c) Zn/HZSM-5; (d) Co/HZSM-5; (e) Cu/HZSM-5.

Table 2
Acidic properties of the series catalysts from NH$_3$-TPD and Py-IR measurements.

Sample	Relative acid sites (%)			200 °C				350 °C			
	Weak	Medium	Strong	L	B	L + B	L/B	L	B	L + B	L/B
HZSM-5	23.3	49.0	27.7	12.5	18.2	30.7	0.69	2.8	6.9	9.7	0.40
Fe/HZSM-5	24.3	49.5	26.2	30.1	98.7	128.8	0.30	6.9	75.4	82.3	0.09
Zn/HZSM-5	37.2	58.7	4.1	176.6	12.0	188.6	14.67	104.5	6.8	111.3	15.29
Co/HZSM-5	29.3	49.8	20.9	86.0	2.2	88.2	38.72	12.3	0.5	12.8	24.86
Cu/HZSM-5	49.5	44.1	6.4	309.8	72.5	382.3	4.27	198.5	66.5	265.0	2.99

the cost of strong acid site, while the acid distribution of Fe/HZSM-5 and Co/HZSM-5 was similar with that of parent HZSM-5. The Py-IR results indicate that HZSM-5 zeolite had both Lewis and Brønsted acids. Loading with transition metals had significant effects on the quantities and distributions of Lewis and Brønsted acids. The amount of Lewis acids on the catalyst increased after loading with Cu, Zn, and Co, while Fe/HZSM-5 didn't show a remarkable increase in Lewis acids. Adding Fe and Cu increased the amount of Brønsted acids on the catalyst. However, interestingly, the Brønsted acids on Zn/HZSM-5 and Co/HZSM-5 dropped compared with parent HZSM-5. According to Wang's conclusion [5], in addition to the amount of acids sites on the catalyst, the L/B ratio also played an essential role in Diels-Alder reaction. It can be found in the table that the L/B ratio increased in the order Fe/HZSM-5 < HZSM-5

< Cu/HZSM-5 < Zn/HZSM-5 < Co/HZSM-5, among which Co/HZSM-5 presented the largest L/B ratio while Fe/HZSM-5 was even lower than parent HZSM-5.

3.3.2. Analysis of the pyrolytic products

The catalytic activities of the prepared metal modified catalysts were investigated under ex-situ catalytic mode with Rubber-to-PAN ratio of 1:1. As shown in Fig. 8(b), compared with parent HZSM-5, the metal modified catalysts increased the BTEX content in various degree, among which Zn/HZSM-5 displayed the highest BTEX content, reaching 69.99%, followed by Cu/HZSM-5, Co/HZSM-5, and Fe/HZSM-5. As reactants, conjugated diene and dienophile accounted for 6.52% and 9.06% in the Fe/HZSM-5 catalyzed products, only 1.35% and 2.33%
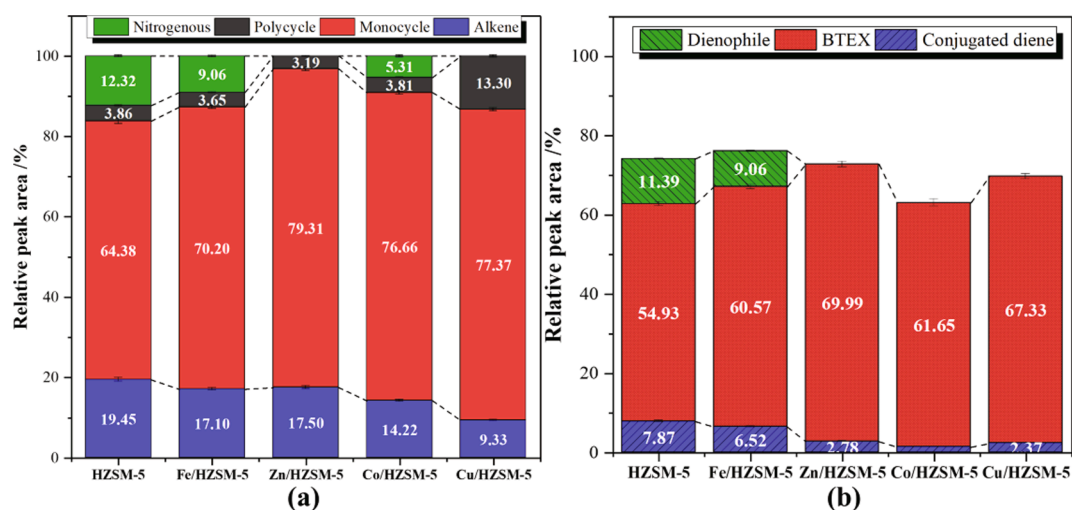

Fig. 8. Products distribution of pyrolytic oil under different metal modified catalysts (Ex-situ catalysis, Rubber-to-PAN ratio of 1:1). (a) Distribution of all products, (b) Distribution of some focused products.

lower than those in parent HZSM-5. It means Fe/HZSM-5 could not effectively promote the Diels-Alder reaction, which may be attributed to its low L/B ratio [19]. In comparison, the catalysts with high L/B ratio converted almost all conjugated diene and dienophile into BTEX, which indicated that high L/B ratio was necessary to promote Diels-Alder reaction. The product distributions of Zn/HZSM-5 and Cu/HZSM-5 in Fig. 8(b) were similar, but it can be observed from Fig. 8(a) that the catalytic products of Cu/HZSM-5 contained 13.30% polycyclic aromatic hydrocarbons, which were undesirable products for their pollution to the air [37]. Therefore, although the BTEX contents of Zn/HZSM-5 and Cu/HZSM-5 were very close, Zn/HZSM-5 was considered a better catalyst in this study due to its relatively low PAHs content.

The specific yield of benzene, toluene, ethylbenzene, xylene, and cumulative BTEX are displayed in Fig. 9. The most striking result to emerge from the figure is that although the BTEX contents were all improved to varying degrees after using metal modified catalysts, the yield of cumulative BTEX decreased for some catalysts. For instance, the BTEX content of Fe/HZSM-5 and Cu/HZSM-5 were both higher than that of HZSM-5 in Fig. 8, but the cumulative BTEX yield of Fe/HZSM-5 and Cu/HZSM-5 were lower than that of HZSM-5, as seen in Fig. 9. The reason is that after catalytic pyrolysis, the oil yield will decrease inevitably as a result of secondary reactions [6,38], which means the high relative content of a certain product is not equal to its high yield.

The conclusion further proves the importance of absolute yield analysis, which however, was often ignored in many previous studies. Another significant result can be obtained is that the selectivity to a certain product differs among the prepared catalysts. According to Fig. 9, Zn/HZSM-5 showed the best catalytic effect as its cumulative BTEX yield was the highest, reaching 19.47 wt%. Zn/HZSM-5 significantly raised the yield of benzene and toluene to 6.18% and 8.05%, respectively. However, compared with HZSM-5, Zn loading did not increase the yield of xylene and ethylbenzene, but reduced them instead. The negative effects were also observed with regard to the yield of toluene, ethylbenzene, xylene, and cumulative BTEX catalyzed by Cu/HZSM-5 and Fe/HZSM-5. The results suggest that metal modified catalysts had both positive and negative effects on the yield of BTEX, for which the reason was twofold. On the one hand, there is no doubt that Zn/Co/Cu modified catalysts could promote the Diels-Alder reaction as has been demonstrated above, which would increase the BTEX yield. On the other hand, the catalysts may further lead to secondary reactions of the formed BTEX, such as dehydrocyclization to generate polycyclic rings, which has been observed in Cu/HZSM-5. In general, considering the better promotion of Diels-Alder reaction and fewer side effects, Zn/HZSM-5 was considered the optimal catalyst in this study.
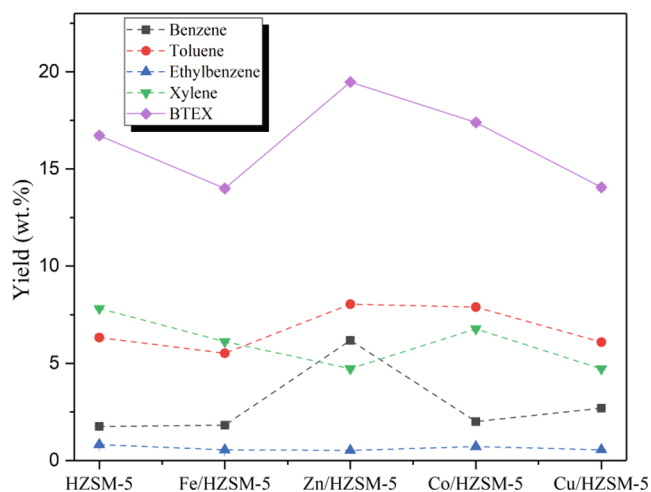
3.4. Effects of Rubber-to-PAN ratio on the pyrolytic products

To further study the influence of Rubber-to-PAN ratio on the oil products, experiments were performed under ex-situ catalysis, using Zn/HZSM-5 as catalyst. As can be seen from Fig. 10, the variation trend of the product distribution is obvious. As the ratio of Rubber-to-PAN decreased, the BTEX content showed an upward trend, while conjugated diene plummeted, which suggested that low Rubber-to-PAN ratio was conducive for promoting Diels-Alder reaction. When no polyacrylonitrile was added, the catalyst still worked in increasing BTEX content during pyrolysis treatment of waste rubber alone, which was in line with previous researches [31,39]. The addition of polyacrylonitrile could further improve the BTEX content at the expense of conjugated diene. However, when the ratio was lower than 1, continuing to increase the amount of polyacrylonitrile had little effect on the increase of BTEX content, for which the reason may be that polyacrylonitrile was excessive. According to the results in Fig. 11, the variation trend of BTEX yield was basically consistent with that of BTEX content. The smaller the Rubber-to-PAN ratio, the greater the BTEX yield. The highest cumulative BTEX yield was obtained at the ratio of 1:3, reaching 22.01 wt%. The cumulative BTEX yield skyrocketed when the Rubber-to-PAN ratio dropped from 2:1 to 1:1, and after that, the increase in BTEX yield was limited. As the increase of polyacrylonitrile had limited contribution to the increase of BTEX yield when the ratio was less than 1, considering the optimization of input and output, the Rubber-to-PAN ratio of 1:1 was considered the most appropriate condition in this study.

3.5. Evaluation of the BTEX yield

To evaluate the effectiveness of the BTEX yield in this study, some similar researches regarding the BTEX production from rubber wastes are listed in Table 3 for comparison. It is worth noting that there have been numerous researches on the recovery of aromatic hydrocarbons from wastes in previous studies. However, most of these researches used qualitative or semiquantitative analysis to discuss the results, namely using the peak area of a certain product to express its relative content, which however, was inaccurate in the strict sense [30]. For this reason, only the literatures involving the quantitative analysis of BTEX yield are presented in Table 3, while those only discussing the relative content of BTEX are not included. As can be seen from the table, same catalysts had different catalytic effects on the BTEX yield, which might be related to the type of reactor, the temperature, and the quantitative analysis method. It can be observed that zeolites were the most commonly used catalysts in promoting the BTEX production for their excellent selectivity to monocyclic aromatic hydrocarbons. The highest BTEX yield was reported by Williams et al. [40], and the BTEX yield could reach up to 17.70 wt% using Y-zeolite as catalyst on a fixed-bed reactor. Compared with pyrolysis of the waste tire alone, the catalytic co-pyrolysis of waste tire and polyacrylonitrile in this study further improved the BTEX yield, up to 22.01 wt%, demonstrating the feasibility and superiority of the strategy in this research.

3.6. Discussion of the catalytic mechanism

The possible catalytic reaction mechanisms of BTEX generation by Diels-Alder reaction are summarized in Fig. 12. The compounds in blue, black, and red dashed boxes represent reactant, intermediate product, and target product, respectively. The conversion of reactants to BTEX requires two steps. The first step is the cycloaddition of conjugated diene and dienophile to form intermediate products, and followed by a series of subsequent aromatization reactions, including elimination, dealkylation, isomerization, etc. In the first step of the reaction, isoprene and dienophile undergo an addition reaction to form a six-membered ring. Because the molecular structures of isoprene and dienophile are asymmetric, two products with different structures will be formed after cycloaddition. Then the six-membered rings are altered into benzene
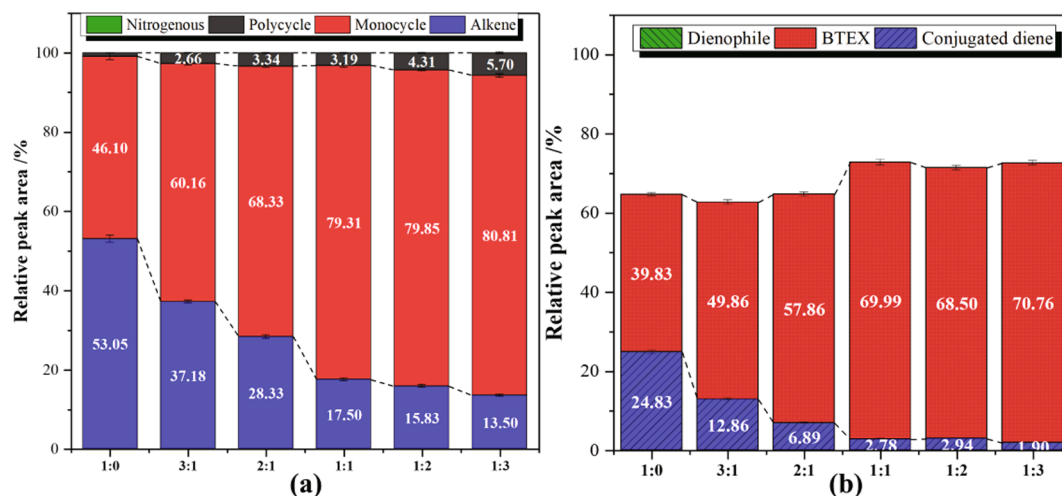

Fig. 9. BTEX yield under different metal modified catalysts (Ex-situ catalysis, Rubber-to-PAN ratio of 1:1).

Fig. 10. Products distribution of pyrolytic oil under different Rubber-to-PAN ratio (Ex-situ catalysis, Zn/HZSM-5 as catalyst). (a) Distribution of all products, (b) Distribution of some focused products.
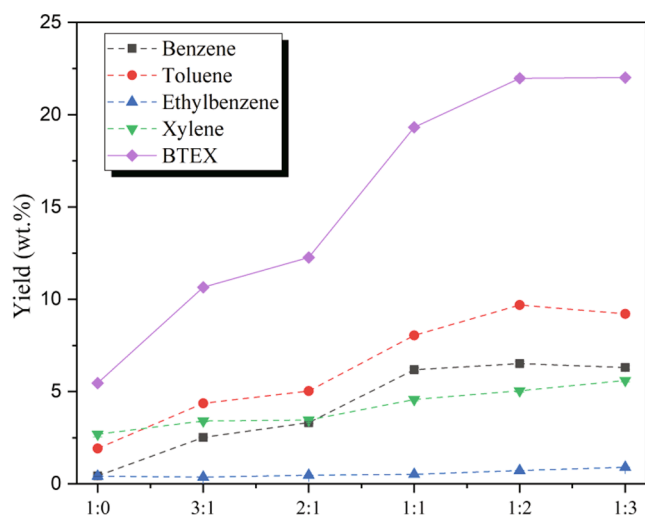

Fig. 11. BTEX yield under different Rubber-to-PAN ratio (Ex-situ catalysis, Zn/HZSM-5 as catalyst).

ring by eliminating a hydrogen cyanide and a hydrogen. It is worth noting that the intermediate product has two para or meta substituents, whose structure is decided by the spatial configuration of the reactants. Of the two substituents, one is methyl, originating from isoprene, and the other is methyl or hydrogen, derived from dienophile, represented by 'R' in the figure. When the 'R' represents hydrogen, both intermediate products generate toluene, while when it is methyl, the intermediate products end up as m-xylene and p-xylene. A small part of the produced m/p-xylene is converted to o-xylene and ethylbenzene through isomerization. Finally, part of the toluene, xylene, and ethylbenzene will be

converted to benzene by dealkylation.

The specific roles of Lewis and Brønsted acids during the conversion pathways of BTEX can be summarized according to the distribution of pyrolytic products and the characterization of the catalysts. It can be observed in Fig. 8(b) that there were many unreacted dienophiles in the group of HZSM-5 and Fe/HZSM-5. This phenomenon was attributed to the incomplete cycloaddition of conjugated diene and dienophile. The incomplete cycloaddition was related to the inadequate Lewis acids on HZSM-5 and Fe/HZSM-5, whose amounts of Lewis acids were much lower than the other three catalysts according to Table 2. In addition, it can be found in Table 2 that the amount of Brønsted acids on Co/HZSM-5 was particularly low compared with the other groups, which could explain its relatively low BTEX content in Fig. 8(b). Based on the above results and analyses, the effects of Lewis and Brønsted acids can be concluded as follows. The Lewis acids mainly functioned in the first step by promoting the cycloaddition of conjugated diene and dienophile to form intermediate products [18]. The Brønsted acids played their roles in the elimination reactions to form aromatic structures [20]. Both Lewis and Brønsted acids played an essential role in the conversion pathways of BTEX and both of them were indispensable. Therefore, it is vital to modify the catalysts to make them own moderate Lewis and Brønsted acids.

The distribution of the catalytic products can be well explained by the reaction mechanism. As can be seen from the reaction pathways, m-xylene, p-xylene, and toluene are the primary products of the Diels-Alder reaction, while benzene and ethylbenzene are secondary products, which can only be generated through the secondary reactions of xylene and toluene. This is the reason why the cumulative BTEX was dominated by xylene and toluene after catalytic pyrolysis in Fig. 4. Moreover, it can be inferred that Zn/HZSM-5 promoted the dealkylation of toluene and xylene, as its benzene yield was significantly higher than other metal modified catalysts while the xylene yield was low. In addition to the

Table 3
The BTEX yields obtained from previous studies.

Raw material	Reactor type	Temperature (°C)	Catalyst type	BTEX yield (wt.%[①])	Calibration?	Ref.
Waste tire and PAN	Py-GC/MS	500	HZSM-5 zeolite	22.01	Yes	This study
Waste tire	Py-GC/MS	500	HZSM-5 zeolite	12.66	Yes	[41]
Waste tire	Py-GC/MS	500	Tire derived char	10.14	Yes	[41]
Waste tire	Fix-bed reactor	500	Y-zeolite	17.70	Yes	[40]
Waste tire	Stainless steel reactor	430	ZSM-5 zeolite	11.37	No	[42]
Waste tire	Fix-bed reactor	500	USY zeolite	9.66	No	[8]

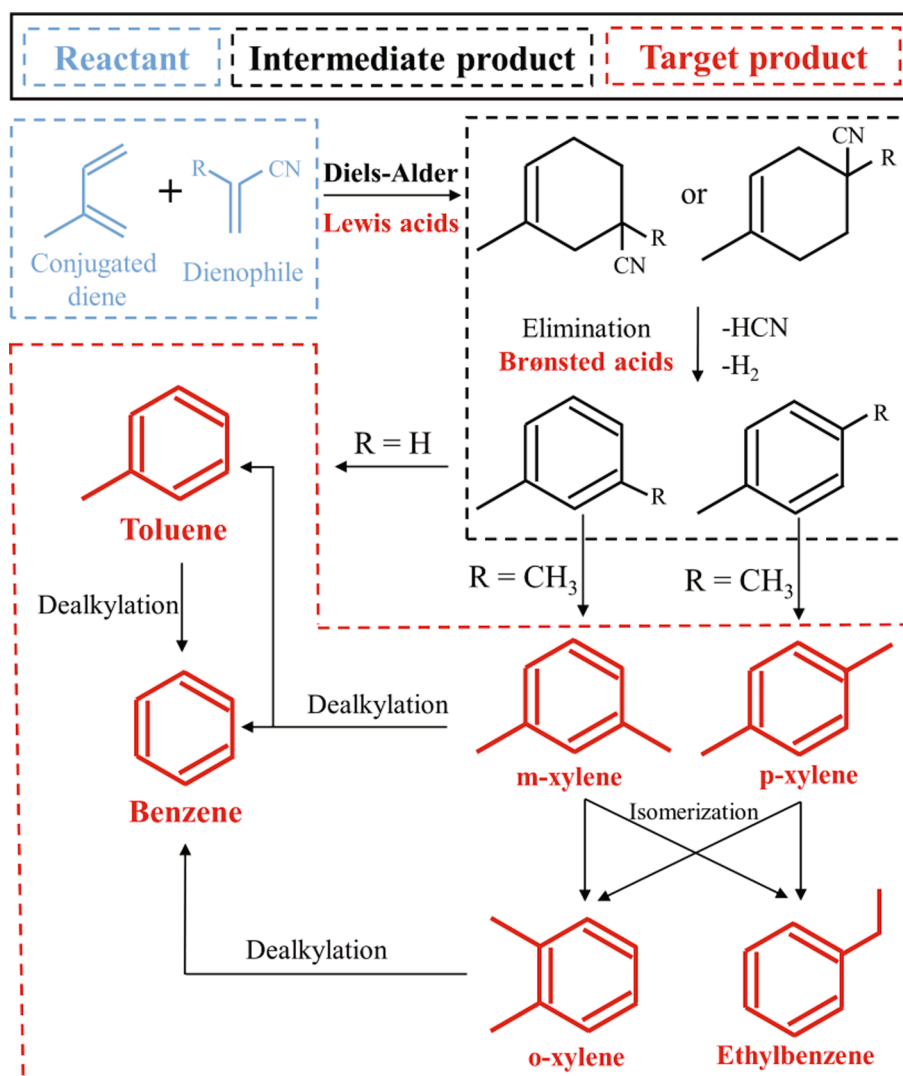① wt.%: $g \cdot (100 \text{ g raw material})^{-1}$.

Fig. 12. Reaction mechanisms of BTEX formation via Diels-Alder reaction.

Diels-Alder reaction, BTEX as well as other monocyclic aromatics can be formed through other pathways such as cyclization and dehydrogenation of chain alkenes, degradation of limonene, and so on, which will also have impact on the BTEX yield [41].

4. Conclusions

In this paper, catalytic co-pyrolysis of rubber waste and polyacrylonitrile using metal modified HZSM-5 zeolites as catalysts was investigated for producing BTEX enriched oil by enhancing the Diels-Alder reaction. Investigations on the effects of catalytic mode, catalyst type, and the mass ratio of feedstocks were conducted on a tandem Py-GC/MS to optimize the catalytic conditions for increasing BTEX yield.

The results revealed that the primary pyrolytic products of rubber waste were rich in isoprene, and those of polyacrylonitrile were abundant in dienophiles. Catalytic co-pyrolysis of rubber waste and polyacrylonitrile could significantly improve the BTEX yield via facilitating the Diels-Alder reaction. Compared with in-situ catalysis, ex-situ catalysis showed better catalytic effect. Both relative content and absolute yield of BTEX under ex-situ catalysis were higher than those under in-situ catalysis. The surface properties of the HZSM-5 catalyst, such as pore structure and acid sites, could be modified and improved by loading with different transition metals. Zn modified HZSM-5 catalyst showed the best catalytic effect in promoting the Diels-Alder reaction for

its highest BTEX content (69.99%) and BTEX yield (19.47 wt%) in catalytic products. In a certain range, increasing the proportion of polyacrylonitrile in the feedstock could improve the BTEX yield, while too much polyacrylonitrile had limited effect in promoting the Diels-Alder reaction. On the whole, the highest BTEX yield was obtained under the condition of ex-situ catalysis, Zn/HZSM-5 as catalyst, and Rubber-to-PAN ratio of 1:3, at which case the BTEX yield reached 22.01 wt%. However, considering the input and output, the optimal condition should be ex-situ catalysis, Zn/HZSM-5 as catalyst, and Rubber-to-PAN ratio of 1:1, at which case the BTEX yield was 19.47 wt%. The results proved that rubber wastes have potential to be an alternative fuel for producing valuable BTEX under this strategy.

CRediT authorship contribution statement

Yuhan Pan: Conceptualization, Methodology, Investigation, Writing – original draft. **Jiaxing Song:** Visualization, Data curation. **Fangfang Lou:** Validation, Investigation. **Jun Xu:** Resources, Funding acquisition. **Yonggang Zhou:** Formal analysis. **Qunxing Huang:** Writing – review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2022.124028.

References

[1] Settle AE, Berstis L, Rorrer NA, Roman-Leshkóv Y, Beckham GT, Richards RM, et al. Heterogeneous Diels-Alder catalysis for biomass-derived aromatic compounds. Green Chem 2017;19(15):3468–92.

[2] Wang J, Jiang J, Wang X, Pang S, Sun Y, Meng X, et al. Enhanced BTEX formation via catalytic fast pyrolysis of styrene-butadiene rubber: Comparison of different catalysts. Fuel 2020;278:118322.

[3] Lee SB, Lee J, Tsang YF, Kim Y-M, Jae J, Jung S-C, et al. Production of value-added aromatics from wasted COVID-19 mask via catalytic pyrolysis. Environ Pollut 2021;283:117060.

[4] Gałko G, Rejdak M, Tercki D, Bogacka M, Sajdak M. Evaluation of the applicability of polymeric materials to BTEX and fine product transformation by catalytic and non-catalytic pyrolysis as a part of the closed loop material economy. J Anal Appl Pyrol 2021;154:105017.

[5] Wang J, Jiang J, Sun Y, Meng X, Wang X, Ruan R, et al. Heterogeneous Diels-Alder tandem catalysis for converting cellulose and polyethylene into BTX. J Hazard Mater 2021;414:125418.

[6] Arabiourrutia M, Lopez G, Artetxe M, Alvarez J, Bilbao J, Olazar M. Waste tyre valorization by catalytic pyrolysis – A review. Renew Sustain Energy Rev 2020;129:109932.

[7] Quek A, Balasubramanian R. Liquefaction of waste tires by pyrolysis for oil and chemicals—A review. J Anal Appl Pyrol 2013;101:1–16.

[8] Boxiong S, Chunfei Wu, Binbin G, Rui W, Liangcai. Liangcai. Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Appl Catal B 2007;73(1-2):150–7.

[9] Miguel GS, Aguado J, Serrano DP, Escola JM. Thermal and catalytic conversion of used tyre rubber and its polymeric constituents using Py-GC/MS. Appl Catal B 2006;64(3):209–19.

[10] Mastral AM, Murillo R, Callén MS, García T, Snape CE. Influence of Process Variables on Oils from Tire Pyrolysis and Hydropyrolysis in a Swept Fixed Bed Reactor. Energy Fuels 2000;14(4):739–44.

[11] Lopez G, Olazar M, Aguado R, Elordi G, Amutio M, Artetxe M, et al. Vacuum Pyrolysis of Waste Tires by Continuously Feeding into a Conical Spouted Bed Reactor. Ind Eng Chem Res 2010;49(19):8990–7.

[12] Unapumnuk K, Lu M, Keener TC. Carbon Distribution from the Pyrolysis of Tire-Derived Fuels. Ind Eng Chem Res 2006;45(26):8757–64.

[13] Zhao Y, Yang X, Fu Z, Li R, Wu Y. Synergistic effect of catalytic co-pyrolysis of cellulose and polyethylene over HZSM-5. J Therm Anal Calorim 2020;140(1):363–71.

[14] Kasipandi S, Cho JM, Park KS, Shin C-H, Wook Bae J. Unprecedented activity and stability on zirconium phosphates grafted mesoporous silicas for renewable aromatics production from furans. J Catal 2020;385:10–20.

[15] Ding K, Zhong Z, Zhang B, Song Z, Qian X. Pyrolysis Characteristics of Waste Tire in an Analytical Pyrolyzer Coupled with Gas Chromatography/Mass Spectrometry. Energy Fuels 2015;29(5):3181–7.

[16] Pan Y, Yang D, Sun K, Wang X, Zhou Y, Huang Q. Pyrolytic transformation behavior of hydrocarbons and heteroatom compounds of scrap tire volatiles. Fuel 2020;276:118095.

[17] Minagawa M, Onuma H, Ogita T, Uchida H. Pyrolysis gas chromatographic analysis of polyacrylonitrile. J Appl Polym Sci 2001;79(3):473–8.

[18] Vermeeren P, Tiezza MD, Dongen M, Fernández I, Bickelhaupt FM, Hamlin TA. Lewis Acid-Catalyzed Diels-Alder Reactions: Reactivity Trends across the Periodic Table. Chemistry – Eur J 2021;27(41):10610–20.

[19] Gao Z, Feng Y, Zhang L, Zeng X, Sun Y, Tang X, et al. Catalytic Conversion of Biomass-Derived 2, 5-Dimethylfuran into Renewable p-Xylene over SAPO-34 Catalyst. ChemistrySelect 2020;5(8):2449–54.

[20] Wang D, Osmundsen CM, Taarning E, Dumesic JA. Selective Production of Aromatics from Alkylfurans over Solid Acid Catalysts. ChemCatChem 2013;5(7):2044–50.

[21] Song S, Wu G, Dai W, Guan N, Li L. Diels-Alder and dehydration reactions of furan derivatives with ethylene catalyzed by liquid Brønsted acids and Lewis acids. J Mol Catal A: Chem 2016;420:134–41.

[22] Pindur U, Lutz G, Otto C. Acceleration and selectivity enhancement of Diels-Alder reactions by special and catalytic methods. Chem Rev 1993;93(2):741–61.

[23] Vichaphund S, Aht-ong D, Sricharoenchaikul V, Atong D. Production of aromatic compounds from catalytic fast pyrolysis of Jatropha residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. Renew Energy 2015;79:28–37.

[24] Lin B, Wang J, Huang Q, Ali M, Chi Y. Aromatic recovery from distillate oil of oily sludge through catalytic pyrolysis over Zn modified HZSM-5 zeolites. J Anal Appl Pyrol 2017;128:291–303.

[25] Arteaga-Pérez LE, Jiménez R, Grob N, Gómez O, Romero R, Ronsse F. Catalytic upgrading of biomass-derived vapors on carbon aerogel-supported Ni: Effect of temperature, metal cluster size and catalyst-to-biomass ratio. Fuel Process Technol 2018;178:251–61.

[26] Wang K, Johnston PA, Brown RC. Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. Bioresour Technol 2014;173:124–31.

[27] Akoueson F, Chbib C, Monchy S, Paul-Pont I, Doyen P, Dehaut A, et al. Identification and quantification of plastic additives using pyrolysis-GC/MS: A review. Sci Total Environ 2021;773:145073.

[28] Olazar M, Aguado R, Arabiourrutia M, Lopez G, Barona A, Bilbao J. Catalyst Effect on the Composition of Tire Pyrolysis Products. Energy Fuels 2008;22(5):2909–16.

[29] Banar M, Akyıldız V, Özkan A, Çokaygil Z, Onay Ö. Characterization of pyrolytic oil obtained from pyrolysis of TDF (Tire Derived Fuel). Energy Convers Manage 2012;62:22–30.

[30] Danon B, van der Gryp P, Schwarz CE, Görgens JF. A review of dipentene (dl-limonene) production from waste tire pyrolysis. J Anal Appl Pyrol 2015;112:1–13.

[31] Ding K, Zhong Z, Zhang B, Wang J, Min A, Ruan R. Catalytic pyrolysis of waste tire to produce valuable aromatic hydrocarbons: An analytical Py-GC/MS study. J Anal Appl Pyrol 2016;122:55–63.

[32] Zheng Y, Wang J, Liu C, Lin X, Lu Y, Li W, et al. Enhancing the aromatic hydrocarbon yield from the catalytic copyrolysis of xylan and LDPE with a dual-catalytic-stage combined CaO/HZSM-5 catalyst. J Energy Inst 2020;93(5):1833–47.

[33] Mekasuwandumrong O, Somboonthanakij S, Praserthdam P, Panpranot J. Preparation of Nano-Pd/SiO2 by One-Step Flame Spray Pyrolysis and Its Hydrogenation Activities: Comparison to the Conventional Impregnation Method. Ind Eng Chem Res 2009;48(6):2819–25.

[34] Zhang H, Yang W, Roslan II, Jaenicke S, Chuah G-K. A combo Zr-HY and Al-HY zeolite catalysts for the one-pot cascade transformation of biomass-derived furfural to γ-valerolactone. J Catal 2019;375:56–67.

[35] Wang X, Xiao C, Zheng P, Zhao Z, Alabsi MH, Shi Y, et al. Dendritic micro–mesoporous composites with center-radial pores assembled by TS-1 nanocrystals to enhance hydrodesulfurization activity of dibenzothiophene and 4,6-dimethyldibenzothiophene. J Catal 2020;384:136–46.

[36] Wang X, Du P, Zhao Z, Mei J, Chen Z, Li Y, et al. Optimal Synthesis of Hierarchical Porous Composite ZSM-5/SBA-16 for Ultradeep Hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene. Part 2: The Influence of Aging Temperature on the Properties of NiMo Catalysts. Energy Fuels 2018;32(7):7800–9.

[37] Chen S-J, Su H-B, Chang J-E, Lee W-J, Huang K-L, Hsieh L-T, et al. Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires. Atmos Environ 2007;41(6):1209–20.

[38] Miandad R, Barakat MA, Rehan M, Aburiazaiza AS, Gardy J, Nizami AS. Effect of advanced catalysts on tire waste pyrolysis oil. Process Saf Environ Prot 2018;116:542–52.

[39] Vichaphund S, Aht-ong D, Sricharoenchaikul V, Atong D. Effect of CV-ZSM-5, Ni-ZSM-5 and FA-ZSM-5 catalysts for selective aromatic formation from pyrolytic vapors of rubber wastes. J Anal Appl Pyrol 2017;124:733–41.

[40] Williams PT, Brindle AJ. Aromatic chemicals from the catalytic pyrolysis of scrap tyres. J Anal Appl Pyrol 2003;67(1):143–64.

[41] Pan Y, Sima J, Wang X, Zhou Y, Huang Q. BTEX recovery from waste rubbers by catalytic pyrolysis over Zn loaded tire derived char. Waste Manage 2021;131:214–25.

[42] Qu W, Zhou Q, Wang Y-Z, Zhang J, Lan W-W, Wu Y-H, et al. Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. Polym Degrad Stab 2006;91(10):2389–95.