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Co-hydropyrolysis of pine and HDPE over bimetallic catalysts: Efficient BTEX production and process mechanism analysis

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ABSTRACT

Co-pyrolysis of plastics and biomass is expected to replace traditional petroleum processing to produce BTEX (benzene, toluene, ethylbenzene, and xylenes) on a large scale, which are important chemical raw materials. The introduction of bimetallic catalysts and hydrogen in co-pyrolysis systems is an effective strategy to increase the content of aromatic hydrocarbons in pyrolysis oils, which has not been studied so far. The present study investigated the efficacy of bimetallic catalysts in enhancing aromatization and Diels-Alder reactions in comparison to Mo/ZSM-5. The synergistic interaction between bimetals contributed to the improved selectivity of aromatic hydrocarbons, particularly BTEX. Results revealed that NiMo/ZSM-5 catalysts led to higher aromatics selectivity in liquid oil, whereas FeMo/ZSM-5 resulted in higher BTEX selectivity for aromatic hydrocarbons. Moreover, metal oxide-supported bimetallic catalysts exhibited lower selectivity for aromatic hydrocarbons in liquid oil, despite facilitating higher liquid-oil yield. Among the metal oxide-supported bimetallic catalysts, FeMo/TiO₂ demonstrated the highest selectivity of BTEX in aromatic hydrocarbons, hus highlighting the significance of hydrogen resulted in 100% selectivity of BTEX. Combined with the experimental results and literature, a possible reaction mechanism was also proposed.

1. Introduction

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are the key organic chemicals, widely used in the production of various chemical products [1–4]. BTEX is also an important blending component to improve the octane number of gasoline [4]. At present, BTEX is generated mainly through the processing of fossil fuel resources, such as thermal fractionation of coal and catalytic reforming and aromatization of petroleum [5–7]. However, as fossil fuel resources are non-renewable and rapidly consumed [8], traditional methods of producing BTEX from fossil fuel resources are gradually limited. As the only renewable energy containing carbon [9], abundant waste biomass is expected to replace fossil fuel resources for large-scale BTEX production [9,10].

Pyrolysis is a thermal decomposition process that converts either biological or synthetic polymers into valuable products [11,12]. Pyrolysis has been well explored by worldwide researchers as an efficient pathway to produce BTEX from lignocellulosic biomass [13–16].

Cárdenas Galindo et al. investigated the effects of Aerosil and MCM-41 catalysts on the production of BTEX from Agave salmiana bagasse pyrolysis [17]. Park et al. investigated the effects of different pyrolysis atmospheres (N2, CH4, and pre-decomposed CH4 stream) on the BTEX production of yellow poplar pyrolysis under two zeolite catalysts [18]. This technology offers a sustainable solution for converting low-cost and abundant biomass feedstocks into high-value chemicals that are used in various fields. However, the oxygen-rich characteristics of biomass lead to low yield of hydrocarbons and excessive coke formation on catalyst [19,20]. Rangel et al. produced BTEX with a yield of 39.35% by catalytic fast pyrolysis of MDF residues on nickel modified beta zeolites [21]. Park et al. produced a maximum BTEX yield of 9.58 wt% under the CH₄ ex-situ decomposition environment over 1 wt% Ga/HZSM-5 [18]. The comprehensive evaluation of ten catalysts used for biomass pyrolysis by Saffron et al. indicated that except for HZSM-5, all the other catalysts had low aromatics yield and different degrees of coke formation [22].

Co-pyrolysis of biomass and hydrogen-rich feedstock is an effective

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strategy to improve aromatics yield and inhibit coke formation [23]. Plastics are widely produced and used in industry, agriculture, and other fields because of their lightweight and high durability [24,25]. Due to the short service life, a large amount of waste plastic accumulates in the environment [26,27]. Waste plastics have the advantages of high H/C effective ratio, abundance and low cost, and can be used as hydrogenrich materials in biomass pyrolysis system [28], which is not only expected to increase selectivity of aromatic hydrocarbons in pyrolysis oil, but also to alleviate the environmental problems caused by waste plastics. Previous studies have indicated that co-pyrolysis of plastics and biomass showed synergistic effects, enhancing the production of pyrolysis oil with lower oxygenates contents compared to individual pyrolysis [29]. Önal and co-workers [30] carried out co-pyrolysis of high density polyethylene and potato skin and observed that co-pyrolysis can produce high calorific value oils with higher H and C content and lower O content. Vibhakar and co-workers [31] demonstrated that co-pyrolysis of agricultural residues and mixed plastics resulted in lower oxygenates in co-pyrolysis oil. The pyrolysis of plastics can promote mass and heat transfer by producing a liquid medium, thus promoting the pyrolvsis of biomass [32].

The addition of catalysts in the co-pyrolysis process helps to promote decarboxylation, dehydration, decarbonylation and hydrogenation, which reduces oxygenates content and improves the selectivity of aromatic hydrocarbons in liquid oil [33]. At present, zeolite, modified zeolite and metal oxides are the main catalysts used in co-pyrolysis of plastics and biomass [34,35]. It was demonstrated that interactions between metals help modify properties of catalysts surface, resulting in increases in catalytic activity and selectivity for target products [36]. Hence, applications of bimetallic catalysts in co-pyrolysis of plastic and biomass are promising options for the generation of bio-oil with high BTEX selectivity. However, bimetallic catalysts have rarely been reported in co-pyrolysis of plastic and biomass [34]. Given the advantages of bimetallic catalysts, it is worth exploring the effects of bimetallic catalysts on co-pyrolysis of plastics and biomass, and screening best bimetallic catalysts to achieve higher reaction rate, BTEX selectivity and liquid oil yield.

The addition of hydrogen in pyrolysis was initially used to study coal and subsequently to biomass for hydrocarbons production [37]. Previous studies have indicated that hydrogen is important in the catalytic pyrolysis of biomass. Reductive hydrogen gas in the pyrolysis can produce hydrogen radicals reacting with volatiles released from biomass to remove oxygen in the form of H₂O, CO and CO₂, and produce aromatic hydrocarbons [38]. Reactive volatile intermediates can also be capped by hydrogen radicals to avoid catalyst coking due to further polymerization [39]. Moreover, the addition of hydrogen leads to exothermic reaction, and the generated heat is conducive to sustaining the endothermic pyrolysis reaction [40]. In view of the unique properties of hydrogen, the introduction of hydrogen in the catalytic co-pyrolysis of plastics and biomass may be beneficial to generations of aromatic hydrocarbons. However, as far as we know, the effect of hydrogen on the catalytic co-pyrolysis of plastics and biomass hasn't been investigated.

In this study, co-hydropyrolysis of biomass and plastics on bimetallic catalysts was performed, aiming to explore the effects of the addition of bimetallic catalysts on the reaction, and screen optimal bimetallic catalysts for highly selective production of aromatic hydrocarbons, especially BTEX in pyrolysis oil. To investigate the effect of hydrogen on catalytic co-pyrolysis of biomass and plastics, the experiments under helium atmosphere were also carried out to confirm the positive effect of the hydrogen on the production of aromatic hydrocarbons. Combined with the experimental results and literature, a possible reaction mechanism was also proposed. This paper has new understandings of the reaction mechanism and process of co-hydropyrolysis pyrolysis of plastics and biomass over bimetallic catalysts, which has a guiding significance for the efficient and large-scale production of BTEX.

2. Material and methods

2.1. Materials

Pine sawdust were bought from a wood mill near Hangzhou and then ground and sifted. After that, fine powder with particle size between 180 and 200 mesh was collected as feedstock for experiments. HDPE with a particle size of about 200 mesh was purchased from Macklin. Pine and HDPE samples were pre-mixed in a mixer for 12 h to form a homogeneous mixture (60 wt% pine and 40 wt% HDPE), which was then dried at 90 °C for 12 h before experiments. Table 1 showed the proximate and ultimate analysis of the feedstock.

The wetness impregnation method was used to prepare Mo/ZSM-5, NiMo/ZSM-5, FeMo/ZSM-5, FeMo/ZrO2, FeMo/y-Al2O3, and FeMo/ TiO₂ catalysts. The preparation of the catalysts involves the dissolution of the metal precursor and metal oxide or zeolite in deionized water. The resulting suspension undergoes a series of treatments including heating, stirring, cooling, and drying, followed by high-temperature calcination, to yield the final catalysts with desired characteristics. Please refer to previous papers and supplementary information for the specific synthesis method of catalysts [41,42]. The nominal Mo and Ni/Fe mass content in catalysts was 4 wt% of the supports mass, respectively. Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), nano zirconia (ZrO₂), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·H₂O), alumina (γ-Al₂O₃), and nano titanium oxide (TiO₂) were purchased from Aladdin. Zeolite ZSM-5 (Si/Al = 27:1, Nankai University Catalyst Co., Ltd) was activated to form HZSM-5 at 550 °C for 4 h.

2.2. Catalyst characterization

The porosity and specific surface area of bimetallic catalysts were determined by Micromeritics ASAP2020 instrument. The acid sites of bimetallic catalysts were measured by Micromeritics Autochem II 2920 Chemisorption analyzer. The crystallization of bimetallic catalysts was measured by Rigaku MiniFlex 600. Please refer to the supplementary information for detailed characterization methods.

2.3. Pyrolysis system

The experiments were carried out on a tandem micro-pyrolyzer (Rx-3050TR, Frontier Laboratory, Japan). This pyrolysis system was described in detail in our previous works [43,44]. At each run, 0.83 mg of a mixture of 60 wt% pine/40 wt% HDPE was loaded into a sample cup which was then placed into 1st pyrolyzer. The pyrolysis vapors then went through the second pyrolyzer, which contained 20 mg of reduced catalyst. The temperatures of the first and second pyrolyzer were set at 600 °C. To prevent condensation of pyrolysis vapors, the interface temperature of the first and second pyrolyzer was set at 350 °C. The upgraded vapors were then purged into a Gas Chromatograph-Mass

Ultimate and proximate analysis of pine and HDPE.

Pine	HDPE
49.74	85.06
6.12	14.05
42.70	0.00
0.11	0.31
2.02	0.20
82.60	99.80
15.34	0.00
0.04	0.00
	Pine 49.74 6.12 42.70 0.11 2.02 82.60 15.34 0.04

^a Calculated by difference.

Spectrometer (GC, 7890B, MS, 5977B, Agilent Technologies, USA) for identification and quantification using external standard method. The detailed quantitative methods can be found in the Supplementary information (2.3 Pyrolysis system).

Product distribution can be seen by carbon yield. The specific calculation formula is as follows. The unaccounted portion includes large molecular weight compounds undetectable by GC–MS, unrecovered char deposited on reactor walls, catalyst surfaces, and catalytic tube sections.

$$Carbon yield = \frac{Moles of carbon in specific species}{Moles of carbon in feedstocks} \times 100\%$$
(1)

$$Carbon \ selectivity = \frac{Moles \ of \ carbon \ in \ specific \ species}{Moles \ of \ carbon \ in \ all \ quantified \ species} \times 100\%$$
(2)

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. XRD analysis

Fig. 1(a) showed XRD patterns of bimetallic catalysts. The XRD patterns of FeMo/ZSM5 exhibited characteristic peaks of ZSM-5 at 2θ of

8.0°, 8.8°, 9.0°, 23.1°, 23.2°, 23.9° and 24.4°, which were indexed as (101), (200), (111), (501), (051), (033), (133) planes (PDF#47-0638). Diffraction peaks with 2-theta values of 31.1°, 33.8° and 37.9° were characteristic peaks of iron oxide (Fe₂O₃) (PDF#40-1139) and the diffraction peaks at 25.8°, 27.4°, 39.0° and 39.2° were characteristic peaks of molybdenum oxide (MoO₃) (PDF#47-1320), which confirmed that Fe and Mo was successfully impregnated on ZSM-5 and existed as metal oxides. In addition to the characteristic peaks of ZSM-5 and MoO₃, the XRD patterns of NiMo//ZSM-5 exhibited the characteristic peaks of nickel oxide (Ni₂O₃) at 32.0°, 44.8°, 51.6° and 56.8° (PDF#14-0481), which indicated that Ni also existed in the form of oxides on the ZSM-5. The XRD patterns of FeMo/ γ Al₂O₃ presented the characteristic peaks of aluminum oxide (Al₂O₃) at the 2-theta values of 19.6°, 31.9°, 37.6°, $39.5^\circ\text{, }45.8^\circ\text{, }60.5^\circ\text{ and }66.8^\circ\text{ (PDF}\#29\text{--}0063\text{)}.$ Molybdenum peaks were detected at 2-theta values of 40.5° and 73.7° (PDF#42–1120), while iron peak was detected at 44.7° (PDF#06–0696). The diffraction peaks of 36.5°, 38.0°, 53.8° and 65.7° were characteristic peaks of molybdenum oxide (MoO₂) (PDF#50–0739). The results implied that Fe and Mo existed mainly as metal elements on the Al₂O₃ support, and a small part of molvbdenum existed as metal oxides. The XRD patterns of FeMo/ZrO₂ showed the characteristic peak of baddelevite at the 2-theta values of 28.2°, 31.5°, 50.1°, 34.2°, 49.3° and 35.3°. The diffraction peak of 44.7° (110) is a characteristic peak of iron (PDF#06-0696), and diffraction peaks at 41.4°, 41.6°, 42.7°, 43.9°, 45.4° and 45.8° were characteristic



Fig. 1. Characterizations of bimetallic catalysts (a) XRD patterns, (b) N₂ adsorption-desorption isotherms, and (c) NH₃-TPD profiles.

peaks of iron molybdenum (Fe₆₃Mo₃₇) (PDF#19–0608), which indicated that Fe and Mo on ZrO₂ support formed alloy structure, and a small part of Fe existed as elemental form. The XRD patterns of FeMo/TiO₂ exhibited the characteristic peaks of anatase at the 2-theta values of 5.3° , 37.8° , 48.0° , 53.9° , 55.0° , 62.7° , 70.3° , and 75.0° (PDF#21–1272). The diffraction peaks at 17.6° , 25.1° , 32.1° , 35.9° , 37.0° , 45.2° and 58.9° are characteristic peaks of Kamiokite (Fe²₂+Mo³⁺₄O₈) (PDF#36–0526), indicating that Fe and Mo existed mainly in alloy structure on TiO₂ support. The XRD results showed that the main forms of metal on ZSM-5 support were metal elements and alloys.

3.1.2. Specific surface area and pore structure

Table 2 and Fig. 1(b) provided the N2-TPD isotherms, specific surface areas, pore volumes, and average pore diameters of the bimetallic catalysts. FeMo/ZSM-5 and NiMo/ZSM-5 catalysts exhibited type I isotherms, showing the existence of micropores in the catalysts, while hysteresis loops indicated the presence of a certain amount of mesopores in the catalyst [45]. FeMo/TiO2 and FeMo/yAl2O3 showed type IV isotherms, showing the existence of mesopores in the catalyst. Compared with catalysts supported by metal oxides, catalysts supported by zeolite had a smaller average pore diameter (\sim 3 nm) and more micropores (\sim 0.1 cm³/g), and larger specific surface area (232.2726 and 256.6446 m^2/g), which can provide more active sites. The type of bimetal coated on the zeolite support affects the specific surface area of the catalyst. The larger the ionic radius of the metal, the higher the probability of pore blockage in the zeolite skeleton. Hence, NiMo/ZSM-5 catalyst had a smaller average pore diameter than FeMo/ZSM-5 catalyst, but a larger specific surface area of micropore (182.8329 m^2/g). However, the FeMo/ZSM-5 catalyst had a higher proportion of mesopores (38.29%), which may have led to more active sites and allowed more macromolecules to pass through. The catalysts supported by metal oxides primarily consisted of mesoporous. FeMo/ γ Al₂O₃ catalyst had the smallest average pore diameter and the largest specific surface area (120.9076 m^2/g), followed by FeMo/TiO₂ and FeMo/ZrO₂.

3.1.3. NH3-TPD

The active sites of catalysts often come from acidic sites in the catalyst structure. Therefore, NH₃-TPD of bimetallic catalysts has been conducted to determine the quantity and strength of acid sites, and the results were presented in Fig. 1(c) and Table 3. The desorption peak 1 in the low-temperature range may be assigned to the adsorption of NH₃ on the Lewis acid site and physical adsorption site [46]. The desorption peak 2 in the high-temperature range could be associated with the adsorption of NH₃ on the strong Brønsted acid site [46]. The catalyst supported by zeolite presented one desorption peak in low temperature, which corresponds to the weak acid site, indicating that the intensity distribution of the acid site is concentrated. The catalysts supported by metal oxides showed both weak and strong acid sites, implying that the intensity distribution of acidic sites on the catalyst surface is wide. Although the catalyst supported by zeolite only had weak acid sites, the density of acid sites was up to about 1.6 mmol/g. The impregnation of metal oxide particles will cover the acid sites on the original ZSM-5 and form new acid sites. Thus, the acid characteristics of metal oxide itself will affect the strength and density of acid sites on the ZSM-5 surface. Compared with FeMo/ZSM-5, NiMo/ZSM-5 catalyst had a stronger acidic site (peak position at 158.9 °C) and a larger acidic site density (1.616 mmol/g). Among the three catalysts supported by metal oxides, although FeMo/ZrO₂ had the strongest acid site, the total density of acid sites was the lowest (0.085 mmol/g), while FeMo/ γ Al₂O₃ showed the highest density of weak acid sites and strong acid sites. The total acid site density of FeMo/ γ Al₂O₃ catalyst was as high as 0.631 mmol/g.

3.2. Evaluation of bimetallic catalysts in co-hydropyrolysis of pine and $\ensuremath{\mathsf{HDPE}}$

Zeolites, in particular ZSM-5, are the most common catalysts selected in the co-hydropyrolysis of biomass and plastics due to their remarkable deoxygenation and aromatization capabilities [34]. Mo has been used in the modification of zeolite catalysts because of its promoting effect on hydrogenation reaction [47]. In order to investigate the effects of bimetallic catalysts on co-hydropyrolysis of pine and HDPE, two bimetallic catalysts (FeMo/ZSM-5 and NiMo/ZSM-5) were synthesized based on Mo/ZSM-5 for co-hydropyrolysis.

As can be seen from Fig. 2(a), the introduction of catalyst in the cohydropyrolysis of pine and HDPE significantly reduced the yield of liquid and increased the yield of gas products, showing that catalyst is favorable to the chemical bond breaking of macromolecular liquid components to form lightweight gas components [48]. The introduction of bimetallic catalysts FeMo/ZSM-5 and NiMo/ZSM-5 led to lower oil yield and higher gas yield than that of monometallic catalysts Mo/ZSM-5, indicating the stronger bond breaking ability of bimetals, which probably due to the higher activity caused by the synergistic effect between bimetals [49]. Compared with FeMo/ZSM-5, the addition of NiMo/ZSM-5 resulted in a lower oil yield, indicating that NiMo/ZSM-5 has strong ability of secondary cracking of organic macromolecules, which may be attributed to the high acidic site density and the more homogeneous active metal sites provided by the large specific surface area of NiMo/ZSM-5.

The carbon selectivity of oxygenates and hydrocarbons in liquid was shown in Fig. 2(b). Without catalyst, the liquid produced in cohydropyrolysis process of pine and HDPE contained more oxygenates of 26%. At the presence of catalysts, the liquid products were 100% hydrocarbons, which reveals that the introduction of catalyst can promote the dehydroxylation, decarboxylation, and decarbonylation reactions in the co-hydropyrolysis process of pine and HDPE [50]. Additionally, the presence of catalysts promoted aromatization and Diels-Alder reactions [51], and hence led to a high selectivity of aromatics (> 60%) in the co-hydropyrolysis process. Compared with Mo/ ZSM-5, bimetallic catalysts FeMo/ZSM-5 and NiMo/ZSM-5 had higher aromatics selectivity in hydrocarbon products, probably because bimetallic synergistic effect enhanced the catalytic activity of the catalysts for aromatization and Diers-Alder reactions. NiMo/ZSM-5 catalyst had a higher aromatic hydrocarbons selectivity of 82% than FeMo/ZSM-5. More active acid sites on the surface of NiMo/ZSM-5 catalyst may also facilitate the aromatization and Diers-Alder reactions.

Aromatic hydrocarbons in liquid were further subdivided into BTEX (benzene, toluene, ethylbenzene, and xylenes), alkylbenzenes (ABs,

Table 2

Specific surface areas, pore volumes and average pore diameters of bimetallic catalysts.

Sample	$S_{BET}^{a} (m^2/g)$	$S_{micro}^{b} (m^2/g)$	S _{Meso} (m ² /g)	V _{total} ^c (cm ³ /g)	V _{micro} ^b (cm ³ /g)	V _{meso} (cm ³ /g)	Average pore diameter (nm)
FeMo/ZSM-5	232.2726	167.5231	48.3436	0.1823	0.1036	0.0698	3.1394
NiMo/ZSM-5	256.6446	182.8329	58.8331	0.1909	0.1130	0.0695	2.9751
FeMo/ZrO2	6.8570	1.2637	5.6975	0.0427	0.0005	0.0421	24.8810
FeMo/TiO ₂	67.3358	3.4889	66.9695	0.2507	0.0010	0.2379	14.8951
FeMo/γAl ₂ O ₃	120.9076	-	122.7674	0.2094	-	0.2003	6.9263

^a Calculated by the BET method in the P/P_0 range of 0.10–0.30.

^b Calculated using the t-plot method.

^c Calculated by measuring the amount of adsorbed nitrogen at $P/P_0 = 0.99$.

Table 3

NH₃-TPD data of bimetallic catalysts.

Samples	Desorption peak 1			Desorption peak 2			Total acidity (mmol/g)
	Peak position (°C)	Area (count)	Density (mmol/g)	Peak position (°C)	Area (count)	Density (mmol/g)	
FeMo/ZSM-5	156.3	4,391,205	1.600	-	-	-	1.600
NiMo/ZSM-5	158.9	4,405,830	1.616	434.4	-	-	1.616
FeMo/ZrO2	170.7	124,758	0.046	750.5	106,139	0.039	0.085
FeMo/TiO ₂	157.2	873,874	0.322	703.6	357,284	0.132	0.454
$FeMo/\gamma Al_2O_3$	132.1	1,121,833	0.414	713.1	588,189	0.217	0.631



(d)

NiMo/ZSM-5

NiMo/ZSM-5

CO

(b)

No catalysts

No catalysts

C₂H₆

Fig. 2. Product yield and distribution of co-hydropyrolysis of pine and HDPE via zeolite supported catalysts (a) liquid and gas yield; (b) hydrocarbons and oxygenates selectivity; (c) different aromatics selectivity; and (d) gas products selectivity.

except BTEX), and polycyclic aromatic hydrocarbons (PAHs), and their selectivity were shown in Fig. 2(c). The selectivity of BTEX in aromatic hydrocarbons was 100% without catalyst, and it decreased after the addition of catalyst. However, considering much higher aromatics selectivity in liquid (Fig. 2(b)), the addition of catalysts still promoted the production of BTEX. The reduced selectivity of BTEX in aromatic hydrocarbons after catalyst addition may be attributed to the promotion of polycondensation and alkylation of BTEX into PAHs and ABs [34]. The addition of bimetallic catalysts FeMo/ZSM-5 and NiMo/ZSM-5 produced more BTEX than that of monometallic catalysts Mo/ZSM-5, further implying the presence of synergistic effects between bimetals, which enhances the catalytic activity and thus improve the selectivity of BTEX in aromatic hydrocarbons. The addition of FeMo/ZSM-5 produced more BTEX than NiMo/ZSM-5, possibly because FeMo/ZSM-5 limited the conversion of BTEX to high-branching ABs by inhibiting the

(c)

methylation/alkylation reaction.

Fig. 2(d) showed the gas products selectivity of the co-hydropyrolysis with/without catalysts. Less alkenes were produced without catalysts during co-hydropyrolysis. However, the selectivity of alkenes (ethylene and propylene) increased obviously after the addition of monometallic catalysts Mo/ZSM-5, which may be due to the high reaction rate of β -scission and termination reactions at the acid site of Mo/ZSM-5 [52]. Compared with monometallic catalyst Mo/ZSM-5, bimetallic catalysts FeMo/ZSM-5 and NiMo/ZSM-5 increased the selectivity of alkanes (i.e. methane, ethane, and propane) in gas products, especially methane, while decreased the selectivity of alkenes (i.e. ethylene and propylene), which was attributed to the enhancement of hydrogen transfer reaction by bimetallic catalysts [53], leading to the saturation of alkenes.

To sum up, compared with Mo/ZSM-5, bimetallic catalysts FeMo/ ZSM-5 and NiMo/ZSM-5 enhanced the cleavage of C-C bond and C—O bond of organic macromolecules due to the synergistic effect between bimetals, and enhanced dehydroxylation, decarboxylation and decarbonization, aromatization and Diels-Alder reactions, etc. This resulted in the formation of hydrocarbons, especially aromatic hydrocarbons, and higher selectivity of BTEX in aromatic hydrocarbons. In terms of the two bimetallic catalysts, NiMo/ZSM-5 had lower liquid yield but higher aromatics selectivity in liquid than FeMo/ZSM-5 due to higher acidic site density and more homogeneous active metal sites. However, the excessive aromatization may lead to the low selectivity of BTEX in aromatic hydrocarbons.

3.3. Effects of metal oxide supports and atmospheres on the product yield and distribution

Bimetallic zeolite catalysts successfully increased the selectivity of BTEX in liquid; however, the liquid yield is low. The properties of catalyst support also have a significant impact on the catalytic performance. Metal oxides with less acidity have been reported to have good hydrodeoxygenation performance [34]. Therefore, bimetallic catalysts supported by different metal oxides (i.e., FeMo/ γ Al₂O₃, FeMo/ZrO₂ and

FeMo/TiO₂) were further synthesized to explore their effects on the product yield and distribution of co-hydropyrolysis of pine and HDPE, and the results were provided in Fig. 3.

The zeolite-supported bimetallic catalyst FeMo/ZSM-5 resulted in a lower liquid yield and a higher gas yield than the metal oxide-supported catalysts (Fig. 3(a)). This is due to the strong acidity of zeolite, which can effectively break the C—C and C—O bonds of organic macromolecules. Bimetals mainly existed in the form of metal oxides on zeolite, and the large specific surface area provided a more uniform active metal site; thus, FeMo/ZSM-5 showed a stronger hydrodeoxygenation ability, which promoted the dehydroxylation, decarboxylation, decarbonization reaction to produce hydrocarbon products (Fig. 3(b)). Additionally, FeMo/ZSM-5 also promoted aromatization and Diels-Alder reaction, leading to high aromatics selectivity of 66% (Fig. 3(c)). It is worth noting that the strong acidity of FeMo/ZSM-5 may cause excessive aromatization [53], resulting in the part conversion of BTEX into PAHs and reducing the selectivity of BTEX in aromatic hydrocarbons. Fig. 3(d) showed that FeMo/ZSM-5 also favored the saturation of alkenes to alkanes, dramatically increasing the selectivity of alkenes in gaseous products and decreasing the alkenes selectivity.



Fig. 3. Product yield and distribution of co-pyrolysis of pine and HDPE under different atmospheres and catalysts (a) liquid and gas contents; (b) hydrocarbon and oxygenates contents; (c) different aromatics contents; and (d) different gas contents.

Fe and Mo existed on the γ -Al₂O₃ support were in the form of metal oxides and metal elements with strong hydrocracking ability, along with the large specific surface area of FeMo/ γ Al₂O₃, which enhanced the hydrogenation of intermediate products to form liquid hydrocarbons with smaller carbon number. Due to the small average pore size of γ Al₂O₃, intermediate products cannot enter the γ Al₂O₃ support, resulting in a low possibility of excessive cracking to produce gas (Fig. 3(d)). Moreover, FeMo/ γ Al₂O₃ decreased the selectivity of CO₂ and improved the selectivity of CO (Fig. 3(d)), probably because it promoted the reforming reaction between methane and carbon dioxide [54], resulting in partial conversion of CO₂ to CO.

Due to the largest average pore size allowing more intermediates to enter and retain in the support and promoting direct cleavage of intermediates into gaseous products, a higher gas yield was observed with FeMo/ZrO₂ as indicated in Fig. 3(a). FeMo/ZrO₂ also showed the lowest selectivity for aromatic hydrocarbons in liquid, but the highest selectivity for BTEX in aromatic hydrocarbons (Fig. 3(b) and (c)). In addition, FeMo/ZrO₂ had the highest selectivity of methane and lowest selectivity of CO (Fig. 3(d)), which be caused by the enhanced hydrogenation and methanation of carbon monoxide with presence of FeMo/ZrO₂ [55].

Among the metal oxide-supported catalysts, FeMo/TiO₂ showed the highest hydrocarbon selectivity of 100% (Fig. 3(b)), possibly due to the strong hydrodeoxygenation capacity of Fe and Mo presented as alloys on TiO₂ support. Although FeMo/TiO₂ has the highest selectivity for aromatic hydrocarbons (56%) in liquid, it had the lowest selectivity for BTEX in aromatic hydrocarbons (Fig. 3(b) and (c)). The results suggested that FeMo/TiO₂ contributed to the production of aromatic hydrocarbons in liquid, but also promoted the conversion of BTEX in aromatic hydrocarbons into heavy PAHs or high-branching ABs. Therefore, in order to achieve high BTEX yield in liquid, it is necessary to properly regulate the acidity of metal oxide-supported catalysts to promote aromatization while avoiding methylation/alkylation and excessive aromatization of BTEX.

Co-pyrolysis of pine and HDPE under different atmospheres were also performed to understand if and how the hydrogen works in the process. As presented in Fig. 3, without catalyst, the gas production of co-pyrolysis under hydrogen atmosphere is higher than that under helium atmosphere, suggesting that hydrogen may promote the hydrocracking of C-C and C-O bonds of intermediates to generate lightweight and non-condensable C1-C3 compounds (Fig. 3(a)) [56]. The selectivity of oxygenate compounds in liquid obtained under hydrogen atmosphere is low (Fig. 3(b)), indicating that hydrogen can promote decarboxylation, and decarbonization reactions, so that oxygen in the condensable organic phase can be removed in the form of CO₂, and CO [57]. In addition, the selectivity of BTEX in aromatic hydrocarbons was 100% under hydrogen atmosphere, and the selectivity of PAHs was significantly reduced (Fig. 3(c)), indicating that many reactive volatile intermediates can be capped by hydrogen radical to avoid polymerization and excessive aromatization to generate PAHs [58].

At the presence of bimetallic catalysts, the effects of hydrogen on the product selectivity were varied with different catalysts. This is because the selective adsorption of intermediate products by catalysts with different characteristics led to the participation of hydrogen in different reactions, and thus the variances of product selectivity. The difference of product distribution in hydrogen and helium atmosphere became larger after the addition of FeMo/ZSM-5 and FeMo/ZrO2, indicating that FeMo/ZSM-5 and FeMo/ZrO2 were conducive to the involvement of hydrogen in hydrocracking and hydrodeoxygenation. This resulted in lower liquid yields with higher selectivity of hydrocarbons and gas yields under hydrogen atmosphere (Fig. 3(a) and (b)). With FeMo/TiO₂ and FeMo/yAl₂O₃, liquid yield under hydrogen atmosphere was higher than that under helium atmosphere, but the gas yield was lower (Fig. 3 (a)). This suggests that these two catalysts may facilitate the hydrogen participation in the C-C coupling reaction, favoring the prodction of components in the liquid. In terms of FeMo/TiO₂, a lower selectivity of BTEX in aromatic hydrocarbons was observed under hydrogen

atmosphere (Fig. 3(c)), which may be due to the promoted participation of hydrogen in alkylation/methylation of BTEX. After adding FeMo/ γ Al₂O₃, the selectivity of aromatic hydrocarbons was lower under hydrogen atmosphere, while the selectivity of aliphatic hydrocarbons was higher than that under helium atmosphere (Fig. 3(b)), implying that FeMo/ γ Al₂O₃ probably be beneficial for hydrogen to involve in the hydrogenation of aromatic hydrocarbons. Moreover, the presence of bimetallic catalyst showed a higher selectivity of alkanes in gas products under hydrogen atmosphere than that under helium atmosphere (Fig. 3 (d)), indicating that bimetallic catalyst is favorable for hydrogen to participate in alkene saturation.

3.4. Proposed reaction mechanism

During the co-hydropyrolysis of pine and HDPE over bimetallic catalysts, the cracking reaction took place initially; however, due to the presence of hydrogen, various complex hydrotreating such as alkylation, C-C coupling, hydrocracking, hydrodeoxygenation, hydrogenation, and recombination occurred simultaneously or successively [56]. After a series of complex reactions described above, HDPE was transformed into chains of alkenes and a small amount of alkanes, and pine was decomposed into ketones, aldehydes, acids, alcohols, phenols, furans and other oxygen-containing substances, as well as some aliphatic and aromatic hydrocarbons [34]. When the above pyrolysis volatiles passed through the active metal sites on the bimetallic catalyst surface, they cracked and entered the pore channel for further transformation. The active sites of the bimetallic catalyst promoted a series of deoxygenation reactions (e. g. decarboxylation, decarbonization and dehydration) to convert some ketones, alcohols, aldehydes, and carboxylic acids into alkenes and alkanes, and some phenols into aromatic hydrocarbons. In the process of dehydration, decarbonization and decarboxylation, oxygen was mainly removed from the oxygenates in the form of H₂O, CO and CO₂. Additionally, the bimetallic catalyst facilitated the hydrogen transfer reaction, where hydrogen was extracted from the HDPE intermediates and transferred to the pine intermediates for hydrogenation. The unstable hydrogen-derived intermediates of HDPE further underwent β-scission to form alkene and hydrocarbon pools. The alkenes generated above react with furan and phenol pools on the acidic active sites of bimetallic catalyst to form aromatic hydrocarbons by aromatization and Diels-Alder reaction. Therefore, under the dual promotion of hydrogen and bimetallic catalyst, the co-pyrolysis of pine and HDPE finally resulted a pyrolysis oil rich in aromatic hydrocarbons (See Fig. 4), and the selectivity of BTEX in aromatic hydrocarbons was up to 94%.

4. Conclusion

The effects of bimetallic catalysts and hydrogen on the performance of co-pyrolysis of pine and HDPE were reported in this study, and the results proved that the introduction of bimetallic catalysts and hydrogen favored the generation of aromatic hydrocarbons and improved the selectivity of BTEX in aromatic hydrocarbons. A reaction mechanism for the above expected results was also proposed through references and speculation, providing further understandings of the reaction process. This study optimized the product yield and selectivity, and provides a sustainable strategy for large-scale production of aromatic hydrocarbons, especially BTEX.

CRediT authorship contribution statement

Jing Su: Data curation, Validation, Investigation, Writing – original draft. Tan Li: Conceptualization, Formal analysis, Data curation, Writing – original draft. Guanqun Luo: Funding acquisition, Validation, Project administration, Writing – review & editing. Yi Zhang: Investigation, Validation. Evgeny R. Naranov: Investigation, Validation. Kaige Wang: Conceptualization, Supervision, Funding acquisition, Validation, Project administration, Writing – review & editing.



Fig. 4. Reaction mechanism diagram of co-hydropyrolysis of biomass and plastics.

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.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

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