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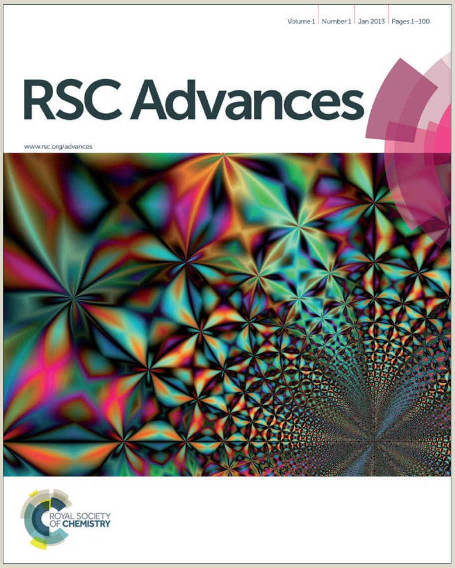

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Thermally stable phosphorus and nickel modified ZSM-5 zeolites for catalytic co-pyrolysis of biomass and plastics

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ABSTRACT

A series of phosphorus (P) and phosphorus/nickel (P/Ni) modified ZSM-5 zeolites were prepared by impregnation of a conventional ZSM-5 zeolite with P and subsequent Ni. The conventional, P-, and P/Ni-modified ZSM-5 zeolites were then tested as the catalysts for petrochemical production from co-feed catalytic fast pyrolysis (CFP) of pine wood and low-density polyethylene (LDPE) mixtures. Results showed that the yield of valuable petrochemicals (olefins and aromatic hydrocarbons) from co-feed CFP increased from 42.9 C% for conventional ZSM-5 to 52.8–54.1 C% for P- and P/Ni-modified ZSM-5, while the yields of low-value alkanes and undesired char/coke decreased from 17.3 C% and 22.6 C% to 9.6–10.2 C% and 18.9–15.7 C%, respectively. ZSM-5 impregnation with P and P/Ni thus significantly improved the product distribution in co-feed CFP of biomass and LDPE. In addition, modification with P and P/Ni improved considerably the hydrothermal stability of zeolites to resist steam-induced catalyst deactivation that may occur in co-feed CFP. When the conventional ZSM-5 zeolite was pretreated with 100% steam at 550 °C for 3–9 h, it produced 26.7–32.1% lower aromatic yields than untreated ZSM-5 in co-feed CFP. In contrast, steam pretreatment did not considerably affect the activity of P- and P/Ni-ZSM-5 zeolites for aromatic production. They maintained comparable aromatic yields in co-feed CFP when they had been steam pretreated for up to 9 h. These results indicate that ZSM-5 modification with P and P/Ni may provide a viable way to improve the catalyst's activity and life time for petrochemical production from co-feed CFP of biomass and plastics.

Keywords: Catalysis; Zeolite; Pyrolysis; Biomass; Plastic; Petrochemical

1. Introduction

Petrochemicals derived from petroleum are important raw materials for manufacturing numerous useful products for everyday life, such as plastics, synthetic fibers, solvents, and medicines. As the petroleum reserves around the world are depleting at a rapid rate, producing petrochemicals from renewable lignocellulosic biomass has gained increasing interests.[1, 2] Catalytic fast pyrolysis (CFP) is promising technology that can rapidly convert solid biomass directly into valuable aromatic hydrocarbons and olefins, which are the two most important classes of petrochemicals.[3-5] During CFP, biomass is rapidly pyrolyzed in the presence of catalysts (e.g., zeolites and metal oxides).[3, 5-8] Volatile intermediates (e.g., furans, aldehydes, and phenols) formed from the initial thermal decomposition of biomass are then catalytically converted over the catalysts to final products.[3, 5, 9, 10] The whole conversion process can be completed in a single reactor at short reaction times (e.g., in seconds). CFP can thus provide an effective way to convert lignocellulose into valuable petrochemicals.

While CFP can rapidly convert biomass into aromatic hydrocarbons and olefins, its carbon efficiency has yet to be improved. Among many catalysts that have been tested in CFP studies, ZSM-5 zeolite has been shown to produce the highest aromatic yield from a variety of lignocellulosic feedstock, and is therefore currently the most commonly used catalyst in CFP.[3, 5, 11, 12] However, even with ZSM-5, CFP of natural lignocellulose (e.g., woods and grasses) can usually produce only ~10–30 C% and ~5–10 C% of aromatic hydrocarbons and olefins, respectively. [3-5, 13]

The low carbon yields of aromatic hydrocarbons and olefins in CPF of lignocellulose are mainly due to its hydrogen deficient (~6–7 wt.%) and oxygen rich (usually >40 wt.%) nature.[3, 5, 14, 15] Therefore, CFP of biomass produces considerable amounts of solid residues (char/coke, ~30–50 C%) during the thermal decomposition of biomass (which produces char) and catalytic conversion of biomass-derived oxygenated volatiles over zeolites (which produces coke).[13, 16-

[19] Moreover, during the conversion of oxygen-rich biomass to hydrocarbons, significant fractions of carbon in the feedstock are released as CO and CO_2 (carbon yields of ~20–30 C%).[13, 20-22] As a result, only ~20–30% of the carbon contents of biomass feedstock can be converted into the final aromatic hydrocarbons and olefins in CFP.[4, 5, 13]

To improve the carbon efficiency for petrochemical production in CFP, we have proposed co-feeding of hydrogen-deficient biomass with hydrogen-rich waste plastics in CFP.[23] It was hypothesized that waste plastics may provide a cheap and abundant hydrogen source to improve the carbon efficiency of petrochemical production from CFP of biomass. Various combinations of biomass (e.g., cellulose, lignin, and pine wood) and plastics (e.g., polyethylene, polypropylene, and polystyrene) have been tested in co-feed CFP.[21, 24-26] The results show that co-feeding of cellulose or pine wood with LDPE has a significant synergy for aromatic production.[21, 23] For example, the aromatic yield increased significantly from 32.9 C% and 28.3 C% for CFP of cellulose alone and LDPE alone, respectively, to 48.4 C% for CFP of their mixture (cellulose-to-LDPE mass ratio of 2:1). However, the synergy for aromatic production is not insignificant for other combinations of biomass and plastics (cellulose/polypropylene, cellulose/polystyrene, and lignin/LDPE).[21] Reaction pathway analysis suggests that the synergy between cellulose or pine wood and LDPE is mainly because in the presence of zeolite catalysts, cellulose-derived furans (e.g., furan and furfural) can react with LDPE-derived linear olefins (e.g., ethylene and propylene) via Diels-Alder reaction and subsequent dehydration reaction to yield aromatic hydrocarbons (see Fig. 1).[21, 23-25] The results indicate that co-feeding of natural biomass (such as pine wood), which usually contains significant cellulose contents (~40–50 wt.%), with LDPE can thus provide a simple and effective way to improve aromatic production in CFP.

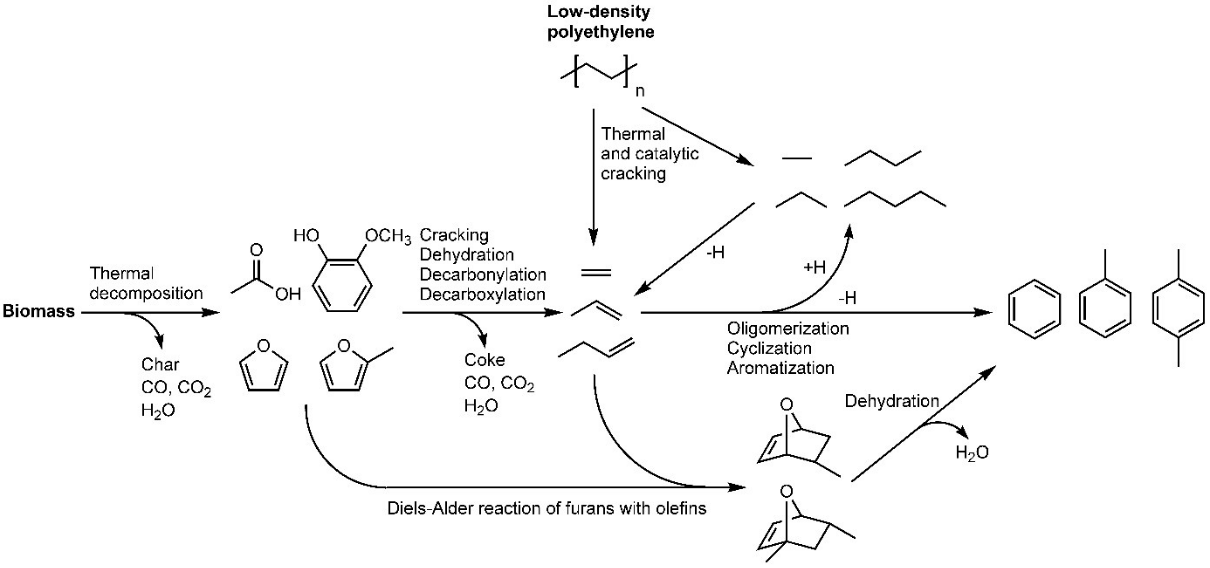

Fig. 1. Schematics of aromatic formation pathway for co-feed CFP of biomass and LDPE mixture with ZSM-5 zeolites.

Although co-feeding of biomass with LDPE can considerably improve aromatic production in CFP, it also raises several issues that need further improvement. For example, co-feed CFP of cellulose and LDPE mixtures with ZSM-5 produces significant amounts of C_1–C_5 alkanes (e.g., 9.1–26.6 C% at LDPE feed ratios of 20–50 wt.% [21]), which are primarily derived from the thermal and catalytic cracking of LDPE (see Fig. 1). Because lower alkanes have much lower value than aromatics and olefins, it is highly desirable to decrease alkane yields in co-feed CFP, for example, by converting them to olefins and aromatic hydrocarbons.

Moreover, previous research has shown that during CFP of biomass, substantial amounts of water can be generated during both the initial thermal decomposition of biomass and subsequent deoxygenation reactions of biomass-derived oxygenates over catalysts.[9, 10, 14, 16, 17, 27] At high temperatures (e.g., ~450–700 °C for CFP), water may cause hydrothermal damage to ZSM-5 structure (e.g., steam-induced dealumination), hence resulting in irreversible catalyst deactivation.[27-30] The hydrothermally-induced catalyst deactivation is expected to be more severe in co-feed CFP of biomass and LDPE, whereby Diels-Alder reactions of biomass-derived oxygenates with olefin-olefins and the following dehydration reaction enhances considerably the formation of not only aromatics, but also water.[21, 31-33] Therefore, catalysts with higher hydrothermal stability than conventional ZSM-5 zeolites may be required to ensure stable operation of co-feed CFP of biomass and plastics.

Previous studies on catalytic cracking of alkanes have indicated that ZSM-5 impregnation with phosphorus (P) can noticeably enhance alkane transformation to olefins,[29, 34, 35] which can in turn be converted to aromatics over zeolite catalysts.[36] In addition, zeolites modification with P is a well-known way to improve the hydrothermal stability and anti-coking property of zeolites.[28, 29, 34] Therefore, we anticipated that ZSM-5 modification with P might have multiple beneficial effects on co-feed CFP of biomass and plastics, e.g., enhancing alkane transformation to olefins and aromatics, as well as resisting hydrothermally- and coking-induced catalyst deactivation. However, due to the complex reaction mechanisms of CFP, these expectations have yet to be systematically evaluated, and much remains to learn, e.g., whether ZSM-5 modification with P would negatively affect the synergy between biomass and plastics for aromatic production in co-feed CFP.

To this end, the main objective of this study was to evaluate how ZSM-5 modification with P would affect the catalyst performance in co-feed CFP of biomass and LDPE mixtures. In addition, to further improve aromatic yields in the co-feed CFP, we also tested co-impregnation of ZSM-5 with P and nickel (Ni); the latter has been shown to be able to enhance aromatic production during catalytic conversion of biomass feedstock due to its high dehydrogenating activity.[14, 37-41] A series of P- and P/Ni-modified ZSM-5 zeolites were prepared by impregnating a conventional ZSM-5 zeolite with different loadings of P and Ni. The conventional and modified zeolites were then tested as the catalysts in co-feed CFP of biomass and plastics. Due to their abundant availability and low cost, pine wood and LDPE were used as the model compounds of biomass and waste plastics, respectively. The product distribution from co-feed

CFP tests were compared to evaluate the effects of P and P/Ni modification on the catalyst performance for petrochemical production in CFP. The effect of P and P/Ni modification on the hydrothermal stability of ZSM-5 was also evaluated.

2. Experimental

2.1. Materials

Pine wood sawdust was provided by a furniture factory in Beijing. LDPE powder ($d < 0.105$ mm) was acquired from Li Yang Technology Corporation (Shanghai, China). The conventional ZSM-5 zeolite (SiO_2/Al_2O_3 ratio of 32, H type, d_{50} of 2 μm) was purchased from the Catalyst Plant of Nankai University (Tianjin, China). All samples (pine wood, LDPE, and catalysts) were (crushed and) sieved through a 140 mesh (0.105 mm) sieve, and then stored in a desiccator prior to use. Elemental composition of pine wood and LDPE were analyzed with an elemental analyzer (CE-440, Exeter Analytical, Inc., North Chelmsford, MA).[21]

2.2. Catalyst preparation

A series of P-modified ZSM-5 zeolites (P-ZSM-5) were prepared by impregnating 3 g of the conventional ZSM-5 with 20 mL aqueous $(NH_4)_2HPO_4$ solutions of different concentrations (0.048, 0.096, 0.144, and 0.240 M) using incipient wetness impregnation method. This produced P-modified ZSM-5 zeolites with the mass fraction ratio of P to ZSM-5 of 1, 2, 3, and 5 wt.%, respectively. The impregnation period was 4 h at 35 °C. After the impregnation treatment, the zeolites were dried at 110 °C, and then calcined at 550 °C for 4 h in air atmosphere. To prepare P/Ni-ZSM-5, the calcinated P-ZSM-5 zeolites were further impregnated with $Ni(NO_3)_2$ solutions. The mass fraction ratio of Ni to ZSM-5 was 1, 2, and 3 wt.%. The impregnation was conducted for 4 h at 35 °C. The resultant P/Ni impregnated ZSM-5 zeolites were dried at 110 °C, and then calcined at 550 °C for 4 h.

To evaluate the hydrothermal stability of catalysts, conventional, P-, and P/Ni-modified ZSM-5 zeolites were treated at 550 °C for 3–9 h under 100% steam in a fixed bed reactor. The hydrothermally treated catalysts were then tested for their catalytic activity for aromatic production in co-feed CFP of pine wood and LDPE mixtures.

2.3. Catalyst characterizations

The actual P and Ni contents on the catalysts after calcination were measured by X-ray fluorescence (XRF) technique (XRF-1800, Shimadzu Co., Japan). X-ray diffraction patterns of the zeolites were recorded by a powder X-RAY diffractometer (Bruker D8 Advanced) using CuKα radiation at 40 kV and 40 mA. The structural properties of the zeolites were characterized by N_2 adsorption at -196 °C on a Quantachrome Autosorb-iQ^2 instrument.[42] Temperature-programed desorption of NH_3 (NH_3-TPD) was performed using Micromeritics Autochem 2920 instrument.[43] The zeolites were firstly flushed with a helium stream at 550 °C for 1 h, then cooled to 100 °C. NH_3 adsorption was then carried out at 100 °C for 1 h. After purging the samples in a He stream for 2 h to completely remove physically adsorbed NH_3, the zeolites were heated to 600 °C at a heating rate of 10 °C/min. The evolution of desorbed NH_3 was detected using a thermal conductivity detector (TCD). Pyridine FT-IR analyses were conducted with a Nicolet 5700 spectrometer.[42] Zeolites were pressed into self-supporting wafers (10 mg, 13 mm diameter). The zeolite wafers were then activated in situ in an IR cell at 400 °C for 2 h under vacuum. The IR cell temperature was then decreased to 100 °C, and the background spectra of the zeolites were recorded. Pyridine was adsorbed on the sample for 10 min, followed by desorption at 200 °C. The concentrations of Brönsted and Lewis acid sites were then calculated on the basis of the intensity of the 1540 cm^{-1} (Brönsted) and 1450 cm^{-1} (Lewis) bands.

2.4. Catalytic fast pyrolysis

CFP tests were conducted with a semi-batch reactor (Pyroprobe 5200, CDS Analytical, Inc.) using a protocol that had been optimized to maximize aromatic production from CFP of biomass and plastics.[18, 42] In brief, zeolite catalysts were thoroughly mixed with a particular reactant (pine wood, LDPE, and their co-feed mixtures) in a catalyst-to-reactant ratio of 15. Approximately 4 mg of the mixtures were then fast pyrolyzed in the pyroprobe reactor at 550 °C for 60 s. Note that due to the small sample size that can be placed in CDS pyroprobe, high catalyst-to-reactant ratios (e.g., 10–20) are required to ensure effective conversion of biomass- and plastic-derived volatile intermediates (e.g., acids and aldehydes) to desired final products (i.e., aromatic and olefin hydrocarbons) within the zeolite framework.[18, 21] In comparison, much lower catalyst-to-reactant ratios (e.g., 3–9) can be used in CFP processes conducted with fluidized bed reactors designed for industrial applications (see Electronic Supplementary Information (ESI) for more information).[44, 45] The volatiles emitted via the fast heating were carried by helium through a heated transporting tube (300 °C) to a gas chromatograph (Agilent 7890A GC). The yields of hydrocarbons (alkanes, olefins, and aromatics) and carbon oxides (CO and CO_2) were quantified with a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively. The yields of solid residue (char/coke) were determined by measuring the carbon contents in the spent catalysts using an elemental analyzer. At least triplicate CFP tests were performed for each sample. All yields are reported in terms of carbon yield (moles of carbon atoms in the products relative to those in the reactants, Eq. (1)). Aromatic selectivity is calculated according to Eq. (2).

$$\text{Carbon yield} = \frac{\text{Moles of carbon in a product}}{\text{Moles of carbon in reactant}} \times 100\% \quad (1)$$

$$\text{Aromatic selectivity} = \frac{\text{Moles of carbon in an aromatic product}}{\text{Moles of carbon in all aromatic products}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Catalyst characterizations

After P- and P/Ni-modified ZSM-5 zeolites (1–5 wt.% of P and 1–3 wt.% Ni loading) were prepared, they were tested for aromatic production in co-feed CFP of pine wood and LDPE mixtures. The result shows that among the P-modified zeolites, ZSM-5 impregnated with 2 wt.% P (2%P-ZSM-5) produced the highest aromatic yield in co-feed CFP (see Fig. S1 in ESI). Subsequent impregnation of P-modified ZSM-5 zeolites with Ni can further enhance aromatic production in co-feed CFP, and ZSM-5 modified with 3 wt.% P and 2 wt.% Ni (3%P/2%Ni-ZSM-5) produced the highest aromatic yield among the P/Ni-ZSM-5 zeolites (see Fig. S2 in ESI). Therefore, 2%P-ZSM-5 and 3%P/2%Ni-ZSM-5, as well as the conventional ZSM-5, were selected for further characterizations (see Table 1) and CFP evaluations.

The chemical and textural properties of the conventional, P-, and P/Ni-modified ZSM-5 zeolites are summarized in Table 1. The SiO_2/Al_2O_3 ratio of the zeolites increased slightly after the P and P/Ni modification. This is because ZSM-5 impregnation with $(NH_4)_2HPO_4$ solutions can cause mild dealumination of zeolites.[29, 34] In addition, it is noticed that although the P-ZSM-5 zeolite was impregnated with a lower P mass ratio (2 wt.% P) during the incipient wetness treatment than the P/Ni-ZSM-5 zeolite (3 wt.% P), they had a comparable actual P content after they were calcinated for subsequent CFP tests (1.54 and 1.87 wt.%, measured by XRF technique). This is probably because some soluble P species (e.g., orthophosphate monoester and pyrophosphate) on P-modified ZSM-5 zeolites would be washed off the zeolites during their subsequent Ni impregnation to obtain P/Ni-ZSM-5 zeolites.[34, 46]

XRD analysis result shows that modification with P and P/Ni does not affect the framework structure of ZSM-5. All samples exhibit the characteristic peaks of MFI type zeolite at ~8° and 23° (see Fig. 2), which indicates that the framework of ZSM-5 is preserved after P and Ni modification. In addition, no crystalline phases of P and Ni oxides are detected in the XRD patterns of modified ZSM-5 zeolites, suggesting that P and Ni species are well dispersed on the zeolites. Notably, the intensity of the two peaks at ~ 7.9° (0 1 1) and ~8.8° (0 2 0) decreased considerably after P modification, but did not further decrease appreciably after Ni impregnation (Fig. 2). This result suggests that P species has penetrated into the channels of ZSM-5 during P impregnation,[46] which would decrease the low-angle XRD intensities of ZSM-5.[47, 48] On the other hand, Ni does not enter into the zeolite channels during subsequent impregnation of the P-ZSM-5 zeolites.

Table 1

Characterizations of the conventional, P-, and P/Ni-modified ZSM-5 zeolites.

	ZSM-5	P-ZSM-5	P/Ni-ZSM-5
SiO_2/Al_2O_3 [a]	37.7	38.2	39.7
P [a] (wt.%)	-	1.54	1.87
Ni [a] (wt.%)	-	-	1.96
BET surface area [b] (m^2/g)	414.4	327.6	322.3
Micropore surface area [c] (m^2/g)	366.8	276.6	270.7
External surface area [c] (m^2/g)	47.6	51.0	51.6
Micropore volume [c] (cm^3/g)	0.158	0.118	0.113
$A_{Brönsted}$ [d]	496.1	304.0	264.9
A_{Lewis} [d]	40.1	75.9	197.7
$A_{Lewis}/(A_{Brönsted} + A_{Lewis})$	0.08	0.20	0.43

[a] Actual P and Ni contents on the zeolites after calcination, measured by XRF analysis.
[b] From N_2 adsorption measurements (BET method).
[c] From N_2 adsorption measurements (t-plot).
[d] Measured by IR spectrum of adsorbed pyridine

The BET surface area and micropore volume of ZSM-5 decreased considerably after P modification (see Table 1). Similar phenomenon have been reported in previous studies on ZSM-5 modification with P, and attributed to the blockage and occupation of zeolite pores by P species.[28, 29, 46] In comparison, subsequent impregnation of P-ZSM-5 with Ni did not further decrease the surface and micropore volume of zeolites considerably (see Table 1). This result suggests that Ni species do not enter the micropores of ZSM-5 during Ni impregnation and are present mainly on the edges and external surface of ZSM-5 zeolites,[29, 39, 49] consistent with the inference of XRD analysis.

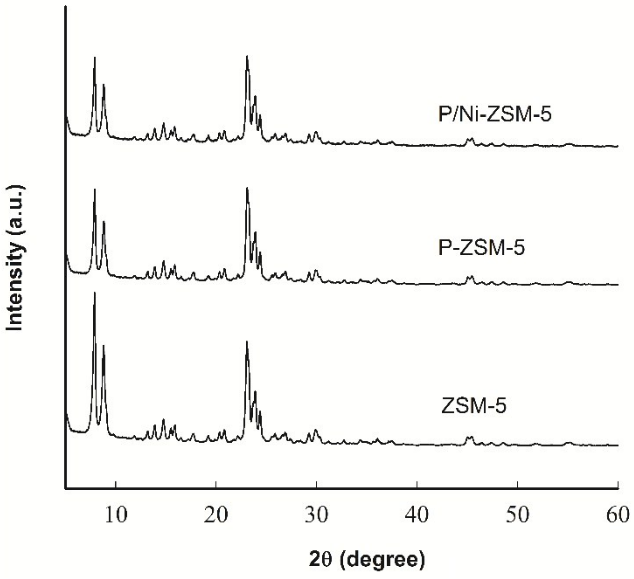

Fig. 2. XRD patterns of conventional, P-, and P/Ni-modified ZSM-5 zeolites.

NH_3-TPD analysis shows that the conventional ZSM-5 exhibited two desorption peaks with centers at approximately 250 °C and 450 °C. Upon modification with P and Ni, the intensity of the high temperature peak decreased considerably, while the low temperature peak was not significantly changed (Fig. 3). Previous work has suggested that the low temperature peak is mainly ascribed to non-framework Lewis acid sites and weaker Brönsted acid sites, whereas the high temperature peak is ascribed to stronger Brönsted acid sites.[20, 50, 51] The result of NH_3-TPD analysis thus suggests that the strong Brönsted acid sites of ZSM-5 zeolites decreased considerably upon P modification, and further declined upon Ni addition. In addition, the high temperature peak of shifted to lower temperature (~400 °C) for the P/Ni-modified ZSM-5 (Fig. 3), suggesting a decrease in the strength of Brönsted acidity.[39, 52]

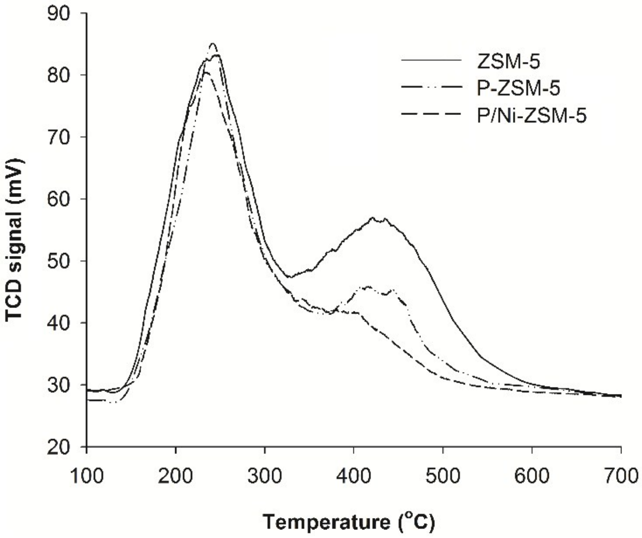

Fig. 3. NH_3-TPD patterns of conventional, P-, and P/Ni-modified ZSM-5 zeolites.

To get more information on the acidity changes, pyridine adsorption was conducted to quantify the Brönsted and Lewis acid sties on the zeolites. The result shows that the density of Brönsted acid sites on ZSM-5 decreased considerably after the zeolite was impregnated with P, and further decreased with Ni impregnation (Table 1). In contrast, the Lewis acid sites on the zeolites increased significantly after P and especially Ni impregnation (see Table 1). Taking into account the results of both NH_3-TPD and pyridine FTIR analysis, it can be discerned that ZSM-5 modification with P and P/Ni decreased considerably the Brönsted acid sites (especially strong ones), but increased the Lewis acid sites of zeolites. These changes are generally in line with the previous findings that P modification can cause dealumination of tetrahedral framework aluminum of zeolites and thus decreases the strong Brönsted acid sites of the catalyst.[28, 46, 52] On the other hand, Ni impregnation would increase the Lewis acid sites of zeolites due to the deposition of nickel species at the external surface of ZSM-5, but decrease the strong Brönsted acidity due to replacement of some protons by nickel ions.[39, 40, 52]

3.2. *Effects of P and P/Ni modification on the product distribution in co-feed CFP*

Co-feed CFP of pine wood and LDPE mixtures with the conventional, P-, and P/Ni-modified ZSM-5 produced similar final products, which consisted mainly of aromatic hydrocarbons, C_2–C_5 olefins, C_1–C_5 alkanes, carbon oxides (CO and CO_2), and solid residue (char and coke) (see Table 2 for detailed lists of the products). This result is consistent with the previous finding that although biomass and plastics have very different compositions and polymer structures, they can be catalytically converted to similar olefins and aromatic products over ZSM-5 zeolites.[10, 16, 17, 21, 24, 53] As shown in Fig. 1, the conversion process generally go through two common reaction stages: (a) thermal decomposition of the polymer structure of biomass and plastic to small primary pyrolysis products, e.g., furans, aldehydes, and phenols for biomass, and alkanes, olefins, and dienes for LDPE, [21, 23-25] and (b) catalytical conversion of the primary products to small olefins, which then evolve as the final olefin products, or go through a series of zeolite-catalyzed reactions including oligomerization, cyclization, and aromatization to yield aromatic hydrocarbons.[10, 16, 17, 21, 25, 53, 54] During the conversion process, alkanes, carbon oxides, and solid residues are also formed from multiple sources (see Fig. 1).[9, 16, 17, 20, 21, 54, 55] Also, it is worth noting that when biomass and LDPE are co-fed in CFP with ZSM-5, LDPE-derived olefins can react with biomass-derived furans via Diels–Alder and subsequent dehydration reactions to yield aromatics;[21, 25, 31-33] this reaction pathway has been considered an important mechanism for enhanced aromatic production in co-feed CFP of biomass and LDPE mixtures with ZSM-5 zeolites.[21, 23, 24]

Notably, compared with conventional ZSM-5, P- and P/Ni-modified zeolites produced much higher yields of aromatic hydrocarbons and olefins, but lower yields of alkanes and solid residues in co-feed CFP (see Fig. 4). ZSM-5 modification with P and P/Ni thus considerably improved the product distribution toward more valuable products (i.e., aromatics and olefins) in co-feed CFP of biomass and LDPE.

Table 2

Detailed product yields in co-feed CFP of pine wood and LDPE mixture (mass ratio of 2) with conventional, P-, and P/Ni-modified ZSM-5 zeolites.

Carbon yield (C%)	ZSM-5	P-ZSM-5	P/Ni-ZSM-5
Aromatic hydrocarbons			
Benzene	4.03 ± 0.03	3.59 ± 0.07	4.85 ± 0.04
Toluene	9.75 ± 0.06	10.1 ± 0.08	11.9 ± 0.10
Ethylbenzene	0.63 ± 0.03	0.92 ± 0.01	1.14 ± 0.05
p-Xylene	2.57 ± 0.11	3.76 ± 0.05	4.69 ± 0.15
m-Xylene	4.39 ± 0.09	4.67 ± 0.04	4.49 ± 0.08
o-Xylene	1.76 ± 0.02	1.76 ± 0.02	1.59 ± 0.03
C_9 monoaromatics	2.53 ± 0.12	3.93 ± 0.08	3.16 ± 0.13
C_{10} monoaromatics	0.31 ± 0.02	0.77 ± 0.03	0.61 ± 0.01
Naphthalene	1.50 ± 0.00	0.91 ± 0.02	1.27 ± 0.00
1-methylnaphthalene	0.43 ± 0.01	0.19 ± 0.02	0.13 ± 0.00
2-methylnaphthalene	1.45 ± 0.02	1.31 ± 0.05	1.63 ± 0.02
C_{12} polyaromatics	0.98 ± 0.02	1.21 ± 0.04	1.23 ± 0.03
Olefins			
Ethylene	3.78 ± 0.09	5.36 ± 0.10	4.62 ± 0.17
Propene	5.15 ± 0.13	8.69 ± 0.05	7.40 ± 0.26
C_4 olefins	2.40 ± 0.08	3.97 ± 0.18	3.70 ± 0.08
C_5 olefins	1.23 ± 0.06	1.68 ± 0.12	1.71 ± 0.02
Alkanes			
Methane	0.86 ± 0.04	0.59 ± 0.02	2.45 ± 0.06
Ethane	0.54 ± 0.01	0.40 ± 0.02	0.92 ± 0.02
Propane	4.33 ± 0.12	2.90 ± 0.06	1.72 ± 0.03
C_4 alkanes	8.57 ± 0.13	4.20 ± 0.31	3.61 ± 0.03
C_5 alkanes	3.02 ± 0.05	1.53 ± 0.12	1.54 ± 0.07
CO and CO_2	7.93 ± 0.26	7.25 ± 0.14	8.93 ± 0.18
Solid (char/coke)	22.6 ± 0.89	18.9 ± 0.89	15.7 ± 0.25

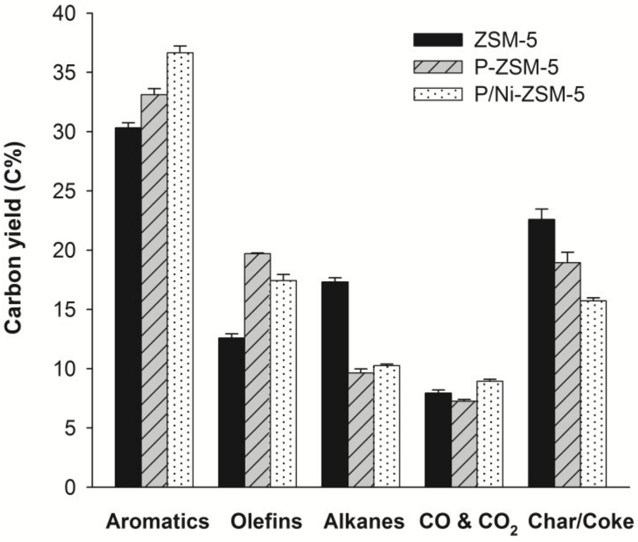

Fig. 4. Carbon yields of major products from catalytic fast pyrolysis of pine wood and LDPE mixture (mass ratio of 2) with conventional, P-, and P/Ni-modified ZSM-5 zeolites.

As shown in Fig. 1, during co-feed CFP of biomass with LDPE, considerable amounts of alkanes can be formed mainly from the initial thermal decomposition of LDPE and subsequent Brönsted acid-catalyzed hydride transfer reactions through which olefins are transformed simultaneously to aromatics and alkanes.[21, 23, 36, 55] However, conventional ZSM-5 zeolites are not effective in converting alkanes to olefins, which is the first and limiting reaction step of alkane aromatization.[36] As a result, alkanes constituted a considerable fraction of the final products in co-feed CFP with the conventional ZSM-5 (see Fig. 4). In comparison, ZSM-5 modification with P and Ni can considerably increase the catalyst's activity for converting alkanes to olefins.[35, 49] In addition, ZSM-5 modification with P and Ni decreased the zeolite's Brönsted acid sites, but increased its Lewis acid sites (see Table 1). Because Lewis acid sites are electron pair acceptor and have strong affinity for hydride ions (dehydrogenation), they may help to accept the hydride ions released during the transformation of alkanes to olefins, as well as subsequent olefins to aromatics.[56] The increase of Lewis acidity of ZSM-5 upon P and Ni modification can therefore prevent some olefins from being hydrogenated to alkanes during CFP conversion process.[43, 56] Due to these reasons, the P- and P/Ni-modified ZSM-5 produced higher olefin yields but lower alkane yields than the conventional ZSM-5 in co-feed CFP (Fig. 4). Olefins can then be further transformed to aromatics via the reaction pathways described previously (see Fig. 1). Consequently, P and P/Ni modification also enhanced aromatic production in co-feed CFP (see Fig. 4). Additionally, because Ni can promote olefin transformation to aromatics,[37] P/Ni-ZSM-5 further increased the yield of aromatics at the expense of olefins as compared to P/ZSM-5 (Fig. 4).

The above result confirms that ZSM-5 modification with P and P/Ni can enhance the conversion of alkanes to olefins and aromatics in co-feed CFP of biomass and LDPE mixtures. In addition, P and Ni modification also decreased solid residue (char/coke) yields in the co-feed CFP (Fig. 4). Previous work has shown that in co-feed CFP of biomass and plastic mixtures, char and coke are mainly generated from the thermal decomposition of biomass and catalytic conversion of biomass-derived oxygenates to hydrocarbons, respectively.[21, 23] In contrast, plastics produce insignificant amounts of char and coke in co-CFP.[21, 23] Assuming that the presence of catalysts would not affect the formation of thermally-derived char,[13, 14] the result suggests that ZSM-5 modification with P and P/Ni decreased considerably the catalytically-derived coke in co-feed CFP. This inference is in line with the previous finding that zeolite modification with P or Ni can generally decrease coke formation during CFP of biomass.[14, 27, 37] Indeed, previous studies have indicated that coke is mainly generated by dehydration of biomass-derived oxygenates (especially those having high oxygen contents),[14, 19, 37] and the strong Brönsted acidity of ZSM-5 are the major catalytic sites for oxygenate dehydration and therefore coke formation during CFP of biomass.[14, 37, 51] To decrease coke formation in CFP of biomass, many researchers have therefore tried modification of zeolites with various transition metals to reduce the acid strength of zeolites.[14, 37, 38, 51, 56] Consistent with these previous studies, Table 1 and Fig. 3 show that ZSM-5 modification with P decreased considerably the strong Brönsted acid sites of the zeolites, and the addition of Ni further reduced the strong acidity. Consequently, the coke yield in the co-feed CFP tests declined in order of ZSM-5, P-ZSM-5, and P/Ni-ZSM-5 (Fig. 4).

The above results indicate that ZSM-5 modification with P and Ni/P can significantly improve the product distribution from co-feed CFP of biomass with LDPE. Upon ZSM-5 modification with P and P/Ni, the yields of valuable aromatics and olefins increased considerably in co-feed CFP of pine wood and LDPE, while the yields of low-value alkanes and undesired coke decreased. ZSM-5 modification with P and P/Ni thus have a beneficial effect on decreasing the rate of coke-induced catalyst deactivation, which has been a major concern in CFP of biomass.

3.3. Evaluation of the hydrothermal stability of P- and P/Ni-modified ZSM-5 zeolites

While co-feed of biomass with LDPE can decrease coke formation in CFP, it enhances water formation, e.g., from the dehydration reaction that follows the Diels–Alder reactions of biomass-derived furans with LDPE-derived olefins.[21, 23, 31-33] Because the in-situ generated water can cause hydrothermal damage to zeolite structure (e.g., dealumination/decomposition of zeolite framework) at high temperatures of CFP,[27, 29, 30, 34] co-feed CFP of biomass and LDPE mixture may require catalysts with high hydrothermal stability to ensure long-term stable operation. To evaluate the hydrothermal stability of the zeolites, we treated the conventional, P-, and P/Ni-modified ZSM-5 with 100% steam at 550 °C for 3–9 h, and then tested their activity for aromatic production in co-feed CFP of pine wood with LDPE (mass ratio of 2).

For the conventional ZSM-5, steam pretreatment considerably degraded its activity for aromatic production in co-feed CFP. As shown in Fig. 5, the yield of aromatics decreased markedly by 27–32% when the conventional ZSM-5 was hydrothermally pretreated for 3–9 h. Moreover, the aromatic product distribution also changed considerably. Fig. 6(a) shows that while the aromatic selectivity decreased for benzene, toluene, and polyaromatics, it increased considerably for larger monoaromatics (e.g., trimethylbenzenes, tetramethylbenzenes, and indane, see Table 2). Because benzene and toluene are two most important primary petrochemicals from which numerous petrochemical intermediates and commercial products can be made, they are generally considered highly desirable aromatic products from CFP.[2, 3, 5] However, as Fig. 6(a) shows, the overall aromatic selectivity for benzene and toluene decreased considerably from 45.5% to 34.0–31.8% in co-feed CFP when the conventional ZSM-5 was hydrothermally pretreated for 3–9 h. This result indicates that hydrothermally-induced deactivation of ZSM-5 zeolites can cause a considerable decrease in both the overall aromatic yield and the selectivities for more valuable aromatic products (benzene and toluene) in co-feed CFP. Furthermore, it is noticed that the deterioration of aromatic yield and distribution occurred mainly within the first 3 h of hydrothermal treatment of the conventional ZSM-5 (Fig. 5 and 6). This result suggests that short duration of severe hydrothermal conditions can cause conventional ZSM-5 zeolite to lose much of its activity for aromatic production in CFP. Similar decay in the catalyst activity of hydrothermally-treated ZSM-5 zeolites has also been reported in CFP of biomass (poplar wood), as well as catalytic cracking of alkane and naphtha, and mainly attributed to the hydrothermal damage (e.g., dealumination/decomposition) of ZSM-5 structure during steam treatment.[27, 29, 30, 34]

In contrast to conventional ZSM-5 zeolite, P- and P/Ni-modified zeolites exhibited excellent hydrothermal stability against steam treatment. No significant changes in the aromatic yield and selectivity were observed for co-feed CFP conducted with P- and P/Ni modified ZSM-5, even when they had been hydrothermally pretreated for up to 9 h (Fig. 5 and 6). This result indicates that P and P/Ni modification can greatly improve the hydrothermal stability of ZSM-5. This improvement can be mainly attributed to the fact that extraframework P species can stabilize the framework aluminum pairs of zeolites, thus preventing dealumination during hydrothermal treatment.[28-30] In addition, impregnation of Ni has also been reported to be able to increase the hydrothermal stability of zeolites because Ni modification can increase the dehydrogenation activity and decrease the acid strength of zeolites.[37, 38]

The above results indicate that ZSM-5 modification with P and P/Ni can considerably improve the hydrothermal stability of the zeolites. This helps the catalysts to resist steam-induced deactivation in CFP of biomass and plastics, as well as in catalyst regeneration in which spent catalysts are exposed to high temperature oxidation in air or steam to remove coke deposits from the catalysts. ZSM-5 modification with P and P/Ni thus has a beneficial effect on improving the catalyst life time for CFP of biomass and plastics.

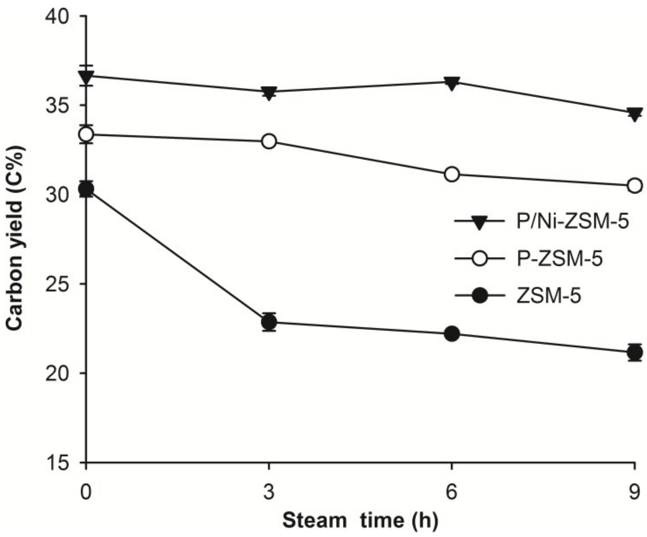

Fig. 5. Carbon yields of aromatic hydrocarbon products from catalytic fast pyrolysis of pine wood and LDPE mixture (mass ratio of 2) with steamed conventional, P-, and P/Ni-modified ZSM-5 zeolites.

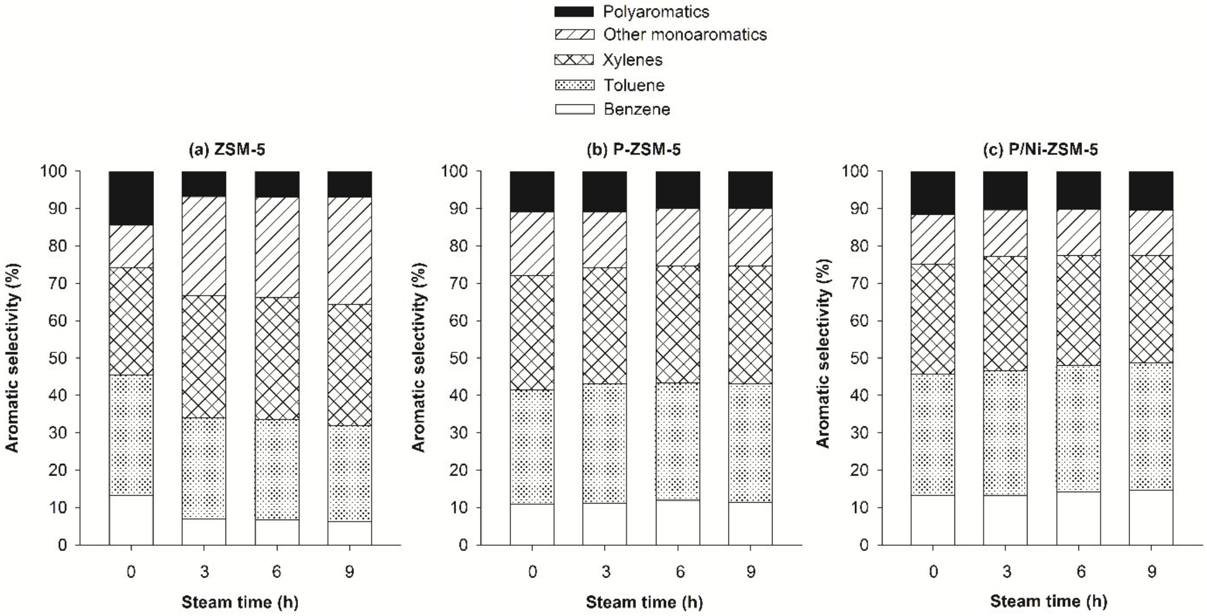

Fig. 6. Aromatic selectivity in catalytic fast pyrolysis of pine wood and LDPE mixture (mass ratio of 2) with steamed (a) conventional ZSM-5, (b) P-modified ZSM-5, and (c) P/Ni-modified ZSM-5 zeolites.

3.4. *Effects of P/Ni modification on the synergy for aromatic production in co-feed CFP*

As described previously, biomass and LDPE have a significant synergy that enhances aromatic production and decreases coke formation when they are co-fed in CFP with ZSM-5 zeolites.[21, 23] To assess whether P/Ni modification would affect this synergy, we investigated CFP of pine wood alone, LDPE alone, and their mixtures (mass ratios of 4–1) with P/Ni ZSM-5 zeolite. The product distribution from these CFP tests are summarized in Table 3. The experimentally-determined yields of aromatics, olefins, alkanes, carbon oxides, and solid residues were then compared to their additive yields that were calculated by linear addition of the corresponding yields determined in CFP of pine wood and LDPE individually according to Eq. (3).[21] Note that the yields are plotted against the effective hydrogen index (H/C_{eff}) of the feedstock in Fig. 7 such that the additive yields changes linearly with the H/C_{eff}.[21] These calculated additive yields would have equaled the experimentally-determined yields if there had been no interactions between biomass and plastics in their co-feed CFP.

$$Y_{additive,(m:n)} = \frac{mY_{bio}C_{bio}\% + nY_{p}C_{p}\%}{(m+n)C_{mix}\%} \times 100\% \qquad (3)$$

where m and n are the mass ratio of pine wood and LDPE in co-feed mixture, respectively; Y_{bio} and Y_{p} are the average carbon yields determined in CFP of pine wood and LDPE, respectively; C_{bio}, C_{p}, and C_{mix}% are the carbon contents in the pine wood, LDPE, and their mixture (pine wood-to-LDPE ratio of m:n).

However, as Fig. 7 shows, the experimental yields deviated considerably from the linear trends of additive yields, indicating that significant chemical interactions occur between pine wood and LDPE in their co-feed CFP. At all three co-feeding ratios, the experimental yields were considerably higher than the additive yields for aromatics (Fig. 7(a)), but lower for alkanes, carbon oxides, and coke (Fig. 7(c–e)). These trends are essentially the same as what have been observed in the previous study on co-feed CFP of biomass and LDPE mixtures with conventional ZSM-5 zeolites.[21] This result indicates that ZSM-5 modification with P and Ni does not negatively affect the synergy between biomass and LDPE for aromatic production and coke reduction in co-feed CFP. In fact, the P- and P/Ni-modified ZSM-5 produced higher aromatic yields and lower coke yields than conventional ZSM-5 (see Fig. 4).

Table 3

Detailed product yields in CFP of pine wood, LDPE, and their mixtures (mass ratio of 4–1) with P/Ni-modified ZSM-5 zeolite.

Ratio of pine wood-to-LDPE	1:0	4:1	2:1	1:1	0:1
H/C_{eff} of the feedstock	0.3	0.8	1.1	1.4	2.0
Carbon yield (C%)					
Aromatic hydrocarbons					
Benzene	3.12 ± 0.05	4.18 ± 0.00	4.85 ± 0.04	5.10 ± 0.09	4.98 ± 0.05
Toluene	5.92 ± 0.04	9.79 ± 0.10	11.9 ± 0.10	12.4 ± 0.14	12.7 ± 0.22
Ethylbenzene	0.40 ± 0.01	0.91 ± 0.01	1.14 ± 0.05	1.09 ± 0.02	1.06 ± 0.02
p-Xylene	2.56 ± 0.00	4.25 ± 0.04	4.69 ± 0.15	4.37 ± 0.07	3.66 ± 0.08
m-Xylene	2.14 ± 0.02	3.67 ± 0.09	4.49 ± 0.08	4.51 ± 0.05	4.71 ± 0.08
o-Xylene	0.75 ± 0.01	1.27 ± 0.04	1.59 ± 0.03	1.61 ± 0.02	1.77 ± 0.03
C_9 monoaromatics	2.41 ± 0.02	2.63 ± 0.02	3.16 ± 0.13	2.50 ± 0.02	2.35 ± 0.01
C_{10} monoaromatics	1.84 ± 0.01	0.79 ± 0.01	0.61 ± 0.01	0.37 ± 0.00	0.00 ± 0.00
Naphthalene	1.90 ± 0.02	1.46 ± 0.02	1.27 ± 0.00	1.14 ± 0.01	0.84 ± 0.01
1-methylnaphthalene	0.07 ± 0.00	0.14 ± 0.00	0.13 ± 0.00	0.41 ± 0.01	0.00 ± 0.00
2-methylnaphthalene	2.36 ± 0.02	1.91 ± 0.05	1.63 ± 0.02	1.36 ± 0.02	0.96 ± 0.02
C_{12} polyaromatics	1.91 ± 0.01	1.49 ± 0.04	1.23 ± 0.03	0.51 ± 0.02	0.29 ± 0.00
Olefins					
Ethylene	2.06 ± 0.05	3.70 ± 0.04	4.62 ± 0.17	5.13 ± 0.03	5.27 ± 0.03
Propene	1.33 ± 0.03	4.79 ± 0.08	7.40 ± 0.26	9.34 ± 0.09	12.3 ± 0.13
C_4 olefins	0.38 ± 0.02	1.95 ± 0.06	3.70 ± 0.08	5.06 ± 0.03	7.76 ± 0.12
C_5 olefins	0.38 ± 0.01	0.88 ± 0.03	1.71 ± 0.02	2.53 ± 0.02	4.45 ± 0.03
Alkanes					
Methane	1.78 ± 0.08	1.84 ± 0.03	2.45 ± 0.06	2.71 ± 0.03	4.18 ± 0.02
Ethane	0.19 ± 0.01	0.51 ± 0.01	0.92 ± 0.02	1.29 ± 0.03	3.08 ± 0.04
Propane	0.15 ± 0.00	0.91 ± 0.02	1.72 ± 0.03	2.82 ± 0.05	6.91 ± 0.10
C_4 alkanes	0.68 ± 0.02	1.73 ± 0.06	3.61 ± 0.03	5.88 ± 0.09	13.2 ± 0.19
C_5 alkanes	0.34 ± 0.02	0.73 ± 0.03	1.54 ± 0.07	2.60 ± 0.03	5.37 ± 0.05
CO and CO_2	20.4 ± 0.03	12.7 ± 0.14	8.93 ± 0.18	5.11 ± 0.04	0.00 ± 0.00
Solid (char/coke)	37.4 ± 0.15	23.9 ± 0.34	15.7 ± 0.25	12.1 ± 0.47	2.06 ± 0.36

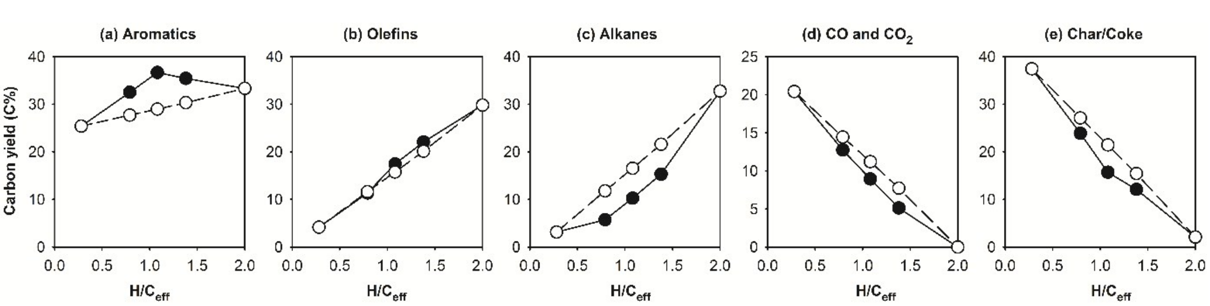

Fig. 7. Comparison between (●) the experimental yields and (○) the calculated additive yields of the major products in catalytic fast pyrolysis of pine wood, LDPE, and their mixtures (mass ratios of 4–1) with P/Ni-ZSM-5 zeolite.

4. Conclusions

This study demonstrates that ZSM-5 modification with P and P/Ni can have several beneficial effects on co-feed CFP of biomass with LDPE. Compared with conventional ZSM-5, the P- and P/Ni-modified ZSM-5 considerably enhanced the production of valuable olefin and aromatic products, and diminished the formation of low-value alkanes and undesired coke in co-feed CFP of pine wood and LDPE mixtures. In addition, modification with P and P/Ni considerably increased the hydrothermal stability of ZSM-5 to resist steam-induced catalyst deactivation that may occur during CFP process. These results indicate that ZSM-5 modification with P and P/Ni can not only improve the product distribution toward more valuable products, but also decrease the rate of coke- and steam-induced catalyst deactivation in co-feed CFP of biomass and LDPE. ZSM-5 modification with P and P/Ni may therefore provide a viable way to improve the catalyst activity and life time for petrochemical production from co-feed CFP of biomass and plastics.

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