Electronic Supplementary Information for:

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

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1. Catalyst-to-reactant ratios used in catalytic fast pyrolysis processes

CDS pyroprobes are commonly used in lab-scale CFP studies mainly to screen catalysts and investigate reaction mechanisms.[1-4] Because the reactors of CDS pyroprobes can hold only tiny amounts of samples (several micrograms), high catalyst-to-sample ratios (e.g., 10–20) are required to ensure that biomass- and plastic-derived volatile intermediates can then be effectively converted to final products (e.g., olefins and aromatic hydrocarbons) within the catalyst framework before the volatile intermediates escape from the reactor.[4-6] It should be noted that the catalyst-to-reactant ratios used for CDS pyroprobe CFP tests are considerably higher than those used for industrial CFP processes. For example, some pilot-scale fluidized bed reactors have recently been developed for continuous CFP operations, in which biomass and catalysts are continuously added into and removed from the reactors.[7-10] The removed catalysts are then regenerated by burning off coke deposit in air and reused in subsequent CFP cycles. The catalyst-to-biomass ratio, which is defined as the ratio between catalyst and biomass feeding rates, is usually between 3 and 9 in these pilot-scale studies.[7, 9, 10]

2. Effects of phosphorus and nickel loading on CFP of pine wood and LDPE mixture

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 (1–3 wt.%) and subsequent Ni (1–3 wt.%). The actual P and Ni contents on the catalysts after calcination (i.e., before the catalysts were used for CFP tests) were measured by X-ray fluorescence (XRF) technique and shown in Table S1.

Table S1
Phosphorus and nickel contents of the zeolites used in this study.

Sample	SiO_2/Al_2O_3	Loading used in impregnation (wt.%)		Actual loading after calcination[a] (wt.%)	
		P	Ni	P	Ni
ZSM-5	37.7	-	-	-	-
1%P-ZSM-5	38.8	1	-	0.91	-
2%P-ZSM-5	38.2	2	-	1.54	-
3%P-ZSM-5	38.0	3	-	3.03	-
5%P-ZSM-5	38.3	5	-	4.96	-
3%P/1%Ni-ZSM-5	39.7	3	1	1.79	1.05
3%P/2%Ni-ZSM-5	39.7	3	2	1.87	1.96
3%P/3%Ni-ZSM-5	38.8	3	3	2.04	3.07

[a] Measured by XRF analysis.

Fig. S1 shows that the aromatic yield in co-feed CFP of pine wood and LDPE mixture (mass ratio of 2) went through a maximum at a phosphorus (P) loading of 2 wt.%. Further increasing P loading over ZSM-5 to 5 wt.% resulted in a considerable decrease in the aromatic yield. This result indicates that ZSM-5 impregnation with appropriate amounts of P can improve aromatic production in co-feed CFP of biomass and LDPE. However, overloading P can cause significant decrease in the catalytic activity of ZSM-5 due to severe pore blockage and acidity decrease of the zeolites.[11-13]

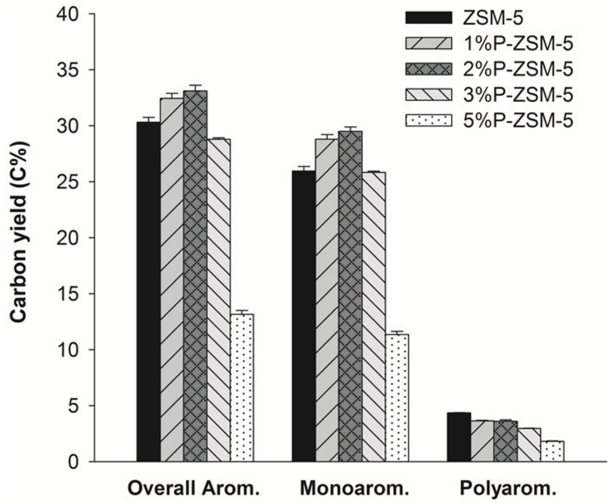

Fig. S1. Effects of phosphorus loading over P-ZSM-5 on aromatic production in co-feed catalytic fast pyrolysis of pine wood and LDPE mixture (mass ratio of 2).

Fig. S2 shows that subsequent impregnation of P-modified ZSM-5 zeolites with Ni can further enhance aromatic production in co-feed CFP. This improvement is probably because Ni modification can increase the dehydrogenation activity of zeolites, thus enhancing olefin transformation to aromatics.[14, 15] Among the P/Ni-ZSM-5 zeolites, ZSM-5 modified with 3 wt.% P and 2 wt.% Ni (3%P/2%Ni-ZSM-5) produced the highest aromatic yield, and was therefore selected for further characterization and CFP evaluations.

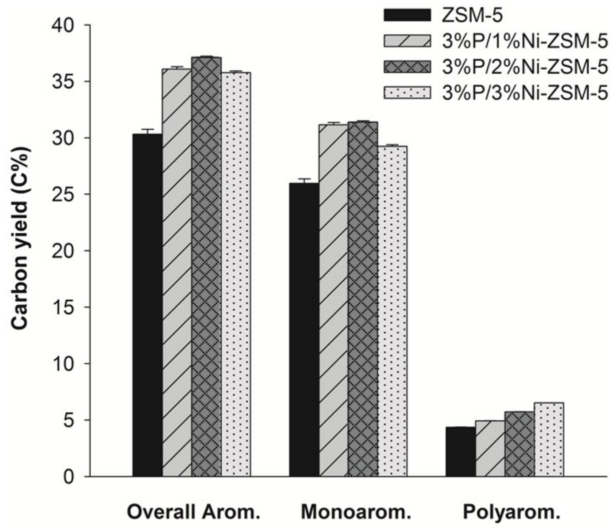

Fig. S2. Effects of phosphorus and nickel loading over P/Ni-ZSM-5 on aromatic production in co-feed catalytic fast pyrolysis of pine wood and LDPE mixture (mass ratio of 2).

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