Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Methanol to aromatics: Isolated zinc phosphate groups on HZSM-5 zeolite enhance BTX selectivity and catalytic stability.

haracterization Details:

Surface area and micropore analysis.

Nitrogen physisorption measurements were performed using a Micromeritics Tristar 3000 apparatus operating at liquid N_2 temperature. Prior to measuring the isotherm, all samples were outgassed under vacuum overnight at 350°C. The surface area was calculated from N_2 isotherm data using the Brunauer-Emmett-Teller (BET) model. The micropore volumes, the micropore and external surface area were measured using t-plot analysis.

Powder X-ray diffraction.

The crystallinity of HZSM-5, P/HZSM and Zn-P/HZSM-5 catalysts was measured with a Bruker Advance D8 X-ray powder diffractometer with Cu K (λ = 1.5418 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. For ZnPHZ catalyst, synchrotron X-ray diffraction pattern was collected on beamline X14A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with a wavelength of 0.7793584 Å. Approximately 1.0 g of sample was placed in the depression in a flat plate. The incident X-ray beam was monochromized at 8.0 eV by the double-crystal monochromator, focused horizontally by a sagittally bent second mono-crystal and focused vertically by a mirror.

Scanning Transmission electron microscopy.

The HAADF-STEM images were taken using JEOL ARM200F aberration-corrected transmission electron microscope (TEM) operated at 200 kV. The semi-convergence angle is about 23 mrad. The inner and outer angles of the detector are 90 and 370 mrad, respectively. A drop of the suspension of powder in acetone was deposited on copper grids coated with an ultrathin carbon film on holey carbon. The images were analyzed using Digital Micrograph (Gatan, Inc.).

NMR measurements.

All NMR spectra were acquired under magic angle spinning (MAS) at room temperature in a Varian VNMR 400 spectrometer (9.39 T) with a spinning rate of 10 kHz. Solid state ^{29}Si spectra were recorded at 79.46 MHz with a pulse length of 2 μs and 4000 scans with 15s repetition time. The ^{27}Al chemical shifts were referenced to an aqueous solution of $Al(NO_3)_3$. The ^{29}Si chemical shifts were referenced to Q8M8. Solid State ^{31}P NMR experiments were operated with a frequency of 161.9 MHz, pulse delay of 15 s, pulse width of 2.6 μs and 4000 scans. The ^{31}P chemical shifts were referenced to an aqueous solution of H_3PO_4. The ^{27}Al MAS spectra were obtained at 104.2 MHz with a pulse length of 0.5 μs and 4000 scans with 1s repetition time.

XAFS measurements.

The catalyst sample was grounded to fine powder and pressed into a pellet, which was mounted in a sample holder. XAFS measurements were performed at beamline X19A at the National Synchrotron Light Source (Brookhaven National Laboratory) and Beamline BL2-2 at the Stanford Synchrotron Radiation Laboratory. The beam was monochromatized using Si(111) double crystal monochromator. Scans were obtained for incident energies varying from 150 eV below and 500 eV above the Zn K-edge energy. A reference Zn foil sample was mounted between the transmission and reference ion chambers. XAFS data in the reference foil were collected simultaneously with the main sample, for energy calibration and alignment. Besides sample of ZnPHZ catalyst, the standard samples of ZnO and anhydrous $Zn_3(PO_4)_2$ were also measured for comparison. All spectra were collected at room temperature after water removal at 430°C in transmission mode.

X-ray absorption coefficient data were processed and analyzed using the IFEFFIT package. All the data were aligned in X-ray energy first. The averaged and background-removed spectra were then edge-step normalized using Athena program. The EXAFS data analysis was done by fitting theoretical signal calculated using FEFF6 code to experimental data in R-space in the first two peak regions, corresponding to the first two nearest neighboring shells. The passive electron reduction factor (S_0^2) was set to 1.0 as determined from EXAFS analysis of the ZnO. The coordination number (N), mean squared bond lenth disorder (σ^2) and the correction (ΔE) to the threshold energy were varied in the fits.

FTIR measurements.

Hydroxyl surface groups of HZ catalysts were characterized by Fourier Transform Infrared Spectroscopy (FTIR), using a Nicolet 5700 spectrometer. Powder samples were pressed at 30 MPa to form disks approximately 13.0 mm in diameter, weighing approximately 17 mg. The sample was treated at 450°C for 2 h under vacuum (1.3×10^{-4} Pa) for dehydration. Spectra were recorded at 40°C with a resolution of 4 cm^{-1} in the region ranging from 4000 to 1300 cm^{-1}. Hydroxyl concentrations of the Brønsted acid sites were estimated by the peak heights.

Py-FTIR.

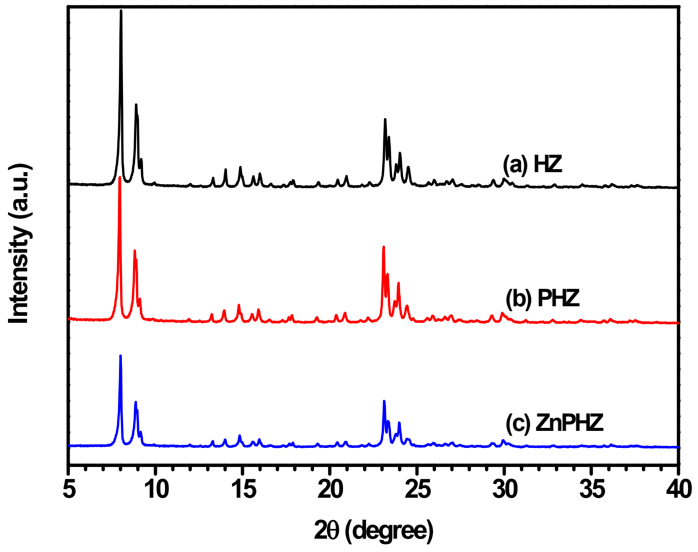
Acidity properties of three zeolites samples were investigated by FTIR spectroscopy using pyridine as a probe molecule. Measurements were performed on a Nicolet 380 spectrometer equipped with a vacuum cell. Zeolite samples were pressed at 30 MPa into thin wafers (24.0 mg, 13 mm in diameter) and were treated for dehydration in the IR cell at 400°C under vacuum (1.3×10^{-4} Pa) for 2 h. After a vacuum treatment and cooling to the temperature of 200°C, a preliminary spectrum was measured at 200°C, 300°C, and 400°C. The absorbance spectra were obtained by using the interferograms of reduced samples as background references. The sample was exposed to pyridine vapor (4 Torr) under static conditions for 10 minutes. The IR spectrum was measured again after vacuum at 200°C. A progressive thermal desorption procedure (steps from 200 to 400°C) was conducted in order to determine the acid amount with different acid strength of Lewis and the Brønsted acid sites by evaluating the amount of remaining adsorbed pyridine as temperature increases. Spectra were recorded with a resolution of 4 cm^{-1} in the region ranging from 1400 to 1700 cm^{-1}. Lewis and Brønsted acid sites detected at 400°C are considered as strong acidic sites (B400, L400); that desorbed from 200°C to 300°C is defined by weak acidic sites (B200, L200); that desorbed from 300°C to 400°C is defined as medium acidic sites (B300, L300). Brønsted and Lewis acid site concentrations were calculated by the integration of the IR bands at 1545 cm^{-1} and at 1450 cm^{-1}, respectively. To allow quantitative comparisons of the peak intensities, all Py-FTIR spectra were normalized using the area of the overtone lattice vibration bands of the zeolites at 1990 cm^{-1} and 1873 cm^{-1}, as conducted in the literatures.[1-3]

NH_3-TPD.

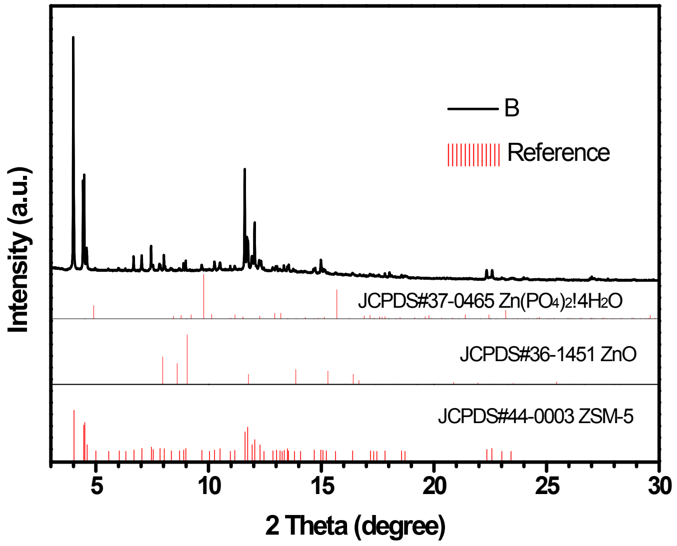
The acidity of the catalysts was determined by temperature programmed desorption of ammonia (NH_3-TPD). A catalyst sample of 100 mg was loaded into a U-shaped micro-reactor and pre-treated at 650°C for 60 min in a flow of helium. After the pre-treatment, the sample was cooled to 150°C and saturated with ammonia. The temperature was increased from 150 to 600°C at a constant heating rate of 10°C/min under a He flow of 20mL/min. The concentration of ammonia in the exit gas was monitored continuously with a TCD detector.

Chemical analysis.

Chemical analysis of the zeolite samples was performed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) on a Varian 725 ES.


(a) HZ
(b) PHZ
(c) ZnPHZ
Intensity (a.u.)
5
10
15
20
25
30
35
40
2θ (degree)

(a)


B
Reference
JCPDS#37-0465 Zn(PO4)2!4H2O
JCPDS#36-1451 ZnO
JCPDS#44-0003 ZSM-5
Intensity (a.u.)
5
10
15
20
25
30
2 Theta (degree)

(b)

Figure S1. XRD patterns of catalysts: (a) HZ, PHZ, ZnPHZ; (b) Synchrotron-based data of ZnPHZ catalyst and reference data from JCPDS.

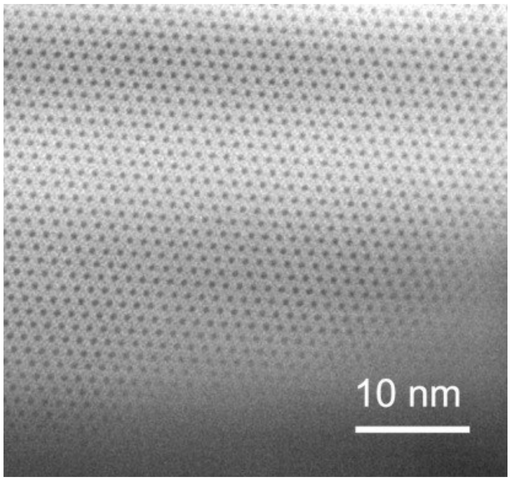
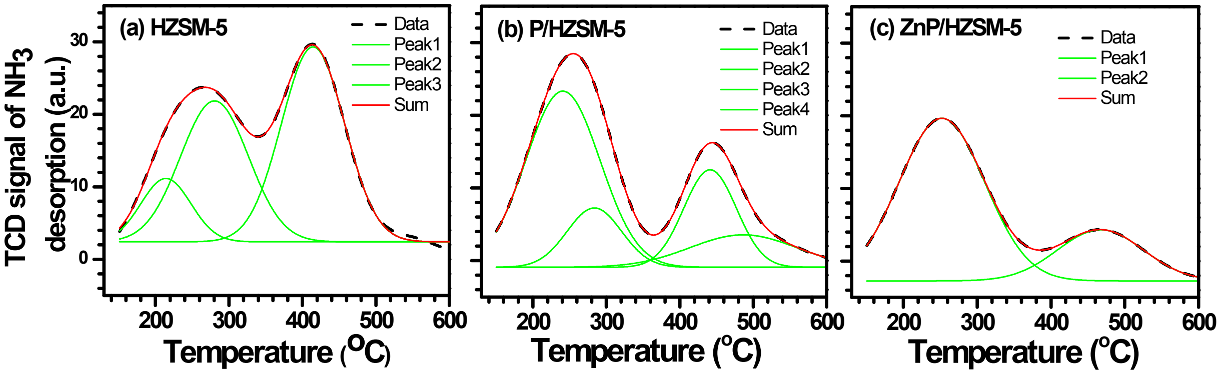


Figure S2. Representative high resolution Scanning Transmission Electron Microscopy images for ZnPHZ catalyst.



F

igure S3. NH_3-TPD profiles of catalysts: (a) HZSM-5, (b) P/HZSM-5, (c) Zn-P/HZSM-5.

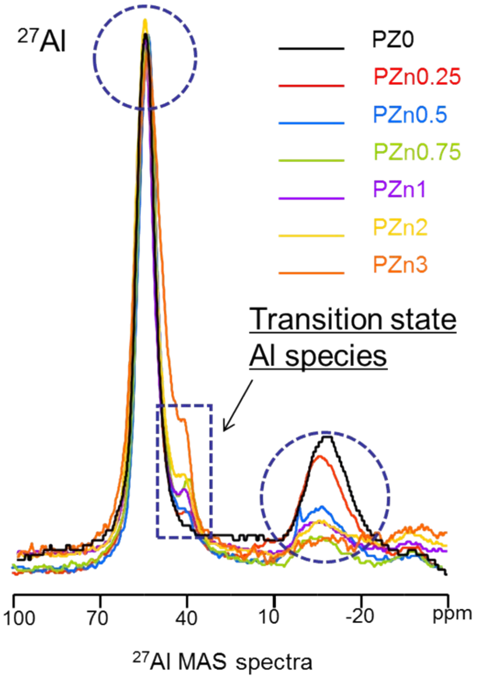


Figure S4. ^{27}Al MAS NMR spectra of ZnPHZ catalysts with zinc loading in the range of 0 to 3.0%, as well as steady phosphorus loading mass.

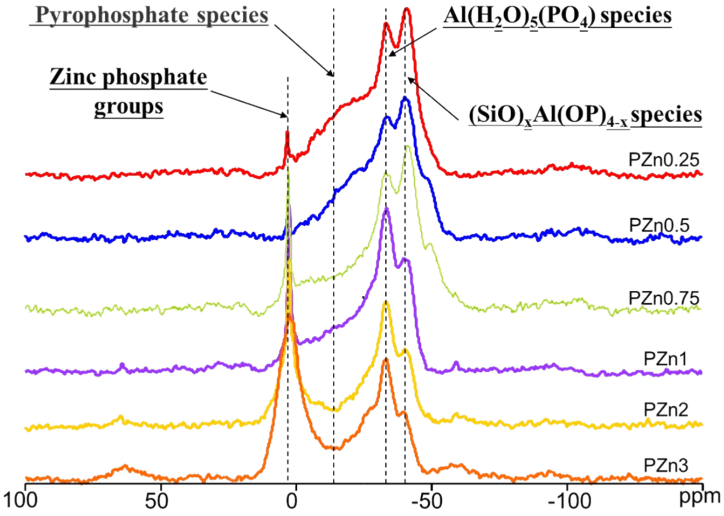
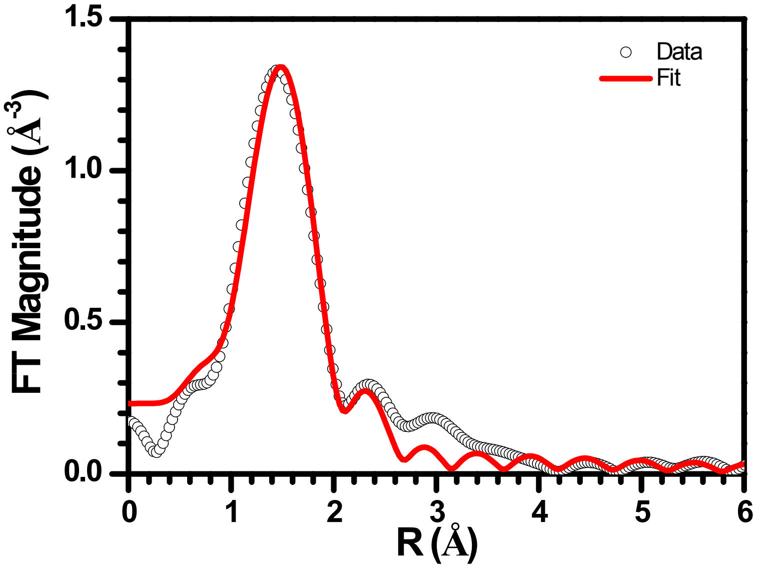
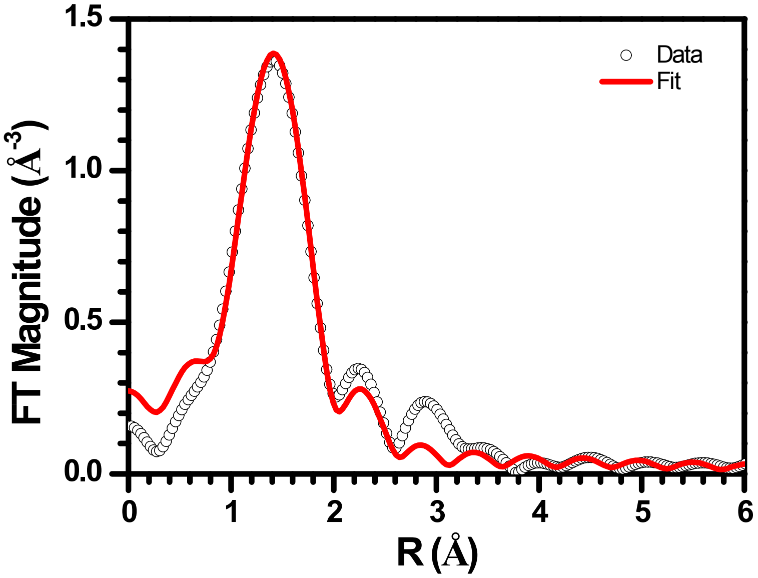


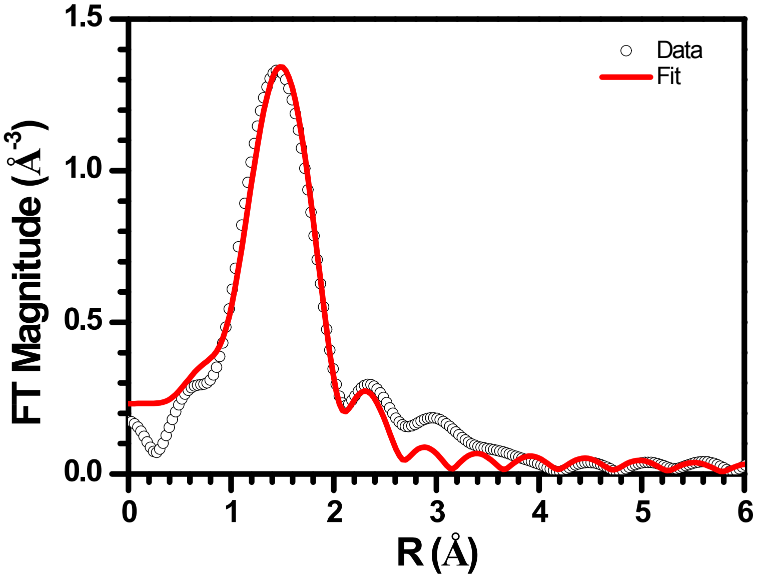
Figure S5. ^{31}P MAS NMR spectra of ZnPHZ catalysts with different zinc loading in the range of 0.25% to 3.0%, as well as steady phosphorus loading mass..


1.5
1.0
0.5
0.0
FT Magnitude ($\mathring{A}^{-3}$)
0
1
2
3
4
5
6
R (Å)
Data
Fit

(a)


1.5
1.0
0.5
0.0
FT Magnitude ($\mathring{A}^{-3}$)
0
1
2
3
4
5
6
R (Å)
Data
Fit

(b)



(c)

Figure S6. k^2-weighted EXAFS data (k-range = 2-10 Å^{-1}) and the fitting curve for zinc K-edge of Zn-P/HZSM-5 sample in r-space: (a) ZnPHZ, (b) PZnHZ, (c) ZnHZ.

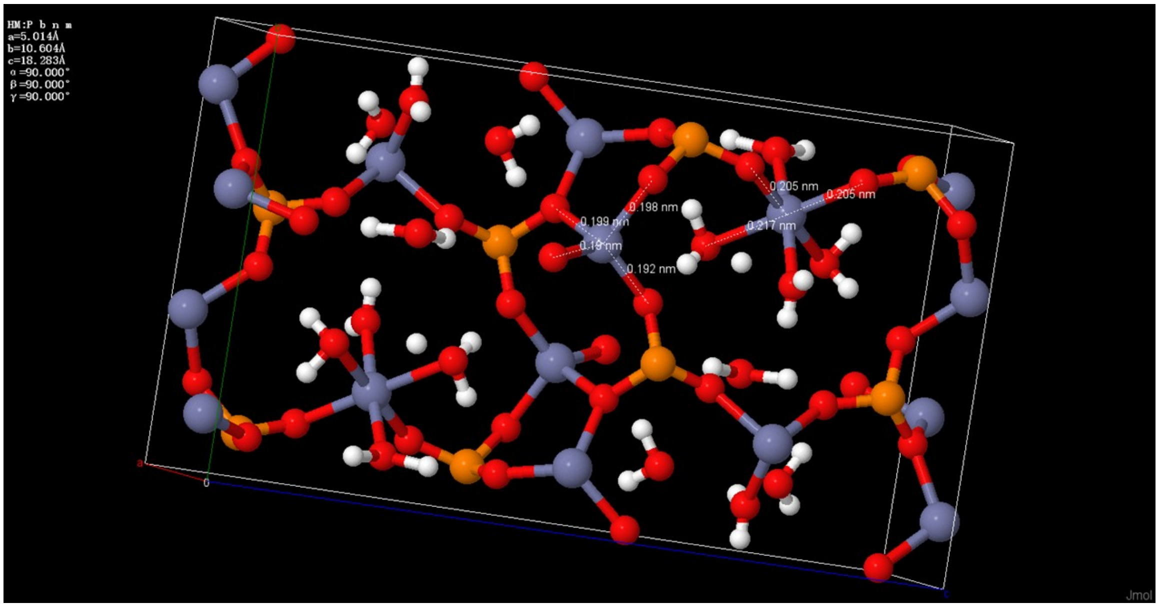
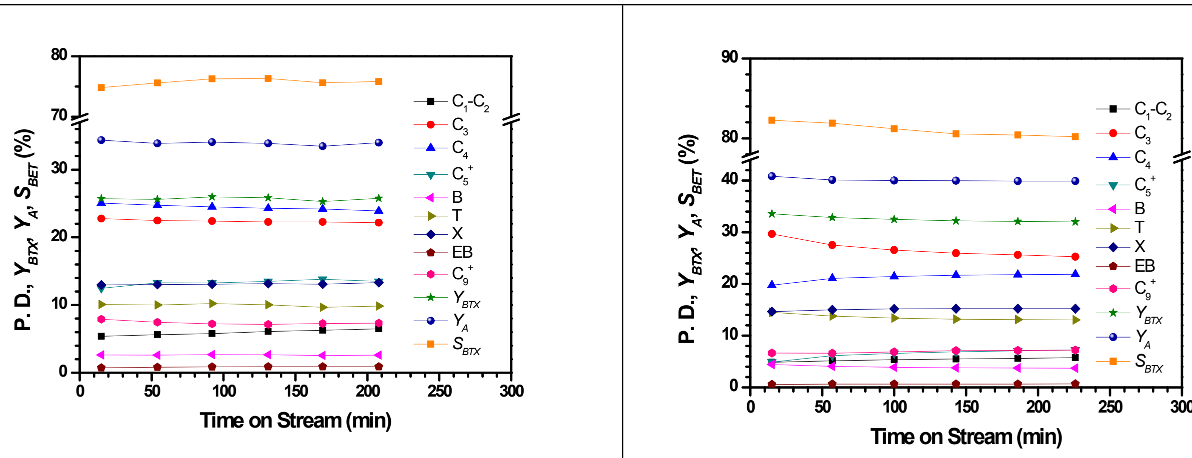
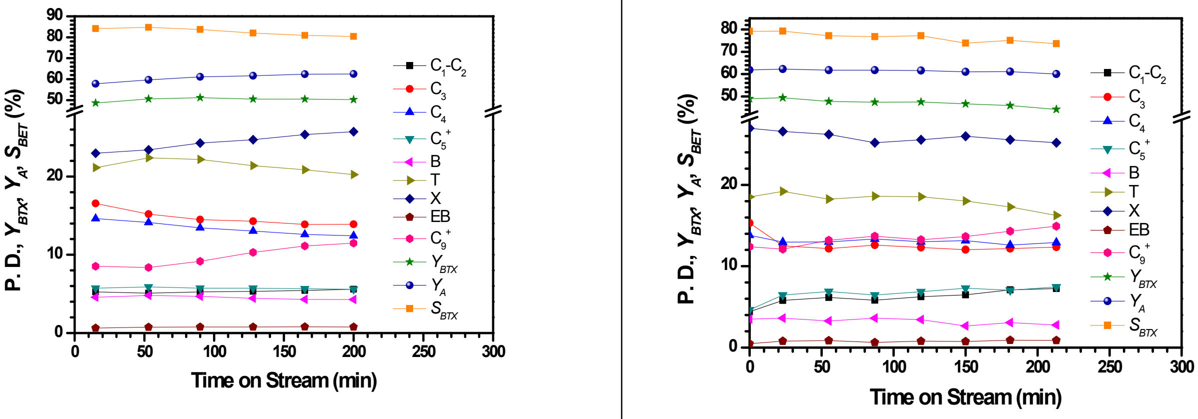


Figure S7. The crystal structure of zinc phosphate hydrates from American Mineralogist Crystal Structure Database code amcsd 0019555).



(a) HZ

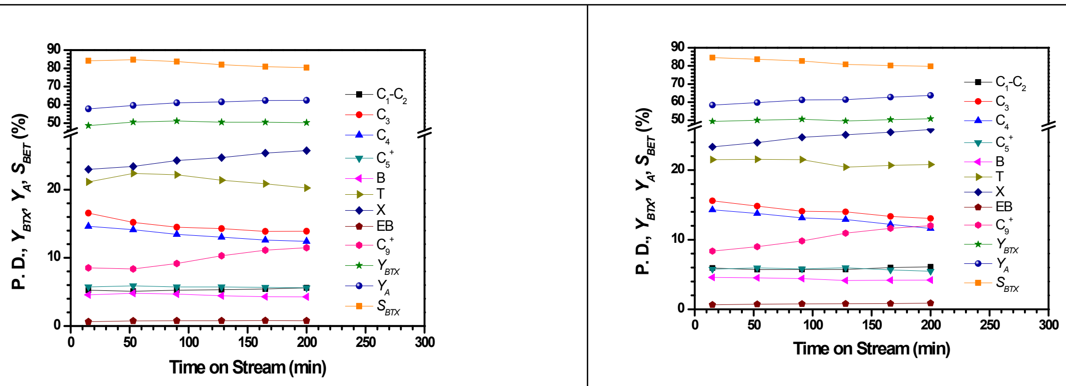
(b) PHZ



(c) ZnPHZ

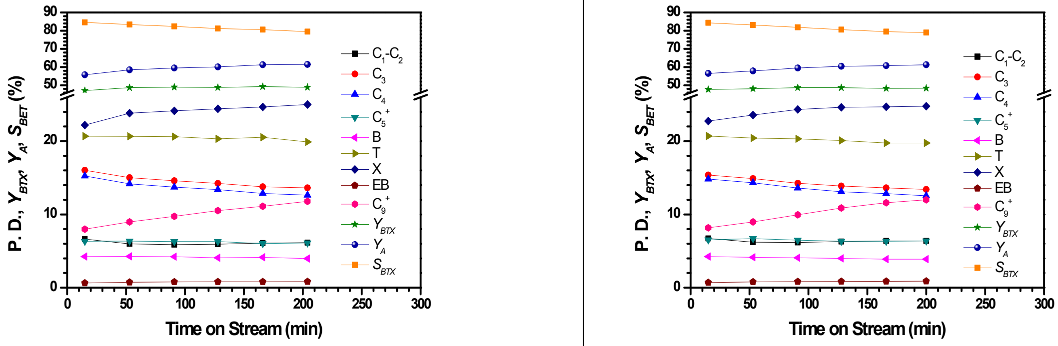
(d) ZnHZ

Figure S8. Time on stream of product distribution (P. D.), yield of BTX (Y_{BTX}), yield of aromatics (Y_A) and selectivity to BTX (S_{BTX}) on: (a) the parent HZ, (b) PHZ, (c) ZnPHZ and (d) ZnHZ catalysts. Reaction conditions: 0.1 MPa, 430°C, 3.0 g catalyst, WHSV = 2.0 h^{-1}.



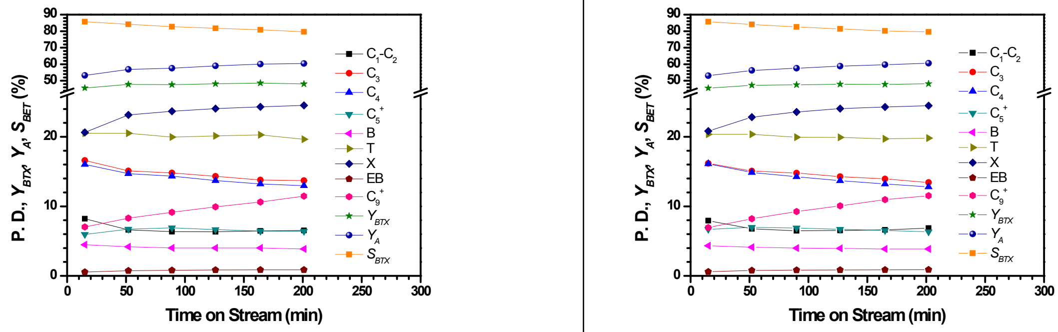
(a) ZnPHZ (0)

(b) ZnPHZ (R1)



(c) ZnPHZ (R2)

(d) ZnPHZ (R3)



(e) ZnPHZ (R4)

(f) ZnPHZ (R5)

Figure S9. Time on stream of product distribution, yield of BTX (Y_{BTX}), yield of aromatics (Y_A) and selectivity to BTX (S_{BTX}) over ZnPHZ catalyst for the fresh catalyst ZnPHZ (0) and five times regeneration (R1~R5). Reaction conditions: 0.1 MPa, 430°C, 3.0 g catalyst, WHSV = 2.0 h^{-1}; Regeneration conditions: calcination at 550°C for 5 h under air atmosphere.

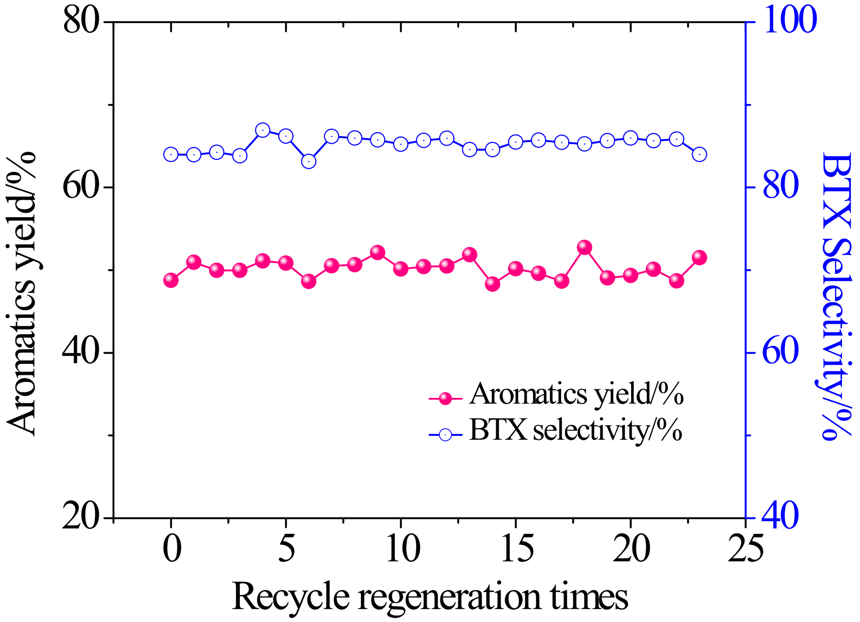


Figure S10. Time on stream of product distribution, yield of aromatics (Y_A) and selectivity to BTX (S_{BTX}) over ZnPHZ catalyst for extended recycle regeneration times. Reaction conditions: 0.1 MPa, 430°C, 3.0 g catalyst, WHSV = 2.0 h^{-1}. Regeneration conditions: calcination at 550°C for 5 h under air atmosphere.

Table S1. Acid amount of different acid strength estimated by Py-FTIR.

Catalysts	B200 Weak	B300 Medium	B400 Strong	L200 Weak	L300 Medium	L400 Strong
HZ	0.046	0.056	0.546	0.173	0.067	0.117
PHZ	0.130	0.065	0.50	0.182	0.071	0.234
ZnPHZ	0.058	0.058	0.077	0.289	0.161	0.354

Table S2. Quantitative analysis data of NH_3-TPD over catalysts.

Items	HZ		PHZ		ZnPHZ	
	Temperature (°C)	Peak Area (a.u.)	Temperature (°C)	Peak Area (a.u.)	Temperature (°C)	Peak Area (a.u.)
HT	414	2899	444	2019	470	1026
LT	--	2996	--	3838	--	3560
TT (LT+HT)	--	5895	--	5857	--	4586
[a]RLT	--	1.000		1.281		1.188
[a]RHT	--	1.000		0.696		0.354
[a]RTA	--	1.000	--	0.994	--	0.783

[a] LT1(2), Low-temperature peak 1 (2); HT1(2), the high-temperature peak 1(2); LT, the total low-temperature peak; TT, the total high- and low-temperature peak; RLT, the relative area of low-temperature Peaks; RHT, the relative area of high-temperature peaks; RTA: Relative Total Acid amount by defining the total acid amount for HZSM-5 as 1.00.

References:

(1) J.G. Zhang, W.Z. Qian, X. P.Tang, K. Shen, T. Wang, X.F. Huang and F. Wei, *Acta Phys. Chim. Sin.* 2013, **29**, 1281.

(2) G. Q. Zhang, T. Bai, T. F. Chen, W. T. Fan and X. Zhang *Ind. Eng. Chem. Res.* 2014**,** **53**, 14932.

(3) S. Zheng, H. R. Heydenrych, A. Jentys and J. A. Lercher, *J. Phys. Chem. B* 2002**, 106**, 9552.