Supplementary Information (SI) for Green Chemistry.
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Supporting Information

Enhanced catalytic aminolysis of polyethylene terephthalate plastic wastes via zeolite acid-base sites regulation

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Supplementary Methods

Chemicals and materials. All chemicals were available with analytical purity and used as received. PET plastic was purchased from Dongwan Huachuang Plastic Co., Ltd. Hβ-25, Hβ-40, SPAO-34, ZSM-5-70, ZSM-5-200 and ZSM-5-300 were purchased from Tianjin Nankai University Catalyst Co., Ltd. $Mg(OH)_2$ was obtained from Shanghai Tongya Chemical Technology Co., Ltd. $Ca(OH)_2$, KOH and NaOH were purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. Propanolamine, N, N-dimethylformamide and N-(2-hydroxyethyl)ethylenediamine were obtained from Macklin. Dichloromethane (>99%) and methanol (>99%) were available from Tianjin Kemiou Chemical Reagent Co., Ltd. Ethylenediamine was purchased from Xilong Science Co., Ltd. Ethanolamine was purchased from Shanghai Rhawn Chemical Reagent Co., Ltd. Besides, Milli-Q water was used in all the experiments.

Characterization

N_2 adsorption-desorption measurements: N_2 adsorption-desorption was conducted on the Micrometrics ASAP 2460 instrument to determine the Brunauer-Emmett-Teller (BET) specific surface area and porous property of the catalysts. Before the measurement, the sample was firstly degassed at 130 °C under vacuum for 6 h. The pore volume and pore size of the samples were determined by the Barrett-Joyner-Halenda (BJH) desorption method.

X-ray powder diffraction (XRD) analysis: XRD was carried out with a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0.1548 nm), which was operated at 45 kV and 40 mA. And the wide-angle patterns were recorded from 10° to 80° (2θ) at a scan rate of 5° min^{-1}.

Scanning electron microscopy (SEM) characterization: SEM image was performed with a JSM-7500F instrument, and the electron beam acceleration voltage was set at 15 kV.

Transmission electron microscopy (TEM) characterization: TEM image was conducted on a FEI Talos F200 transmission electron microscope instrument, the electron beam acceleration voltage was 200 kV.

Nuclear magnetic resonance (NMR) characterization: NMR spectra of ^{13}C and ^{1}H were performed on a Bruker ADVANCE III 400 MHz spectrometer at 25 °C. The sample was dispersed in [D_6]DMSO (0.5 mL), and the data was treated with MestReNova software.

Solid-state ^{29}Si and ^{27}Al magic-angle spinning (MAS) NMR characterization: ^{29}Si and ^{27}Al MAS NMR experiment were conducted on a Bruker AVANCE NEO 400 spectrometer. ^{29}Si MAS NMR spectra was obtained with the resonance frequency and spinning rate of 79.5 MHz and 6 kHz, respectively. In addition, ^{27}Al MAS NMR spectra was obtained with the resonance frequency and spinning rate of 104.3 MHz and 8 kHz, respectively. MestReNova software was used to simulate all the spectra and fit the peaks.

X-ray photoelectron spectroscopy (XPS) characterization: XPS spectra were obtained from Thermo ESCALAB 250Xi instrument. The catalysts were dried at 80 °C for 12 h. The operation conditions were as follows: Al Kα radiation line as the excitation source was set at 15.0 kV and 150 W. The data was analyzed by Avantage software. The C_{1s} was used as the internal standard at 284.8 eV to calibrate the data.

NH_3 temperature programmed desorption (NH_3-TPD) measurements: NH_3-TPD was measured on Micromeritics AutoChem II 2920. The catalysts were pretreated at 150 °C for 0.5 h in He, which was further cooled to 90 °C. And then the catalyst was saturated in flowing 10% NH_3/He for 0.5 h and followed by flushing in N_2 for 1 h. The NH_3-TPD measurement was then carried out at 100-600 °C with the heating rate of 10 °C/min in the flow of N_2.

Fourier transform infrared spectrometer (FT-IR) characterization: FT-IR analysis was carried out with a Bruker Tenser II spectrometer. The catalysts were firstly mixed with KBr powder, which were pressed into a wafer and placed into an infrared cell. The scan range was collected from 2000 to 400 cm^{-1}. For the FT-IR spectra of hydroxyl region, the catalyst was directly grinded and pressed into a wafer without KBr powder, which was loaded into the infrared cell and activated at 450 °C for 1 h under vacuum. After cooling to 50 °C, the spectrum of dehydrated samples was recorded about the hydroxyl region, which was also the background spectrum for probe adsorption. For pyridine adsorption on catalysts, the catalyst was directly grinded and pressed into a wafer without KBr powder, which was suffered from the pyridine vapor for 15 min and then evacuated under vacuum at 150 °C for 0.5 h. The spectra were collected when the sample was cooled down to 50 °C again. When $CHCl_3$ was used as the probe molecule, the vapor was introduced into the cell and kept for 0.5 h, and then the spectra were collected after evacuation at room temperature. And the acid site amounts of M-ZSM-5-70 catalysts from Py-FTIR analysis was estimated with integrated IR peak areas and values using the following equation:

$$\text{Acid site density } (\mu\text{mol} \cdot \text{g - 1}) = \frac{\text{integrated peak area}}{\text{E}} \times \frac{a_{CS}}{\text{m}} \qquad (1)$$

where E, a_{CS} and m were the molar extinction coefficients, cross-sectional area and mass of the wafer, respectively.

Supplementary Figures

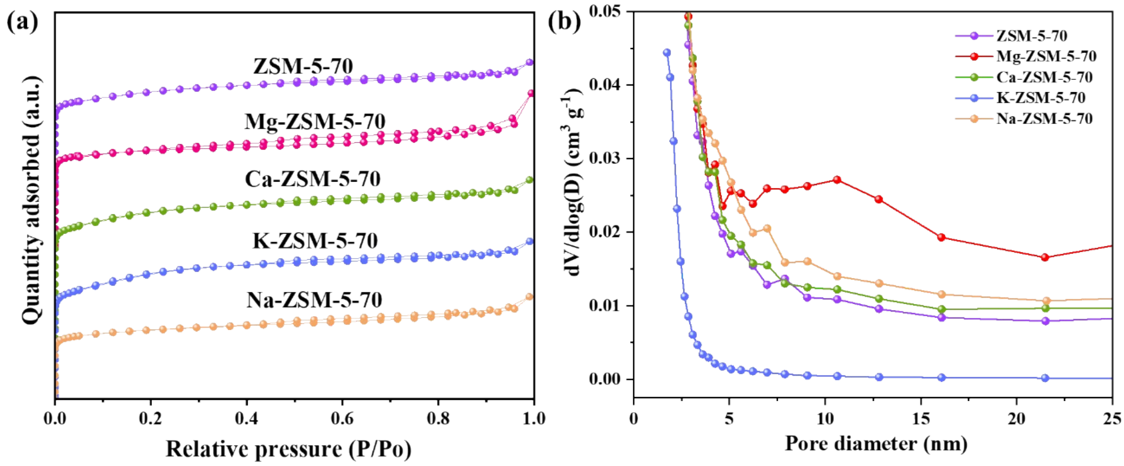

Fig. S1 BET profiles of M-ZSM-5-70 catalysts.

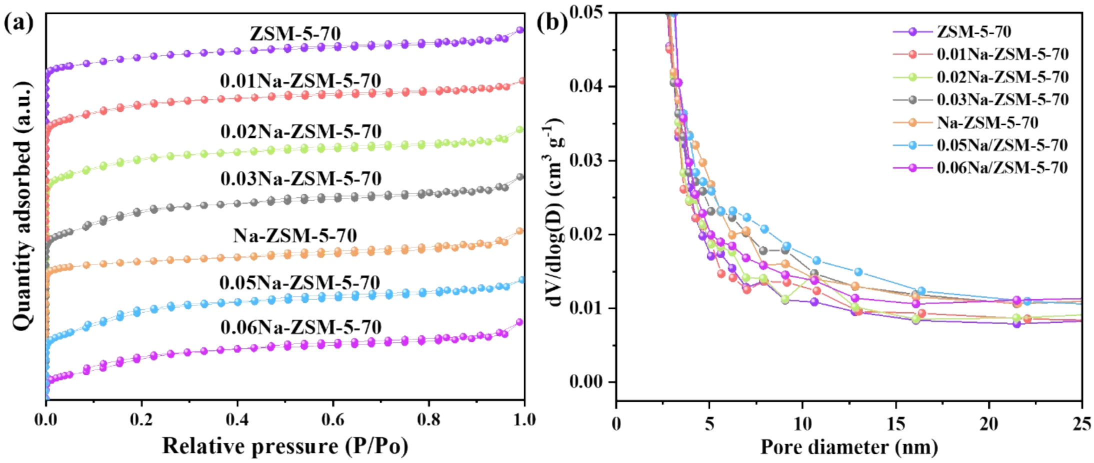

Fig. S2 BET profiles of Na-ZSM-5-70 catalysts with the different Na content.

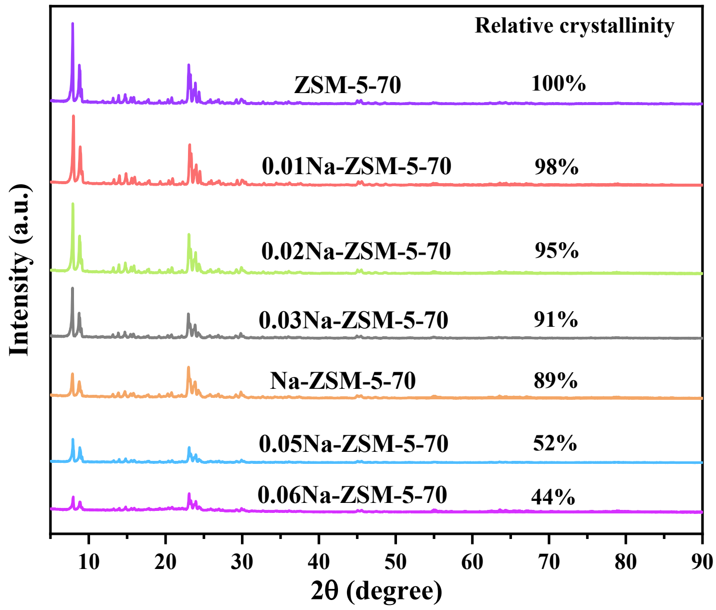

Fig. S3 XRD patterns of Na-ZSM-5-70 catalysts.

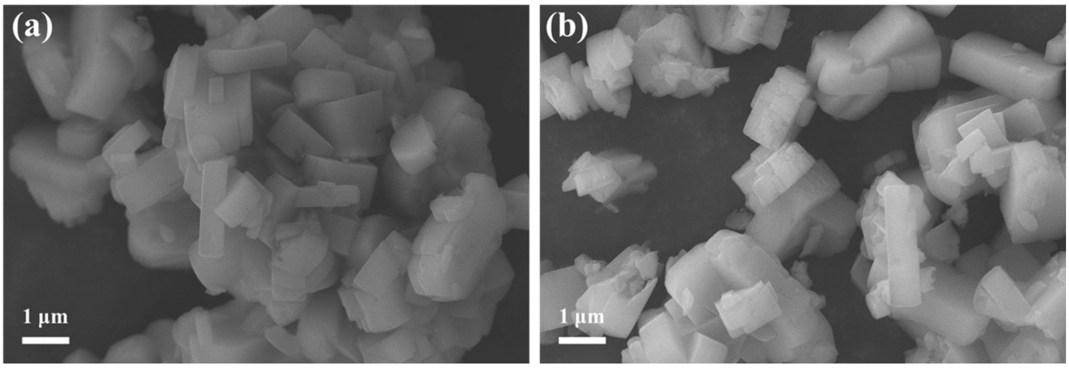

Fig. S4 SEM images of (a) ZSM-5-70 and (b) Na-ZSM-5-70 catalysts.

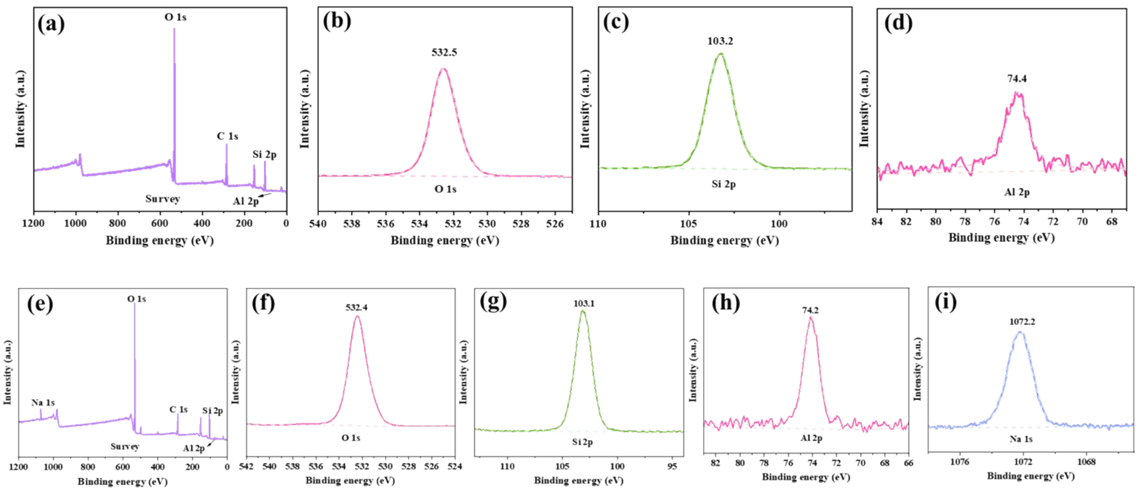

Fig. S5 XPS spectrum of (a-d) ZSM-5-70. (e-i) Na-ZSM-5-70.

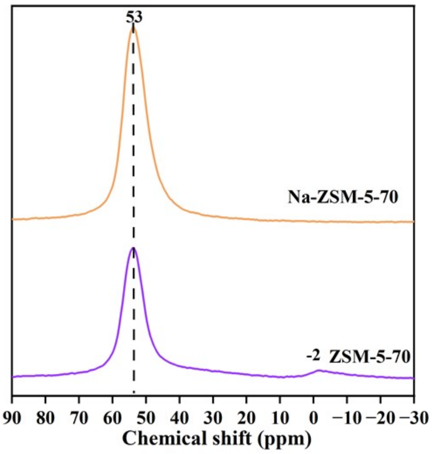

Fig. S6 Solid-state ^{27}Al MAS NMR spectra of ZSM-5-70 and Na-ZSM-5-70.

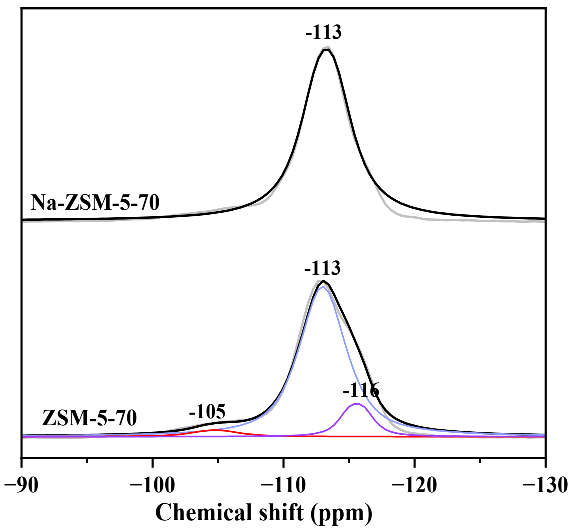

Fig. S7 Solid-state ^{29}Si MAS NMR spectra of ZSM-5-70 and Na-ZSM-5-70.

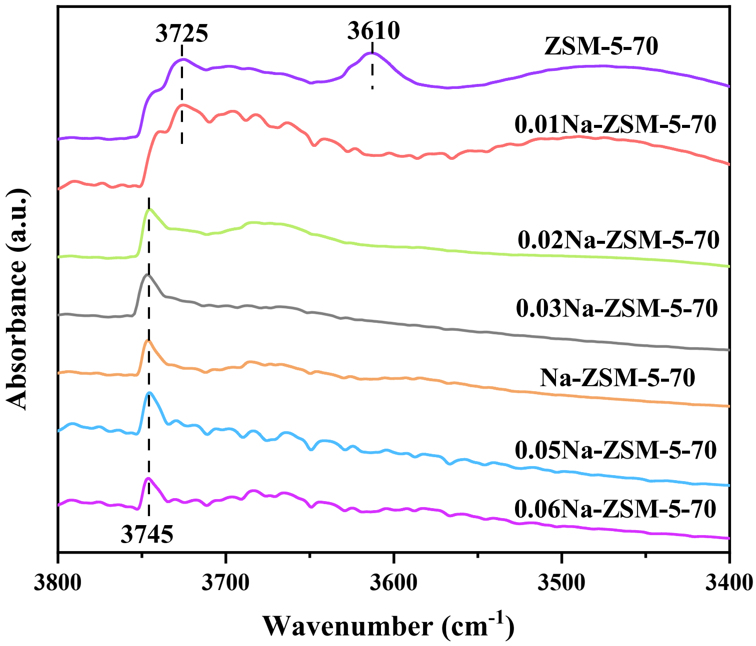

Fig. S8 FT-IR spectra of Na-ZSM-5-70 catalysts in the hydroxyl stretching region.

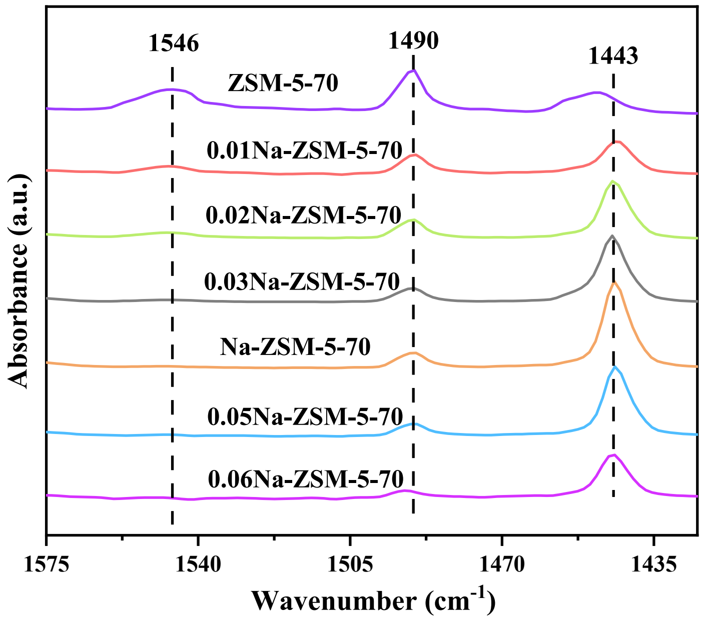

Fig. S9 FT-IR spectra of pyridine adsorption over Na-ZSM-5-70 catalysts.

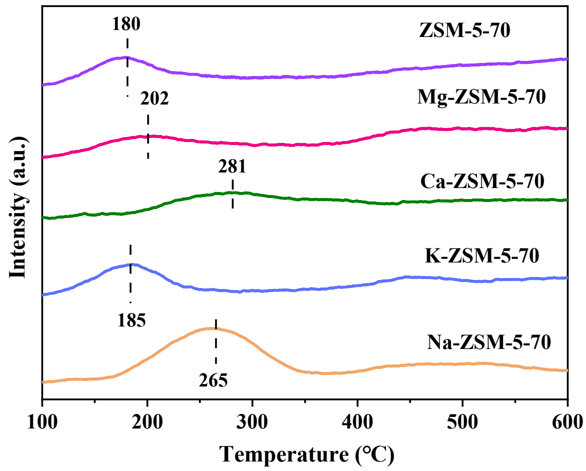

Fig. S10 CO_2-TPD profiles of M-ZSM-5-70 catalysts.

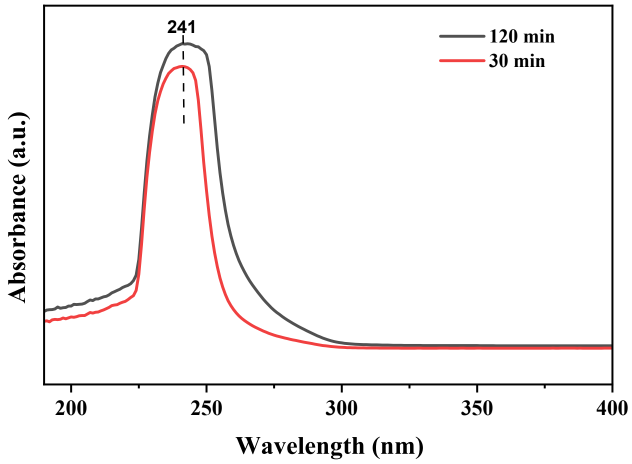

Fig. S11 UV-vis spectrum of reaction liquid after the separation of BHETA product with different reaction time. Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 130 °C.

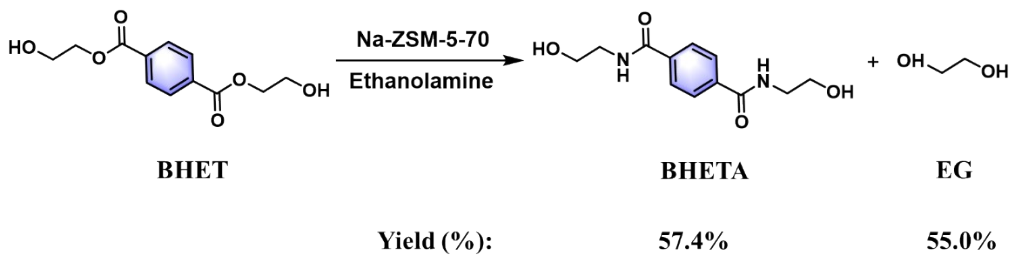

Fig. S12 Catalytic aminolysis of BHET to BHETA and EG. Reaction condition: 0.50 g BHET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 60 ℃, 30 min.

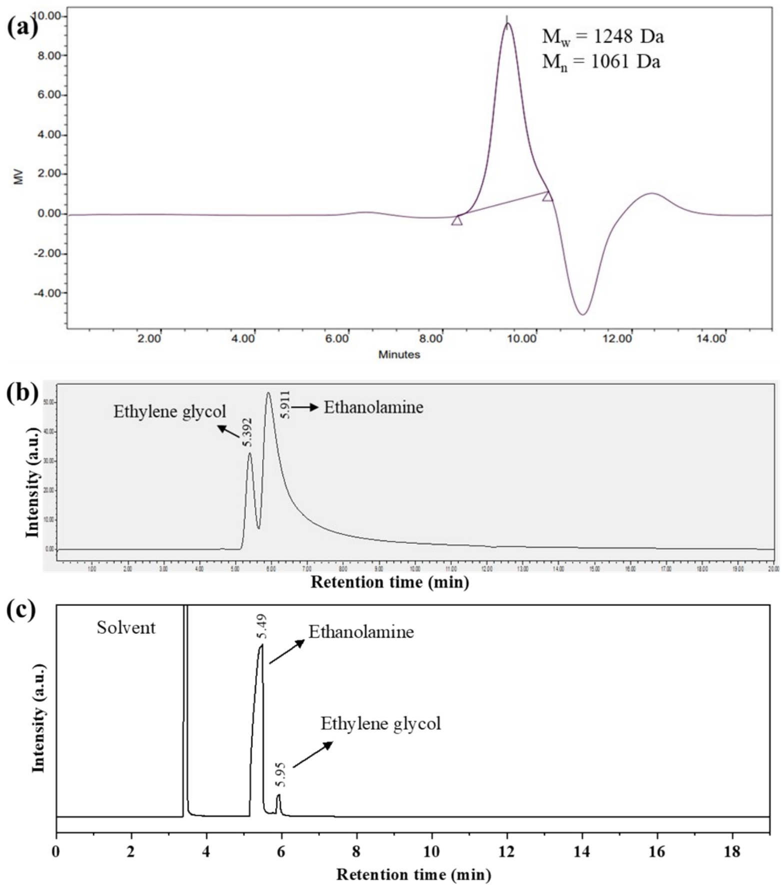

Fig. S13 Reaction liquid after the separation of BHETA was analyzed by (a) GPC. (b) HPLC and (c) GC with the standard samples. Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 100 °C, 30 min.

Supplementary Tables

Table S1 The textural properties of M-ZSM-5-70 catalysts.

Entry	Catalyst	S_{BET} $(m^2 \cdot g^{-1})^a$	S_{micro} $(m^2 \cdot g^{-1})$	S_{ext} $(m^2 \cdot g^{-1})^b$	V_{total} $(cm^3 \cdot g^{-1})^c$	V_{micro} $(cm^3 \cdot g^{-1})$	V_{meso} $(cm^3 \cdot g^{-1})^d$	Pore size (nm)[e]	M content (wt%)[f]
1	ZSM-5-70	209	142	67	0.12	0.07	0.05	2.33	-
2	Mg-ZSM-5-70	226	142	84	0.14	0.07	0.07	2.32	2.44
3	Ca-ZSM-5-70	248	160	88	0.15	0.09	0.06	2.36	3.48
4	K-ZSM-5-70	295	183	112	0.17	0.10	0.07	2.30	1.59
5	Na-ZSM-5-70	311	170	141	0.18	0.09	0.09	2.27	1.03

[a] Calculated by the BET equation.

[b] $S_{ext} = S_{BET} - S_{micro}$.

[c] BJH desorption pore volume.

[d] $V_{meso} = V_{total} - V_{micro}$

[e] BJH desorption average pore diameter.

[f] Measured by ICP-OES.

Table S2 The textural properties of Na-ZSM-5-70 catalysts.

Entry	Catalyst	S_{BET} ($m^2\cdot g^{-1}$)[a]	S_{micro} ($m^2\cdot g^{-1}$)	S_{ext} ($m^2\cdot g^{-1}$)[b]	V_{total} ($cm^3\cdot g^{-1}$)[c]	V_{micro} ($cm^3\cdot g^{-1}$)	V_{meso} ($cm^3\cdot g^{-1}$)[d]	Pore size (nm)[e]	M content (wt%)[f]
1	0.01Na-ZSM-5-70	243	153	90	0.15	0.09	0.06	2.29	0.66
2	0.02Na-ZSM-5-70	270	164	106	0.16	0.09	0.07	2.32	0.90
3	0.03Na-ZSM-5-70	277	167	110	0.16	0.09	0.07	2.38	0.96
4	0.05Na-ZSM-5-70	291	151	139	0.18	0.09	0.09	2.31	1.12
5	0.06Na-ZSM-5-70	243	111	132	0.14	0.06	0.08	2.38	1.23

[a] Calculated by the BET equation.

[b] $S_{ext} = S_{BET} - S_{micro}$.

[c] BJH desorption pore volume.

[d] $V_{meso} = V_{total} - V_{micro}$

[e] BJH desorption average pore diameter.

[f] Measured by ICP-OES.

Table S3 The effect of different catalysts on the conversion of PET to BHETA.

Entry[a]	Catalyst	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	No	36.8	3.7	1.4
2	Hβ-25	24.6	70.4	17.3
3	Hβ-40	32.7	75.1	24.6
4	SPAO-34	41.9	72.3	30.3
5	ZSM-5-70	39.8	84.6	32.7
6	ZSM-5-200	49.9	50.3	25.1
7	ZSM-5-300	20.6	46.5	9.6

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g catalysts, 100 °C, 30 min.

Table S4 The effect of incorporated metal ions on the conversion of PET to BHETA.

Entry[a]	Catalyst	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	ZSM-5-70	$39.8_{\pm 0.9}$	$84.6_{\pm 0.3}$	$32.7_{\pm 0.8}$
2	Mg-ZSM-5-70	$43.4_{\pm 1.4}$	$83.2_{\pm 0.1}$	$36.1_{\pm 1.1}$
3	Ca-ZSM-5-70	$44.6_{\pm 1.2}$	$77.3_{\pm 0.3}$	$34.5_{\pm 1.0}$
4	K-ZSM-5-70	$38.7_{\pm 1.1}$	$76.5_{\pm 0.7}$	$29.6_{\pm 1.0}$
5	Na-ZSM-5-70	$50.3_{\pm 0.9}$	$81.0_{\pm 0.1}$	$40.8_{\pm 0.7}$

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g catalysts, 100 °C, 30 min.

Table S5 The acid site amounts of M-ZSM-5-70 catalysts from NH_3-TPD measurement.

Entry	Catalyst	Acid sites (μmol·g^{-1})		
		Weak acid	Strong acid	Total
1	ZSM-5-70	112.6	101.8	214.4
2	Mg-ZSM-5-70	121.8	83.5	205.3
3	Ca-ZSM-5-70	161.0	55.7	216.7
4	K-ZSM-5-70	47.6	-	47.6
5	Na-ZSM-5-70	287.0	-	287.0

Table S6 The acid site amounts of M-ZSM-5-70 catalysts from pyridine adsorbed FT-IR spectra.

Entry	Catalyst	Brønsted acid sites ($\mu mol \cdot g^{-1}$)	Lewis acid sites ($\mu mol \cdot g^{-1}$)
1	ZSM-5-70	107.5	104.7
2	Mg-ZSM-5-70	105.6	97.4
3	Ca-ZSM-5-70	96.0	127.4
4	K-ZSM-5-70	-	76.9
5	Na-ZSM-5-70	-	256.1
6	0.01Na-ZSM-5-70	17.6	146.9
7	0.02Na-ZSM-5-70	10.3	207.4
8	0.03Na-ZSM-5-70	-	247.3
9	0.05Na-ZSM-5-70	-	200.3
10	0.06Na-ZSM-5-70	-	122.6

Table S7 The basic site amounts of M-ZSM-5-70 catalysts from CO_2-TPD measurement.

Entry	Catalyst	Basic sites (μmol·g^{-1})		
		Weak base	Medium base	Total
1	ZSM-5-70	69.6	-	69.6
2	Mg-ZSM-5-70	73.8	-	73.8
3	Ca-ZSM-5-70	-	69.2	69.2
4	K-ZSM-5-70	68.3	-	68.3
5	Na-ZSM-5-70	-	136.6	136.6

Table S8 The effect of Na content on the conversion of PET to BHETA.

Entry[a]	Catalyst	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	0.01Na-ZSM-5-70	40.9	76.7	31.4
2	0.02Na-ZSM-5-70	39.9	82.7	33.0
3	0.03Na-ZSM-5-70	44.0	79.5	35.0
4	Na-ZSM-5-70	50.3	81.0	40.8
5	0.05Na-ZSM-5-70	41.4	82.9	34.3
6	0.06Na-ZSM-5-70	31.2	50.2	15.6

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g catalysts, 100 °C, 30 min.

Table S9 The effect of reaction temperature on the conversion of PET to BHETA.

Entry[a]	Reaction temperature (℃)	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	90	30.9	78.6	24.3
2	100	50.3	81.0	40.8
3	110	61.0	96.5	58.8
4	120	77.2	96.8	74.7
5	130	100.0	98.1	98.1

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 30 min.

Table S10 The effect of reaction time on the conversion of PET to BHETA.

Entry[a]	Reaction time (min)	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	5	24.4	47.1	11.5
2	10	52.4	86.1	45.1
3	20	84.5	86.7	73.3
4	30	100.0	98.1	98.1
5	40	98.4	93.9	92.5
6	60	97.2	87.2	84.8
7	120	97.2	84.1	81.7

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 130 °C.

Table S11 The effect of PET unit and ethanolamine mole ratio on the conversion of PET to BHETA.

Entry[a]	PET unit/ethanolamine mole ratio	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	1/10	100.0	98.1	98.1
2	1/8	99.3	96.1	95.5
3	1/6	94.4	91.3	86.2
4	1/5	91.2	94.0	85.7

[a] Reaction condition: 0.50 g PET, ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 130 °C, 30 min.

Table S12 The reusability of Na-ZSM-5-70 catalyst for the conversion of PET to BHETA.

Entry[a]	Cycle	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	1	100.0	98.1	98.1
2	2	97.0	96.0	93.1
3	3	96.9	93.0	90.2
4	4	93.0	95.9	89.2
5	5	92.8	95.9	89.0

[a] Reaction condition: 0.50 g PET, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 130 ℃, 30 min.

Table S13 The effect of different purity PET plastic wastes for the production of BHETA.

Entry[a]	Substrate	Purity (%)	PET conversion (%)	BHETA selectivity (%)	BHETA yield (%)
1	Packing tape	79.4	98.2	91.8	90.1
2	Bottles	97.1	99.2	90.5	89.8
3	Granules	99.3	99.0	92.3	91.4
4	Boxes	98.8	99.4	92.7	92.1

[a] Reaction condition: 0.50 g substrate, 3.18 g ethanolamine, 0.10 g Na-ZSM-5-70 catalyst, 130 °C, 30 min.