Supporting Information

Enhanced cleavage of C-C bonds in polycarbonate plastic wastes to valuable phenolics over potassium modified triazine-based strong base catalyst

This file includes:

Supplementary Methods

Supplementary Fig. S1 to S10

Supplementary Table S1 to S13

Supplementary Methods

Chemicals and materials

Potassium nitrate (98%) was obtained from Xilong Scientific Co., Ltd. Polycarbonate plastic (99.9%) was purchased from Guangzhou Huayu Trading Co., Ltd. Methanol was obtained from Tianjin Yongda Chemical Reagent Co., Ltd. γ-aluminium oxide (99%), phenol (99%), isopropenyl phenol (97%), isopropylphenol (98%) and n-dodecane (99%) were purchased from Aladdin Biochemical Technology Co., Ltd. Terephthalonitrile (98%) and anhydrous zinc chloride (98%) were purchased from Macklin Biochemical Technology Co., Ltd. All commercial reagents, unless otherwise noted, were used without further treatment.

Catalyst characterization

X-ray powder diffraction (XRD) was tested by the Bruker D8 Advance (Bruker, Germany). The scanning speed was 10° min^{-1}, and the scanning range was 5-90°. The N_2 adsorption-desorption isotherm was determined using the Micrometrics ASAP 2460 physical adsorption instrument. The test was conducted in liquid nitrogen (77 K) after vacuum degassing at 200 ℃ for 6 h. The specific surface area and pore size of the sample were calculated using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively. Fourier transform infrared (FT-IR) spectrum was collected by Bruker Tensor II Fourier transform infrared spectrometer. Temperature programmed desorption of CO_2 (CO_2-TPD) was tested on a Micromeritics AutoChem II 2920 chemical adsorption instrument. The sample then

underwent degassing at 200 ℃ for 1 h. CO_2 was introduced and adsorbed for 0.5 h until saturation. The atmosphere was then switched to helium. The temperature increased from 50 to 800 ℃ at a rate of 10 ℃ min^{-1}. During this process, the thermal conductivity detector (TCD) combined with mass spectrometry (MS) was used. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were taken by the Zeiss Sigma 300 scanning electron microscope and FEI Tecnai G2 F20 type transmission electron microscope, respectively. The potassium content was detected using the Agilent 5110 type inductively coupled plasma optical emission spectrometer (ICP-OES).

Supplementary Figure

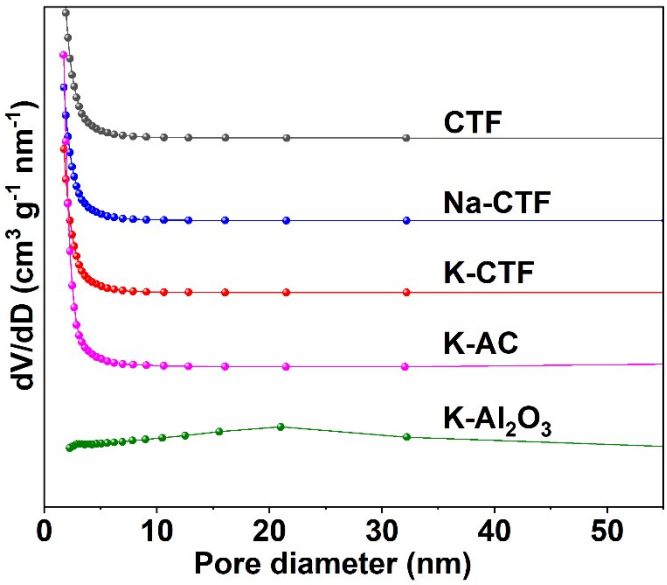

Fig. S1 Pore size distributions of different samples.

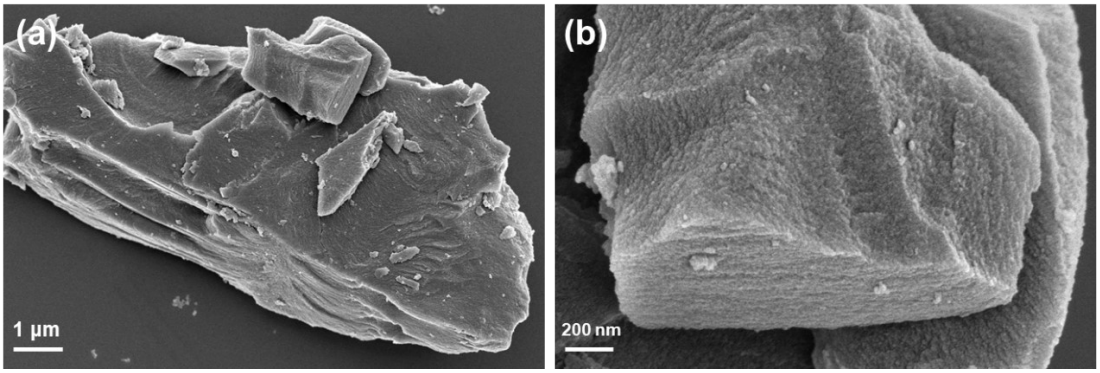

Fig. S2 SEM images of CTF.

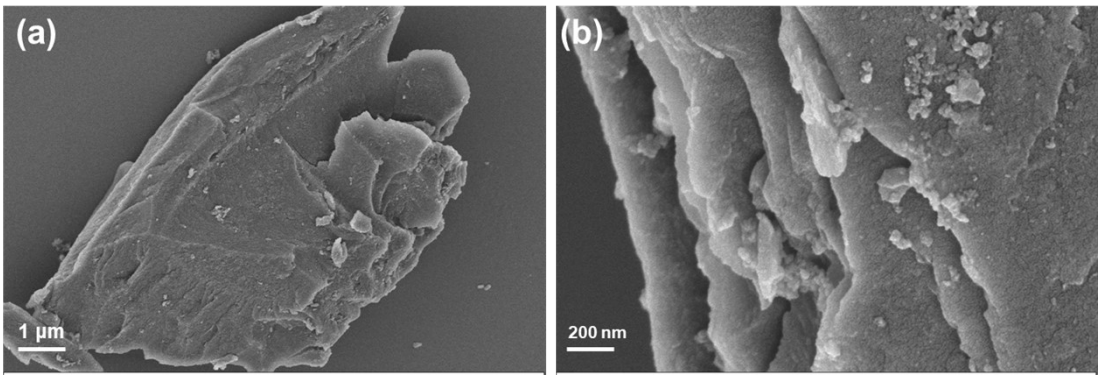

Fig. S3 SEM images of 15K-CTF.

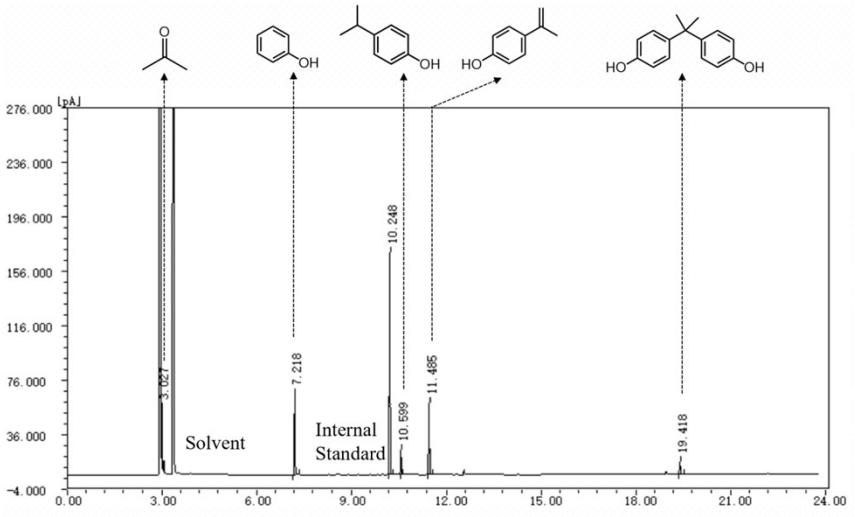

Fig. S4 GC analysis for the catalytic conversion of PC plastic. Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (7:3), 250 ℃, 3 h.

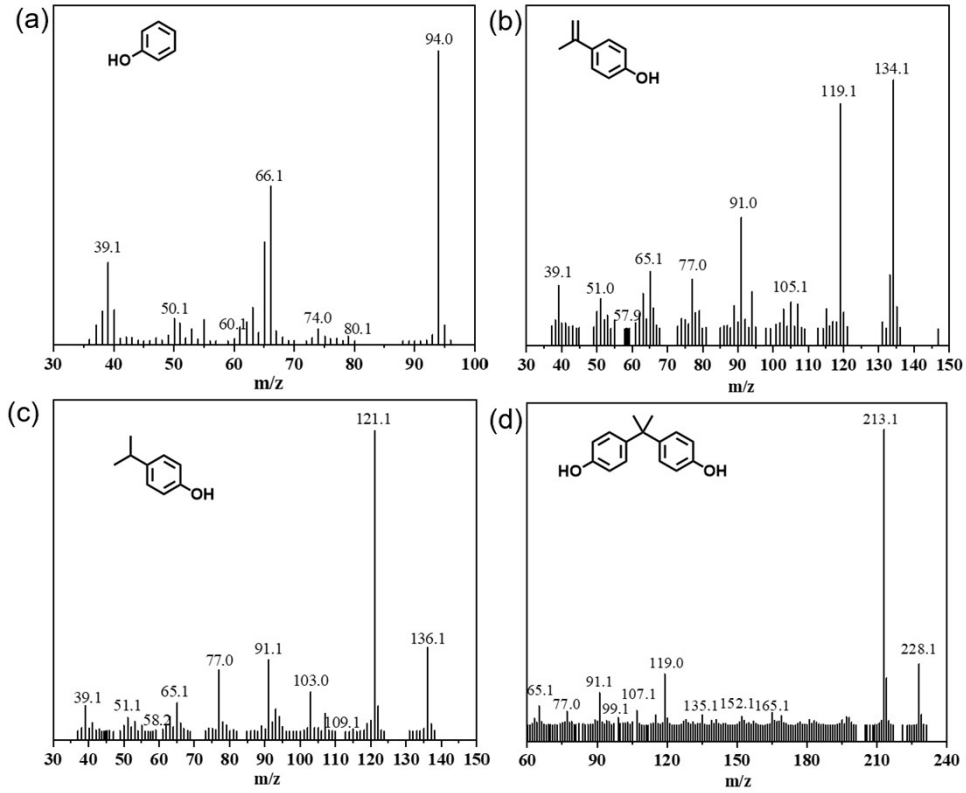

Fig. S5 Mass spectrometry of phenol, IPP, iPrP and BPA for the catalytic conversion of PC plastic. Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (7:3), 250 ℃, 3 h.

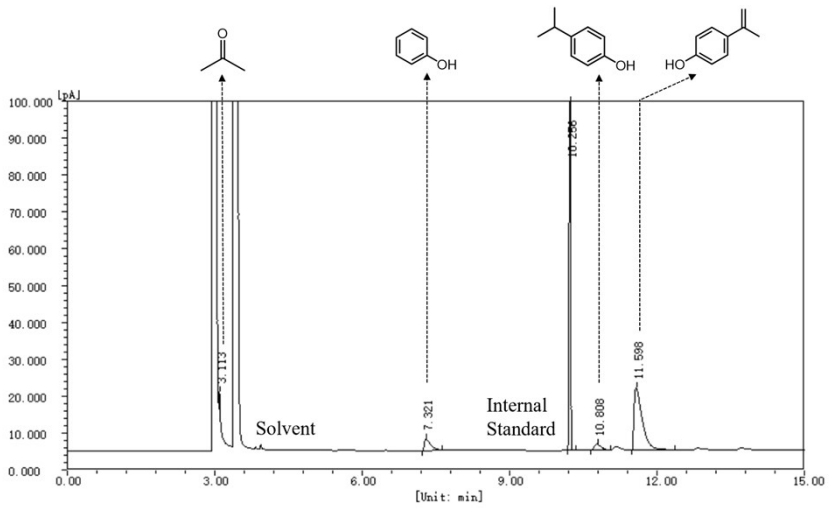

Fig. S6 GC analysis for the catalytic conversion of IPP. Reaction condition: 0.20 g IPP, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 ℃, 3 h.

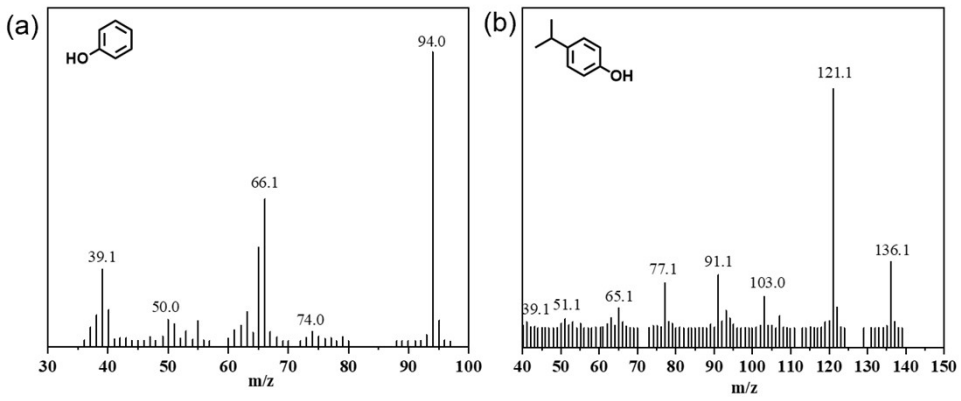

Fig. S7 Mass spectrometry of phenol and iPrP for the catalytic conversion of isopropenyl phenol (IPP). Reaction condition: 0.20 g IPP, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 ℃, 3 h.

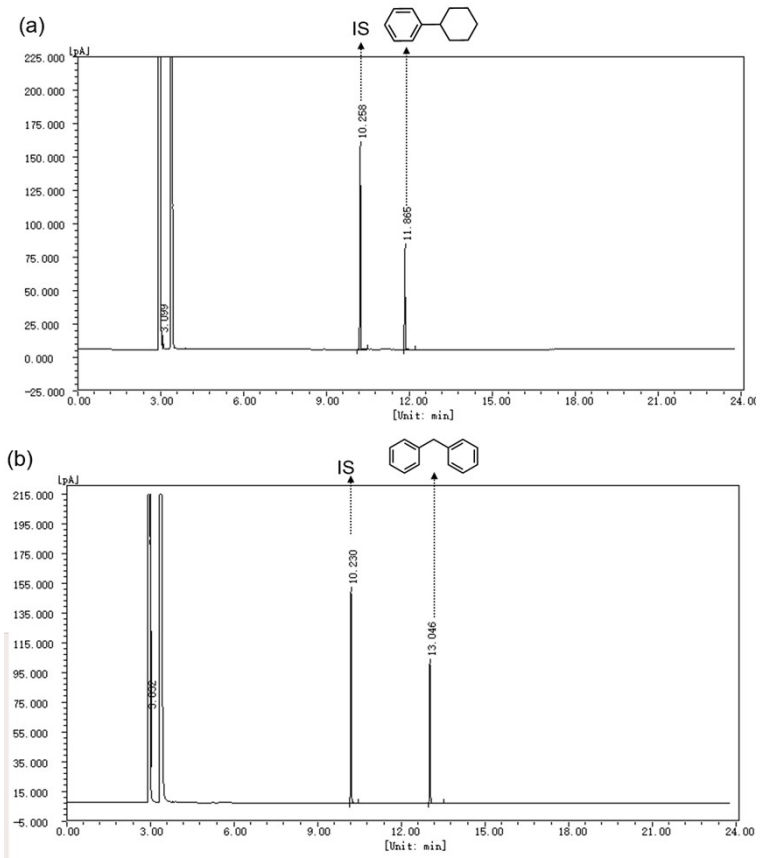

Fig. S8 GC results for the conversion of (a) phenylcyclohexane and (b) diphenylmethane. Reaction condition: 0.20 g substrate, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 °C, 3 h.

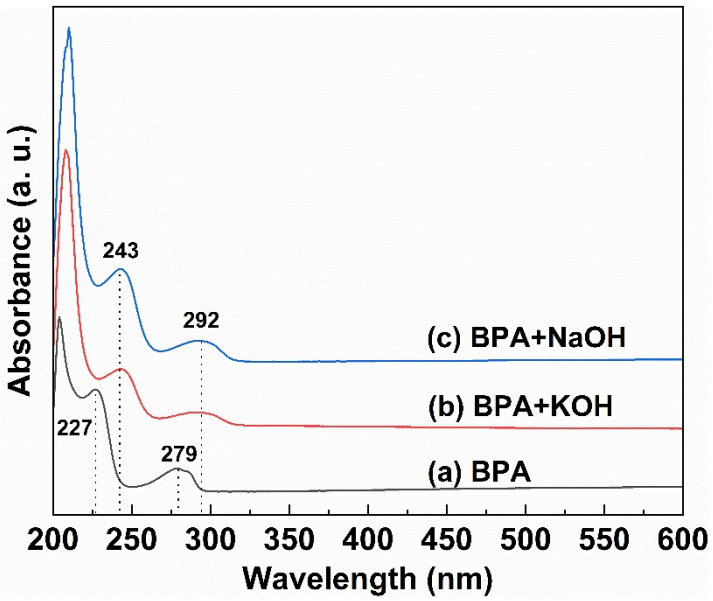

Fig. S9 UV-vis spectra of BPA interacted with the base in methanol solvent as well as BPA.

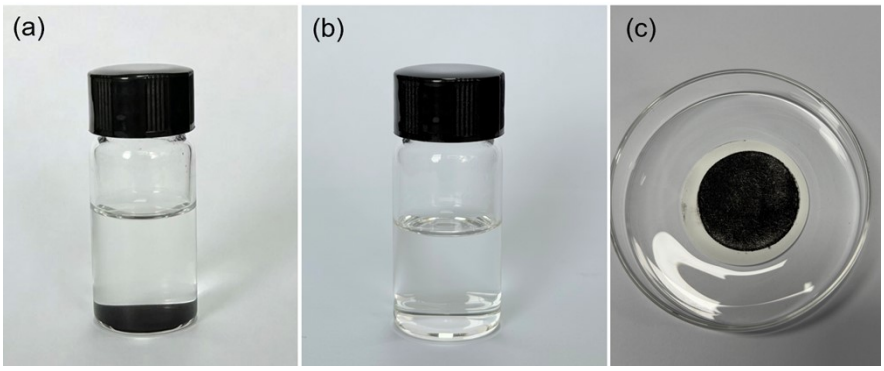

Fig. S10 (a) The reaction mixture. (b) The filtered upper solution and (c) solid precipitate of the filtered catalyst. Reaction conditions: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 °C, 3 h.

For the catalytic conversion of PC plastic over 15K-CTF, the substrate could be completely converted into soluble phenolic products. The reaction mixture clearly exhibited a stratification phenomenon when the mixture cooled down for a period of time (**Fig S10a**). The supernatant was a colorless and transparent solution and small amount of black residue at the bottom was the added catalyst without other insoluble substance (**Fig S10b** and **10c**). The catalyst could be separated from the reaction mixture through a simple filtration process.

Supplementary Table

Table S1. Physical property parameters of different samples.

Entry	Sample	S_{BET} (m^2 g^{-1})[a]	V_t (cm^3 g^{-1})[b]	Pore size (nm)[c]
1	CTF	551	0.32	2.29
2	Na-CTF	540	0.30	2.25
3	K-CTF	537	0.30	2.24
4	K-AC	609	0.16	13.75
5	K-Al_2O_3	111	0.52	18.57

[a] Calculated by the BET equation.

[b] BJH desorption pore volume.

[c] BJH desorption average pore diameter.

Table S2. K content in different samples.

Entry	Sample	Theoretical loading(wt%)	Measured loading (wt%)
1	K-CTF	2.05	1.85
2	15K-CTF	6.83	3.67

Table S3. The amounts of basic sites for potassium modified CTF with different loadings.

Entry	Sample	Amounts of basic sites (mmol g^{-1})
1	CTF	0.50
2	K-CTF	1.15
3	10K-CTF	1.64
4	15K-CTF	2.30
5	20K-CTF	2.85

Table S4. Catalytic activity for PC conversion with potassium modified different catalysts.

Entry[a]	Catalyst	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	K-AC	22.6	41.5	31.0	2.1	74.6
2	K-ZrO_2	14.5	43.8	33.4	0.9	78.1
3	K-ZnO	2.0	45.3	36.1	0.6	82.0
4	K-Al_2O_3	2.1	47.8	35.2	0.7	83.7
5	K-CTF	2.2	52.0	35.5	1.1	88.6

[a] Reaction condition: 0.20 g PC plastic, 0.02 g catalyst, 20 mL methanol/H_2O (1:1), 240 ℃, 3 h.

Table S5. Catalytic activity for PC conversion with different alkali metal modified CTF.

Entry[a]	Catalyst	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	Mg-CTF	22.9	40.6	30.7	1.0	72.3
2	Na-CTF	21.7	40.8	33.8	0.8	75.4
3	Ca-CTF	8.9	45.6	35.0	0.7	81.3
4	K-CTF	2.2	52.0	35.5	1.1	88.6

[a] Reaction condition: 0.20 g PC plastic, 0.02 g catalyst, 20 mL methanol/H_2O (1:1), 240 ℃, 3 h.

Table S6. Catalytic activity for PC conversion over potassium modified CTF with different loadings.

Entry[a]	Catalyst	Yield of dimers product (%)	Yield of monomers product (%)				Mass specific activity (mmol g^{-1} h^{-1})
		BPA	Phenol	IPP	iPrP	Total	
1	CTF	23.6	40.2	29.2	1.1	70.5	18.5
2	K-CTF	2.2	52.0	35.5	1.1	88.6	23.2
3	10K-CTF	1.8	54.0	36.0	1.7	91.7	24.0
4	15K-CTF	0.9	56.9	36.5	2.2	95.6	25.1
5	20K-CTF	1.7	57.9	35.1	3.1	96.1	25.2

[a] Reaction condition: 0.20 g PC plastic, 0.02 g catalyst, 20 mL methanol/H_2O (1:1), 240 ℃, 3 h. Note: Mass-specific activities (mmol g^{-1} h^{-1}) are calculated from the moles of monophenol generated per gram per hour of catalyst.

Table S7. Catalytic activity for PC conversion over homogeneous bases, physical mixture of homogeneous bases with CTF, and 15K-CTF heterogeneous catalyst.

Entry[a]	Catalyst	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1[b]	KOH	9.9	47.0	42.3	0.6	89.9
2[c]	NaOH	4.6	50.9	40.9	0.9	92.7
3[d]	KOH+CTF	13.2	47.5	35.9	2.6	86.0
4[e]	NaOH+CTF	6.0	46.4	39.6	2.1	88.1
5[f]	15K-CTF	0.9	56.9	36.5	2.2	95.6

[a] Reaction conditions: 0.20 g PC plastic, 20 mL methanol/H_2O (1:1), 240 °C, 3 h.

[b] 0.53 mg.

[c] 0.41 mg.

[d] 0.53 mg KOH, 19.47 mg CTF.

[e] 0.41 mg NaOH, 19.59 mg CTF.

[f] 20 mg 15K-CTF. Note: the mole of K was calculated by the actual content of 15K-CTF based on the ICP result.

Table S8. Influence of methanol/H_2O ratio on PC conversion to phenolics.

Entry[a]	Ratio of methanol to H_2O	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	7:3	27.2	37.2	31.0	3.4	71.6
2	6:4	5.3	51.5	37.7	3.6	92.8
3	5:5	1.7	58.4	36.2	3.5	98.1
4	4:6	3.5	53.2	32.1	3.3	88.6
5	3:7	4.8	51.3	19.2	3.6	74.1

[a] Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O, 250 ℃, 3 h.

Table S9. Influence of different organic solvent/H_2O on PC conversion to phenolics.

Entry[a]	Solvent	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	1,2-propylene glycol/H_2O	56.1	19.8	8.9	13.3	42.0
2	ethylene glycol/H_2O	29.6	33.8	15.6	14.3	63.7
3	isopropanol/H_2O	1.5	52.0	34.0	8.1	94.1
4	propanol/H_2O	1.8	53.0	34.1	6.6	93.7
5	ethanol/H_2O	2.2	52.4	33.7	10.6	96.7
6	methanol/H_2O	1.7	58.4	36.2	3.5	98.1

[a] Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL alcohol/H_2O (1:1), 250 ℃, 3 h.

Table S10. Influence of reaction temperatures on PC conversion.

Entry[a]	Temperature (°C)	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	220	48.2	27.5	21.4	1.0	49.9
2	230	33.0	37.1	26.0	1.4	64.5
3	240	0.9	56.9	36.5	2.2	95.6
4	250	1.3	54.1	38.6	3.6	96.3
5	260	1.8	58.1	36.3	3.7	98.1

[a] Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 3 h.

Table S11. Influence of reaction times on PC conversion to phenolics.

Entry[a]	Time (h)	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	1	20.4	32.8	28.5	1.4	62.7
2	2	1.3	46.5	34.9	1.3	82.7
3	3	0.9	56.9	36.5	2.2	95.6
4	4	1.6	58.5	34.8	4.1	97.4

[a] Reaction condition: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 240 ℃.

Table S12. Catalytic conversion of polycarbonate plastic wastes over 15K-CTF catalyst.

Entry[a]	Substrate	Yield of dimers product (%)	Yield of monomers product (%)			
		BPA	Phenol	IPP	iPrP	Total
1	Powders	2.0	55.5	37.8	3.6	96.9
2	Optical disks	1.8	54.3	35.8	3.5	93.6
3	Tubes	1.8	55.3	36.8	3.5	95.6
4	Boards	2.1	55.7	38.7	3.4	97.8

[a] Reaction condition: 0.20 g substrate, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 ℃, 3 h.

Table S13. Reusability of 15K-CTF catalyst.

Run[a]	Yield of dimers product (%)	Yield of monomers product (%)			
	BPA	Phenol	IPP	iPrP	Total
1	1.3	54.1	38.6	3.6	96.3
2	1.4	53.0	39.8	3.1	95.9
3	1.4	53.8	39.1	2.6	95.5
4	1.4	53.7	39.2	2.4	95.3
5	1.4	53.5	39.5	2.2	95.2

[a] Reaction conditions: 0.20 g PC plastic, 0.02 g 15K-CTF, 20 mL methanol/H_2O (1:1), 250 °C, 3 h.