

# Transforming PVC plastic wastes to benzene via hydrothermal treatment in a multi-phase system

Bo Feng, Yong Guo, Xiaohui Liu, Yanqin Wang\*

State key laboratory of green chemical engineering and industrial catalysis, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, P. R. China.

E-mail: wangyanqin@ecust.edu.cn

## Experimental procedures

### Catalyst preparation

ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 56$ ) was purchased from Nankai University Catalyst Co.Ltd. Montmorillonite K-10 was purchased from Boer Chemistry Reagent Co., Ltd (the surface area was  $240 \text{ m}^2/\text{g}$ ). PVC was purchased from Macklin Reagent ( $M_w=114465$ , measured by GPC). THF was purchased from Macklin Reagent Co., Ltd (Shanghai, China). Decane was purchased from Maryer Reagent Co., Ltd (Shanghai, China). Pentadecane was purchased from Macklin Reagent Co., Ltd (Shanghai, China).  $\text{La}(\text{oTf})_3$  was purchased from JiuDing Chemistry Reagent Co., Ltd (Shanghai, China).  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , NaOH and  $\text{Na}_2\text{CO}_3$  was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). All purchased chemicals were analytical grade and used without further purification.

$\text{Nb}_2\text{O}_5$  was synthesized according to our previous reported procedures<sup>1</sup>. Typically, 19.2 g of prepared niobium oxalate and 0.711 g of ammonium oxalate were dissolved in 50 mL deionized water, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at  $180^\circ\text{C}$ . After cooling down, the solid was filtered, washed with distilled water and then dried at  $50^\circ\text{C}$  overnight. Finally, the  $\text{Nb}_2\text{O}_5$  sample was obtained by calcination at  $400^\circ\text{C}$  for 4 h in air with a linear heating ramp of  $10^\circ\text{C min}^{-1}$ .

$\text{NbPO}_5$  was synthesized also according to our previous reported procedures<sup>2</sup>. Typically, 1.32

g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 ml water and then the pH was adjusted to 2 using phosphoric acid. With vigorous stirring, 20 ml of 0.5M niobium tartrate (pH = 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of cetyltrimethyl ammonium bromide (CTAB) which was previously prepared by dissolving 1.0 g of CTAB in 13 ml of distilled water. The pH value of the final solution was about 2. Afterwards, this mixture was stirred for additional 60 min at 35 °C, and then the transparent solution was aged in a Teflonlined autoclave for 24 h at 160 °C. After cooling down, the solid was filtered, washed with distilled water and then dried at 60 °C. Finally, the NbPO<sub>5</sub> sample was obtained by calcination at 500 °C for 5 h in air to remove organic species.

MgAl-LDH was prepared by precipitation method. Typically, 23.08 g Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.09 mol) and 11.25 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.03 mol) was added to a beaker containing 100ml of deionized water. The precipitant was obtained by dissolving 9.6 g NaOH (0.24 mol) and 3.18 g Na<sub>2</sub>CO<sub>3</sub> (0.03mol) into 100ml deionized water. With vigorous stirring, the precipitant was added to the above solution at 70 °C, and the solution was left for overnight aging. After that, the solid was obtained by filtration, and the MgAl-LDH sample was obtained after overnight drying in an oven at 60 °C.

## Characterization

X-ray powder diffraction (XRD) patterns were recorded in the  $\theta$ -2 $\theta$  mode on a D8 Advance Focus diffractometer (*CuK $\alpha$ 1* radiation,  $k = 1.5406 \text{ \AA}$ ), operated at 40 kV and 40 mA, respectively, within scattering angles of 10–90°. Transmission electron microscopy (TEM) images and EDS scanning of samples were obtained on a Talos F200X TEM at 200 kV.

Scanning electronic microscopy (SEM) images were obtained from JEOL JSM-63602 V and Hitachi S-3400N microscopes operated at 5 kV or 15 kV, respectively.

Raman spectra were recorded on a Renishaw Raman spectrometer under ambient conditions, and the 325 nm line of the Spectra Physics Ar<sup>+</sup> laser was used as the excitation wavelength. The laser beam intensity and spectrum slit width was 2mW and 3.5 cm<sup>-1</sup>, respectively.

Infrared spectra of pyridine adsorption (Py-IR) were recorded on Nicolet NEXUS 670 FT-IR spectrometer. The samples were pressed into self-supporting disks and placed in an IR cell attached to a closed glass-circulation system. The disk was dehydrated by heating at 400 °C, for 1 h under vacuum in order to remove the physically adsorbed water. After the cell was cooled to room temperature, the IR spectrum was recorded as background. Pyridine vapor was then introduced into the cell at room-temperature until equilibrium was reached, and then a second spectrum was recorded. Subsequent evacuation was performed at 100 °C, for 10 min followed by spectral acquisitions. The spectra presented were obtained by subtracting the spectra recorded before and after pyridine adsorption.

### **Catalytic test and product analysis.**

The detailed reaction conditions are described in the figure captions and table footnotes. In a typical reaction with PVC conversion as example, solid additive 50mg, PVC (50 mg), decane (3g) and 10% THF aqueous solution (2g) were loaded into a stainless-steel autoclave reactor. After the reactor was purged with N<sub>2</sub> three times and charged to the target N<sub>2</sub> pressure (2 MPa), the reaction was conducted at target temperature (280 °C) with a magnetic stirring speed of 600 r.p.m. After the reaction, the reactor was quenched to ambient temperature in an ice-water bath, and after cooling. Then the organic products were analyzed by gas chromatography (GC) and GC-MS on an Agilent 7890B gas chromatograph with flame ionization detector and an Agilent 7890A GC-MS instrument, both equipped with HP-5 capillary columns (30m\*250mm). The liquid solution was separated from the solid catalyst by centrifugation and was directly analyzed. Pentadecane was used as an internal standard for the quantification of liquid products.

The product yield was calculated by using the equation:

$$\text{Yield}(\text{benzene}) = (\text{mole of C in benzene}) / (\text{mole of C in PVC feedstock}) \times 100\%.$$

Each experiment was repeated at least three times to take the average and calculate the error.

After absorbing part of the organic phase of the system after the reaction, the remaining liquid was slowly poured into the funnel for filtration to collect the carbon material floating

between the water phase and the organic phase after the reaction. The carbon materials collected by filtration were washed three times with 5ml ethanol and water, respectively, and dried overnight in a 60 °C oven. The dried carbon material was collected for use.

The carbonization process of the carbon material after the reaction was referred to the article of He et al<sup>3</sup>. Specifically, 0.5g of the carbon material after the reaction was taken, heated to 800 degrees Celsius at a rate of 5 °C/min in N<sub>2</sub> atmosphere, carbonized for two hours, and naturally cooled to room temperature to obtain the carbonized material.

The carbon material yield was calculated by using the equation:

$$\text{Yield (carbon material)} = \frac{(\text{mass of carbon material}) \times (\text{Carbon mass fraction of carbon material})}{(\text{mass of C in PVC feedstock})} \times 100\%.$$

The carbon mass fraction of carbon material was measured by elemental analysis.

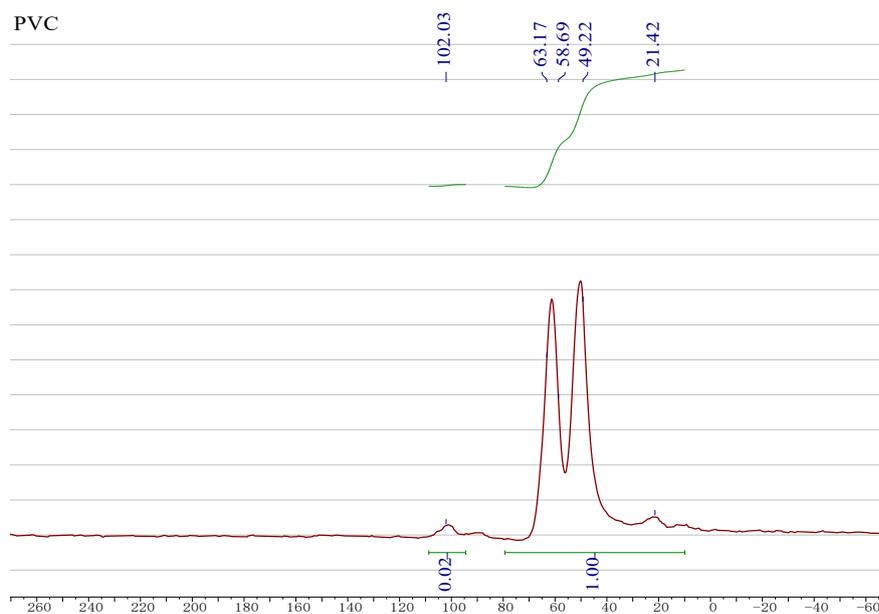


Figure S1. The <sup>13</sup>C NMR spectrum of raw PVC.

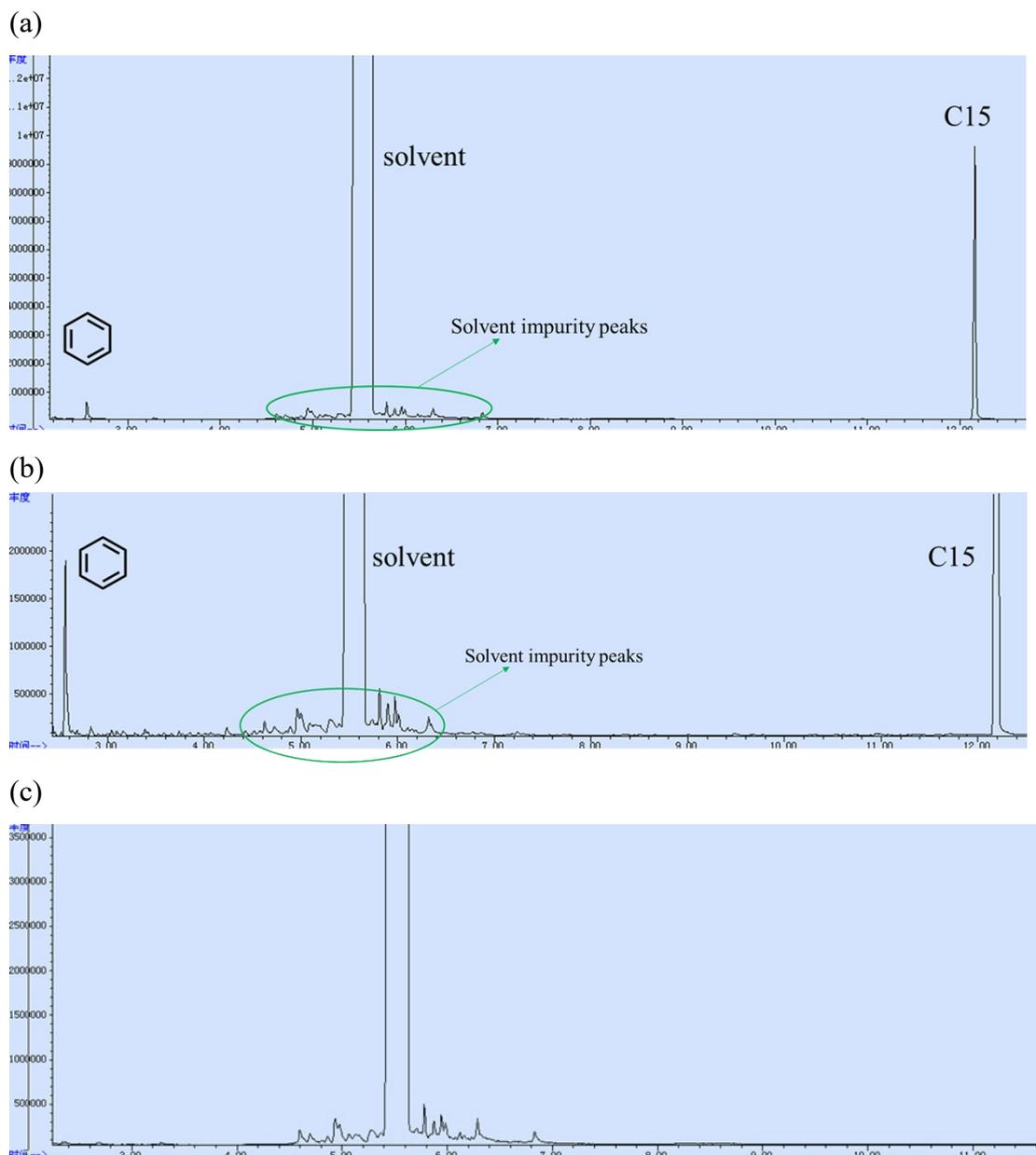


Fig. S2. The GC-MS spectra of the organic phase over ZSM-5(a),  $\text{Nb}_2\text{O}_5$ (b) and pure solvent (c). Conditions: a, b) Catalyst 50mg, PVC 50mg,  $\text{H}_2\text{O}$  3.0g, Decane 3.0g, 2Mpa  $\text{N}_2$ , 280 °C, 1h; c) ZSM-5 50mg,  $\text{H}_2\text{O}$  3.0g, Decane 3.0g, 2Mpa  $\text{N}_2$ , 280 °C, 1h.

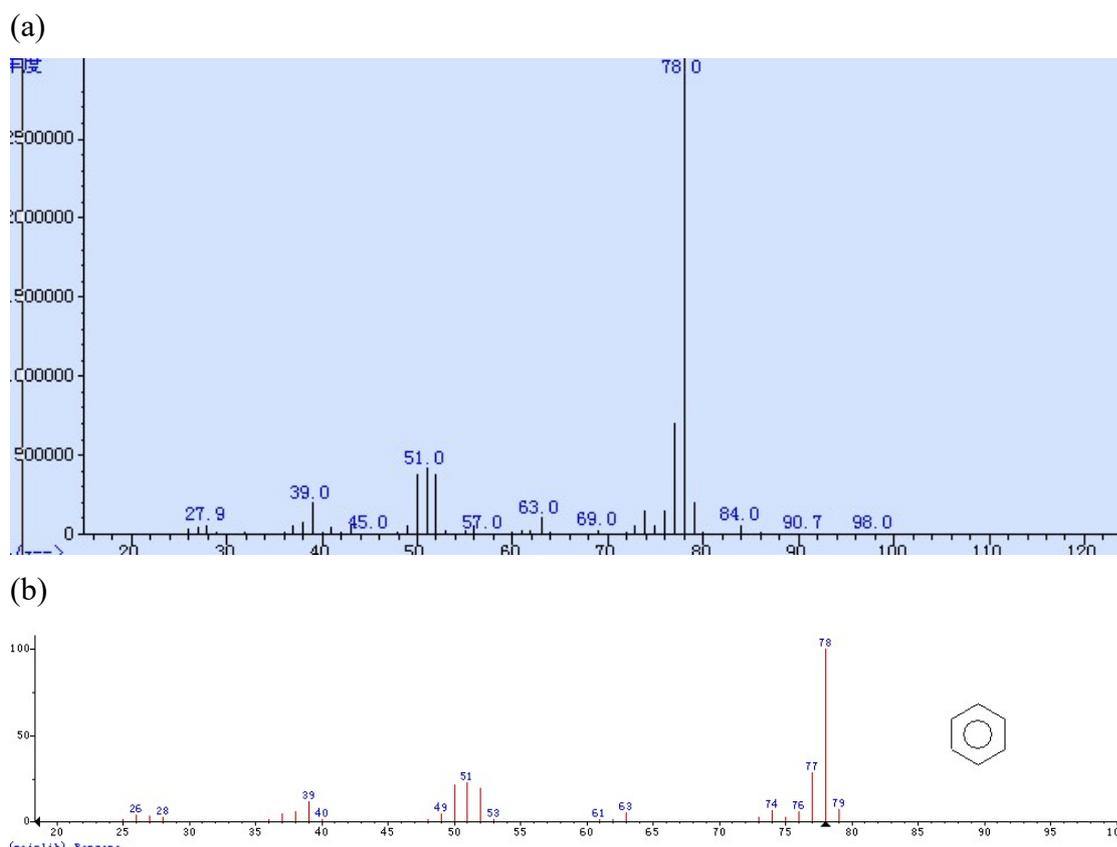


Fig. S3. The MS spectra of the product in organic phase.(a) Ion fragmentation peaks of reaction product; (b) Standard ion fragmentation peaks for the product benzene in the spectral library.

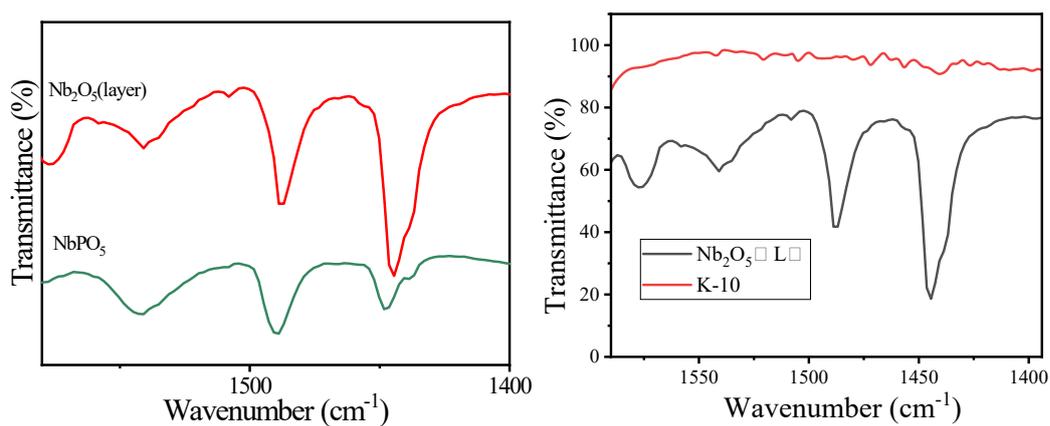


Fig. S4. Py-IR results of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbOPO}_4$  and K-10.

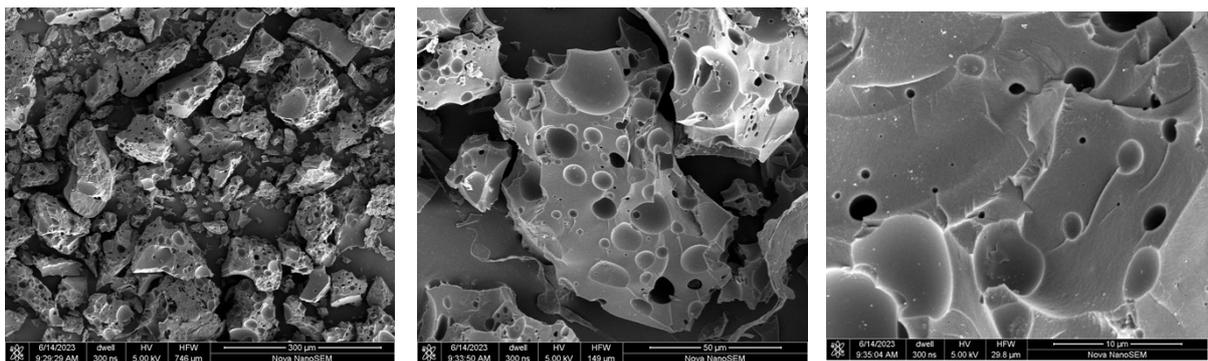


Fig. S5. The SEM image of carbon material after hydrothermal treatment.

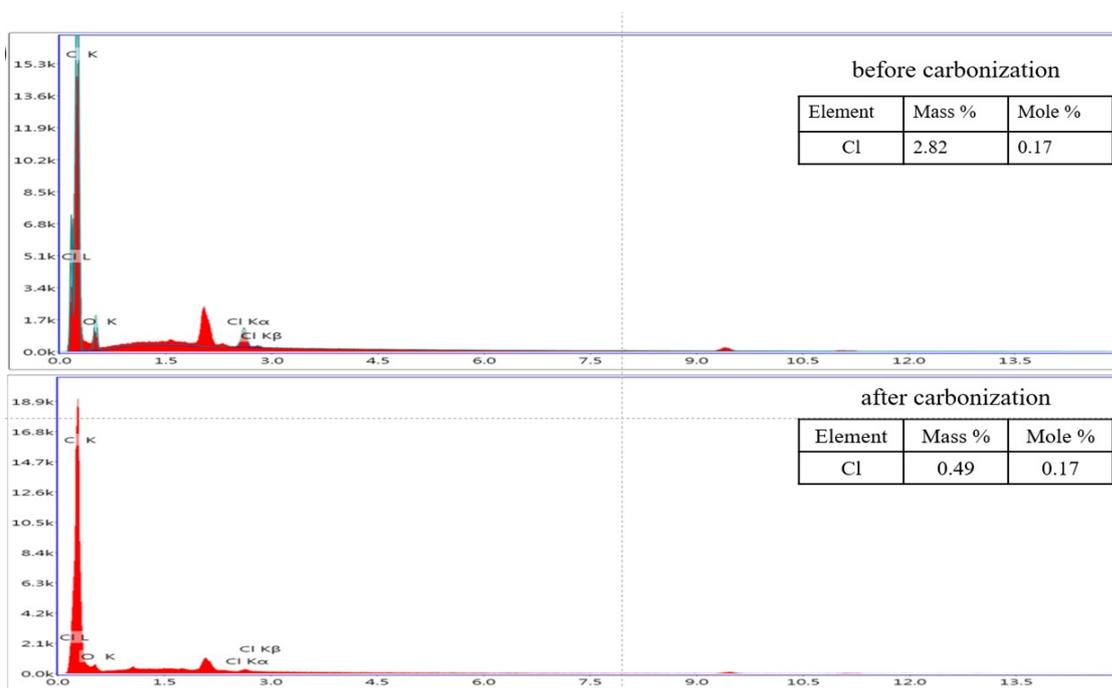


Fig. S6. SEM-EDX elemental point-scanning mode spectrum.



Fig. S7. Photographs of carbon materials after reaction over  $\text{Nb}_2\text{O}_5$  (left) and  $\text{La}(\text{OTf})_3$  (right).

Table S1. Detailed data of Fig. 1.

| Entry  | Benzene yield<br>(mol%) | Absolute error range |
|--|-------------------------|----------------------|
| H <sub>2</sub> O   | 0.1                     | 0.0                  |
| H <sub>2</sub> O/C10   | 6.1                     | 0.1                  |
| H <sub>2</sub> O/C10+ZSM-5                                   | 7.8                     | 0.8                  |
| 10% THF-H <sub>2</sub> O/C10+ZSM-5                           | 11.4                    | 0.5                  |
| 10% THF-H <sub>2</sub> O/C10+NbOPO <sub>4</sub>              | 12.9                    | 0.5                  |
| 10% THF-H <sub>2</sub> O/C10+Nb <sub>2</sub> O <sub>5</sub>  | 23.5                    | 0.5                  |
| 10% NMP-H <sub>2</sub> O/C10+Nb <sub>2</sub> O <sub>5</sub>  | 6.6                     | 0.3                  |
| 10% MeMZ-H <sub>2</sub> O/C10+Nb <sub>2</sub> O <sub>5</sub> | 0.1                     | 0.0                  |
| 10% BDO-H <sub>2</sub> O/C10+Nb <sub>2</sub> O <sub>5</sub>  | 19.1                    | 0.8                  |
| 10% THF-H <sub>2</sub> O/C10                                 | 10.1                    | 0.5                  |
| 10% THF-H <sub>2</sub> O/C10+La(OTf) <sub>3</sub>            | 11.5                    | 0.6                  |
| 10% THF-H <sub>2</sub> O/C10+HCl                             | 10.3                    | 1.0                  |
| 10% THF-H <sub>2</sub> O/C10+K10                             | 24.8                    | 0.5                  |
| 10% THF-H <sub>2</sub> O/C10+MgAILDH                         | 18.7                    | 0.8                  |

Conditions: Catalyst 50 mg, PVC 50 mg, 10% THF/H<sub>2</sub>O 3.0 g, Decane 3.0 g, 2 MPa N<sub>2</sub>, 280 °C, 1 h. Other organic additives: N-methyl-2-pyrrolidone (NMP), N-methylimidazole (MeMZ), 1,4-butanediol (BDO).

Table S2. Detailed data of Fig. 3a and Fig. 3b.

| Runing cycle | Benzene yield (mol%) |
|--------------|----------------------|
| cycle 1      | 24.8                 |
| cycle 2      | 21.4                 |
| cycle 3      | 25.2                 |
| cycle 4      | 21.4                 |
| cycle 5      | 24.4                 |

Conditions: PVC 50 mg, K-10 50 mg, 10%THF/H<sub>2</sub>O 3.0 g, Decane 3.0 g, 280 °C, 1 h.

| Scale-up Times    | Benzene yield (mol%) |
|-------------------|----------------------|
| X 1 <sup>a</sup>  | 24.8                 |
| X 5 <sup>a</sup>  | 20.4                 |
| X 20 <sup>b</sup> | 18.1                 |
| X 50 <sup>b</sup> | 17.5                 |

Conditions: a, PVC n \*50 mg, K-10 n \*50 mg, 10%THF/H<sub>2</sub>O n \*3.0 g, Decane 3.0 g (n= 1, 5), N<sub>2</sub> 2 MPa, 280 °C, 1 h; b, PVC m\*50 mg, K-10 m\*50 mg, 10%THF/H<sub>2</sub>O 100.0 g, Decane 25.0 g, (m= 20, 50), N<sub>2</sub> 2 MPa, 280 °C, 3 h.

Table S3. Elemental analysis and quantification results of PVC and carbon material.

| Sample          | C (wt%) | H (wt%) | O (wt%) |
|-----------------|---------|---------|---------|
| Carbon material | 76.7    | 3.2     | 4.7     |
| PVC             | 38.8    | 4.8     | -       |

1. Y. Xin, L. Dong, Y. Guo, X. Liu, Y. Hu and Y. Wang, *Journal of Catalysis*, 2019, **375**, 202-212.
2. Y. Zhang, J. Wang, J. Ren, X. Liu, X. Li, Y. Xia, G. Lu and Y. Wang, *Catalysis Science & Technology*, 2012, **2**.
3. H. Xing, Z. Lei, Q. Xue Qing, W. Fuwang, S. Shirong, Z. Xihong and W. Zhang, *ChemSusChem*, 2023, DOI: 10.1002/cssc.202300646, e202300646.