# Electronic Supplementary Information

# High value utilization of biomass: selective catalytic transformation of lignocellulose to bio-based 2,5-dimethylphenol

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# 1. Experimental details

## 1) Catalyst preparation

The magnetic metal-organic framework catalyst (Cu-MOF@$Fe_3O_4$) used for the hydroxylation of the cellulose-derived aromatics had been prepared by the method of hydrothermal synthesis [1]. Firstly, the magnetic supporter (0.5 g $Fe_3O_4$) were dispersed in a 50 ml 20 mM $Cu(NO_3)_2 \cdot 6H_2O$ solution of water/DMF (N,N-dimethylformamide) (1 : 1). Then, 20 mM of 1,3,5-benzene-tricarboxylic acid (organic ligand) in water/DMF (1 : 1) solution (50 ml) was added slowly and stirred for 1 h. Then, the mixed solution was put into an autoclave, which was reacted at 120 °C for twelve hours. The precipitate was collected by magnetic separation and washed with deionized water/ethanol until no foam was generated, and dried under vacuum for twelve hours. The sample was noted as the Cu-MOF@$Fe_3O_4$ catalyst (typically containing ~ 40 wt% Cu-MOF and ~ 60 wt% $Fe_3O_4$).

On the other hand, the magnetic oxides-modified zeolite catalyst ($Fe_3O_4$@$SiO_2$@HZSM-5) was chosen for the cellulose catalytic pyrolysis. HZSM-5 zeolite was ordered from Nankai catalyst plant (Tianjin, China). Firstly, the silicon oxide-coated HZSM-5 catalyst was prepared by means of CLD (chemical liquid deposition) method [1]. 10 g HZSM-5 was added to the mixed solution, which TEOS (tetraethyl orthosilicate) was dissolved in n-hexane (2 M). Then, the mixed solution was reacted in an autoclave at 180 °C for twelve hours. After cooling to room temperature, the precipitate ($SiO_2$@HZSM5) was washed, dried (120 °C for twelve hours), and calcined in a furnace (at 550 °C for five hours). Finally, to prepare magnetic catalyst, the component of ferroferric oxide was further doped to the silica-coated zeolite by hydrothermal synthesis [1]. The sample obtained was labeled as $Fe_3O_4@SiO_2@HZSM$-5 (typically containing ~ 20 wt% $SiO_2$ and ~ 5 wt% $Fe_2O_3$).

**2) Catalyst characterization**

Powder X-ray diffraction analysis (XRD) was conducted with Philips/PW3040 diffractometer (Philips, Netherlands), which was equipped with a Cu Kα radiation (40 mA, 45 kV, 0.154 nm, scanned range: $5^{o} < 2\theta < 80^{o}$) [2].

X-ray photoelectron-spectroscopy data (XPS) were accessed on ESCALab220iXL electron spectrometer (VG scientific, UK), using 300W AlKα radiation and referencing to C1s line at 284.8 eV.

Fourier transform infrared spectra (FTIR) were measured by a Nicolet 6700 infrared spectrometer (Thermo Scientific, Massachusetts, USA) within the scanning range of 400 ~ 4000 $cm^{-1}$.

BET specific surface-area as well as pore-texture of the catalysts was tested on the COULTER-SA-3100 analyzer (Krefeld, Germany), on the basis of Brunauer–Emmett–Teller method.

The catalyst's acidity was analyzed by the method of $NH_3$−TPD (ammonia temperature programmed desorption) [2].

TGA (Thermogravimetric-analysis) characterization was carried out by using a MettlerToledo TGA/DTA-851e analyzer [2].

Transmission electron-microscope (JEOL JEM-2100 LaB6, Japan) and/or scanning electron-microscope (FEI-Quanta-200 SEM, Netherlands) were used to obtain the morphology characteristics of the catalysts [2].

### 3) Experimental method for preparation of bio-based p-xylene intermediate

First, the preparation of p-xylene intermediate was tested by lignocellulose catalytic pyrolysis over the magnetic oxides-modified zeolite catalyst ($Fe_3O_4$@$SiO_2$@HZSM-5). The experimental procedure has been described in detail in our previous work [3]. Briefly, the catalytic pyrolysis experiments were conducted using a fixed-bed reactor. Prior to the experiment, the biomass samples were dried in an oven at 110 °C for 12 h to remove moisture. Then, the $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst of 15 g was added to the catalytic pyrolysis reactor. When heated to a set reaction temperature, the lignocellulose raw material (5 g) was fed to the reactor (feed rate: 10 g/h). The liquid reactant such as methanol was added through the syringe pump (TS260 liquid injection pump, Baoding, China). For the catalytic pyrolysis experiments, typical conditions were described as follows: mass ratio of catalyst/biomass (3:1); temperature (450 °C); nitrogen gas (100 mL/min). The liquid products were detected by a gas chromatography/mass spectrometer with a DB-5 capillary column (Thermo/Fisher Scientific GC-MS; ThermoTrace-GC/ISQ MS; USA). The gas products were detected by a GC-SP689 gas chromatograph (TCD/FID two detectors; Shandong; China). The carbon yield and the product's selectivity were calculated, based on the calculation formula described in our previous paper [3]. The experiments generally repeated 3–5 times under the same conditions and the average values were obtained. The standard deviation and/or the carbon balance were calculated to evaluate the experimental precision.

**4). Experimental method for preparation of biomass-based 2,5-dimethylphenol**

In the second step, the preparation of bio-based 2,5-dimethylphenol was performed by means of the catalytic oxidation/hydroxylation of cellulose-derived aromatic intermediates using the metal-organic framework catalyst (like Cu-MOF@$Fe_3O_4$) or other hydroxylation catalysts. The hydroxylation/oxidation experiments were carried out in a two-necked round flask (50 ml), which was equipped with a reflux condenser in water bath. When the temperature reached the set value, hydrogen peroxide aqueous solution (30 wt%) was added (dropwise) into reaction flask, which typically contained the reactant of 1.0 g with the hydroxylation catalyst of 0.5 g.

After the oxidation/hydroxylation reactions, the catalyst can be separated from the mixture by high-speed centrifugation. The liquid products were detected by GC-MS (gas chromatography/mass spectrometry, ThermoTrace GC/ISQMS, USA) using a DB-5MS capillary column, which the oven was programmed to 200 °C at a rate of 5 °C/min, then to 280 °C at 10 °C/min and finally maintained at 280 °C for 10 min. Some high-boiling point's products were detected by means of the LC10A/HPLC system (high performance liquid chromatography, Agilent Phenogel column, 250 nm UV detector, Japan).

The conversion, yield as well as product's selectivity were calculated by formula (1-3) [3].

$$C\ (\%)=\frac{Carbon\ moles\ of\ substrate\ fed\ in-\ Carbon\ moles\ of\ substrate\ in\ products}{Carbon\ moles\ of\ substrate\ fed\ in}\times 100 \qquad (1)$$

$$S_{\mathrm{i}}\ (\%)=\frac{Carbon\ moles\ in\ a\ product}{Carbon\ moles\ in\ all\ products}\times 100 \qquad (2)$$

$$Y_{\mathrm{i}}\ (\%)=\frac{Carbon\ moles\ in\ a\ product}{Carbon\ moles\ in\ substrate}\times 100 \qquad (3)$$

**5) Experimental method for detection of OH radical**

In addition, the ROS such as hydroxyl radicals generated in the liquid phase reaction were detected by applying the spin-trapping technique [4]. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (Sigma-Aldrich) was chosen as a suitable spin-trap because of its well-documented high trapping ability and selectivity toward oxygen-containing radicals. For the EPR (electron paramagnetic resonance) analysis, 100 μL of the sample was collected from the resulting reaction mixture and mixed with 20 μL of 0.2 M DMPO to form DMPO-OH adducts. The liquid sample was immediately transferred into a quartz capillary. The EPR spectra were obtained on an electron spin resonance spectroscopy (ESR, JES-FA200, JEOL, Japan).

The experiments generally repeated 3~5 times under the same conditions and the average values were obtained. The standard deviation and/or the carbon balance were calculated to evaluate the experimental precision.

## References

1. Y. He, L. Zhu, Y. Luo, M. Fan, M. Yang, Y. Zhang and Q. Li, *Fuel Process. Technol.*, 2021, 213, 106674.
2. Y. He, Y. Luo, M. Yang, Y. Zhang, L. Zhu, M. Fan and Q. Li, *Appl. Catal., A*, 2022, 630, 118440.
3. L. Zhu, Y. Luo, Y. He, M. Yang, Y. Zhang, M. Fan and Q. Li, *Mol. Catal.*, 2022, 517, 112063.
4. K. Sobańska, P. Pietrzyk and Z. Sojka, *ACS Catal.*, 2017, 7, 2935−2947.

## 2. Supplementary data

**Table S1.** Elemental compositions of feedstocks..

| Feedstock | Effective H/C ratio [a] | Elemental analysis (wt%) [b] | | | |
|---|---|---|---|---|---|
| | | C | H | N | O [c] |
| Cellulose | 0.03 | 45.04 | 6.21 | 0.01 | 48.74 |
| Lignin | 0.01 | 51.76 | 5.40 | 0.02 | 42.82 |
| Hemicellulose | 0.03 | 40.00 | 6.76 | 0.00 | 53.24 |

[a] Effective H/C ratio is defined by the following equation: $H/C_{eff} = \frac{H - 2O}{C}$, where H, C and O are the moles of hydrogen, carbon and oxygen in the feedstock respectively.

[b] Dry biomass.

[c] Determined by difference.

**Table S2.** Valence distribution of copper in different Cu-based catalysts. [a]

| Catalysts | $Cu^{2+}$ (%) | $Cu^{+}$ (%) | $Cu^{0}$ (%) |
|---|---|---|---|
| Cu-MOF@$Fe_3O_4$ | 99.2 | 0.7 | 0.1 |
| Cu-MOF | 98.8 | 0.9 | 0.3 |
| Cu-MOF-0.2 [b] | 74.1 | 20.5 | 5.4 |
| Cu-MOF-0.5 | 53.6 | 32.4 | 14.0 |
| Cu-MOF-1 | 44.5 | 34.2 | 21.3 |
| Cu-MOF-2 | 10.2 | 43.8 | 46.0 |

[a] Fitting the Cu-AES spectra in Fig. 1b.

[b] The number in the catalyst indicates the molar ratio of hydrazine hydrate/copper.

**Table S3.** Assigmments of FTIR Infrared bands identified from the magnetic metal-organic framework catalyst of Cu-MOF@$Fe_3O_4$.

| Wavenumber range (cm$^{-1}$) | Peak (cm$^{-1}$) | Assigmment |
|---|---|---|
| 3000-3650 | 3430 | O–H stretch |
| 2870-2950 | 2918 | C–H aromatic |
| 1550–1600 | 1562 | C=C stretching of benzene rings |
| 1420-1480 | 1444 | O–C=O symmetrical stretching vibration |
| 1410-1330 | 1373 | O–C=O symmetrical stretching vibration |
| 900-1200 | 1112 | C–H bending vibrations of benzene rings |
| 600-700 | 637 | Fe–O band stretching modes |
| 550-600 | 590 | Fe–O band stretching modes |
| 400-550 | 537 | Cu–O band stretching modes |

**Table S4.** Properties of the fresh $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst and the used one.

| Catalysts | Fresh catalyst | Used catalyst [a] |
|---|---|---|
| *Content (wt%)* | | |
| $Fe_3O_4$ | 5.1 | 5.0 |
| $SiO_2$ | 93.3 | 93.6 |
| $Al_2O_3$ | 1.6 | 1.4 |
| *Acidity (μmol $NH_3$/g)* | 198.3 | 129.4 |

[a] "Used catalyst" represents the $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst used for catalytic pyrolysis under the conditions: catalyst/cellulose mass ratio of 3:1, cellulose/methanol mass ratio of 1:1, 450 °C for 2 h.

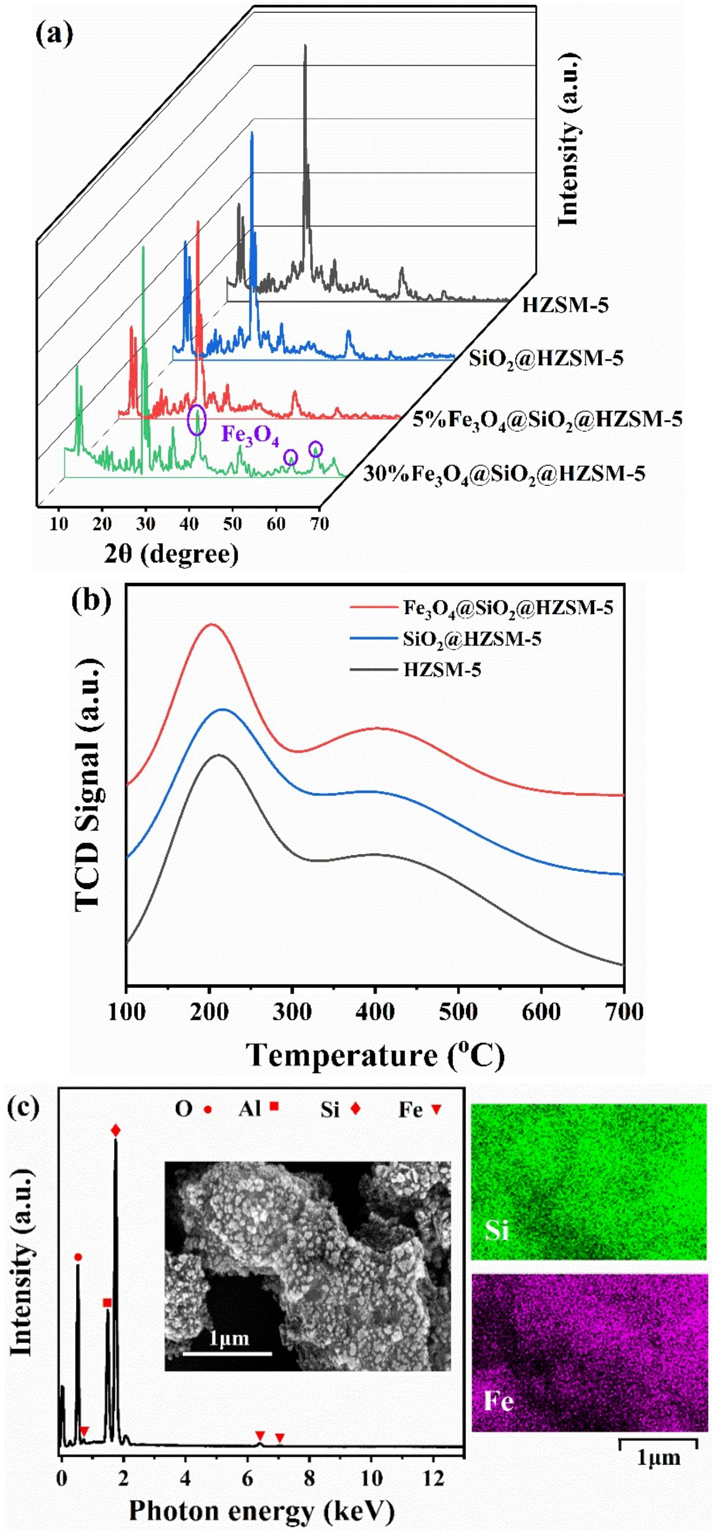

**Fig. S1.** (a) XRD patterns of different zeolite catalysts; (b) $NH_3$-TPD profiles of different zeolite catalysts; (c) SEM characterization for the $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst.

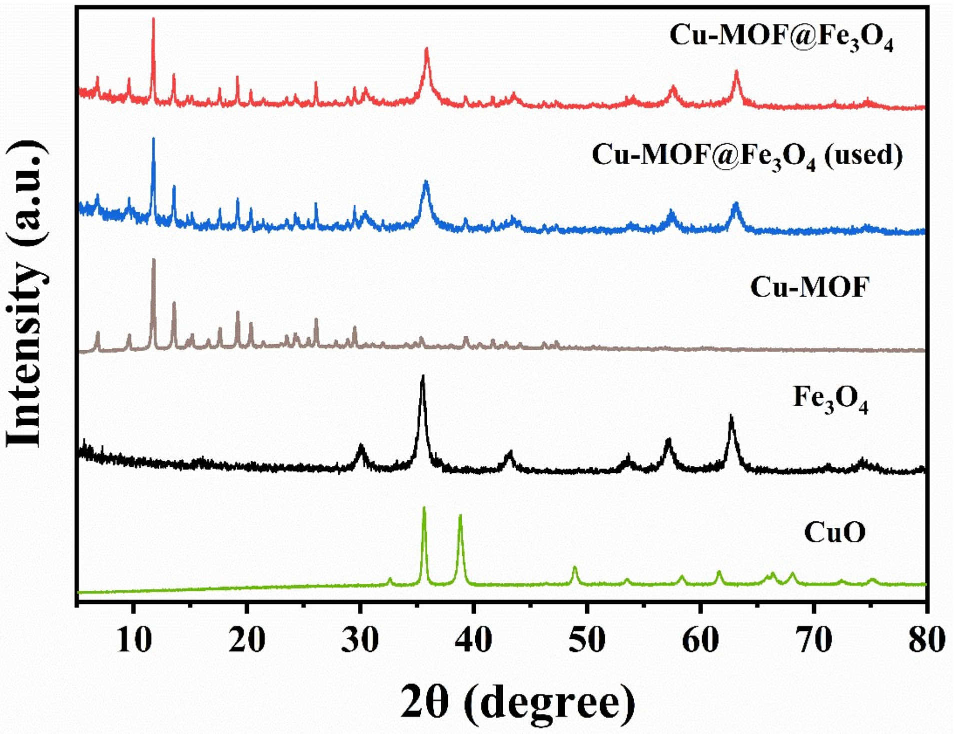

**Fig. S2.** XRD patterns obtained from five samples: (a) Cu-MOF@Fe$_3$O$_4$ catalyst; (b) Cu-MOF@Fe$_3$O$_4$ catalyst used for the catalytic hydroxylation at 80 °C for 32 h; (c) Cu-MOF catalyst; (d) Fe$_3$O$_4$ catalyst; (e) CuO catalyst.

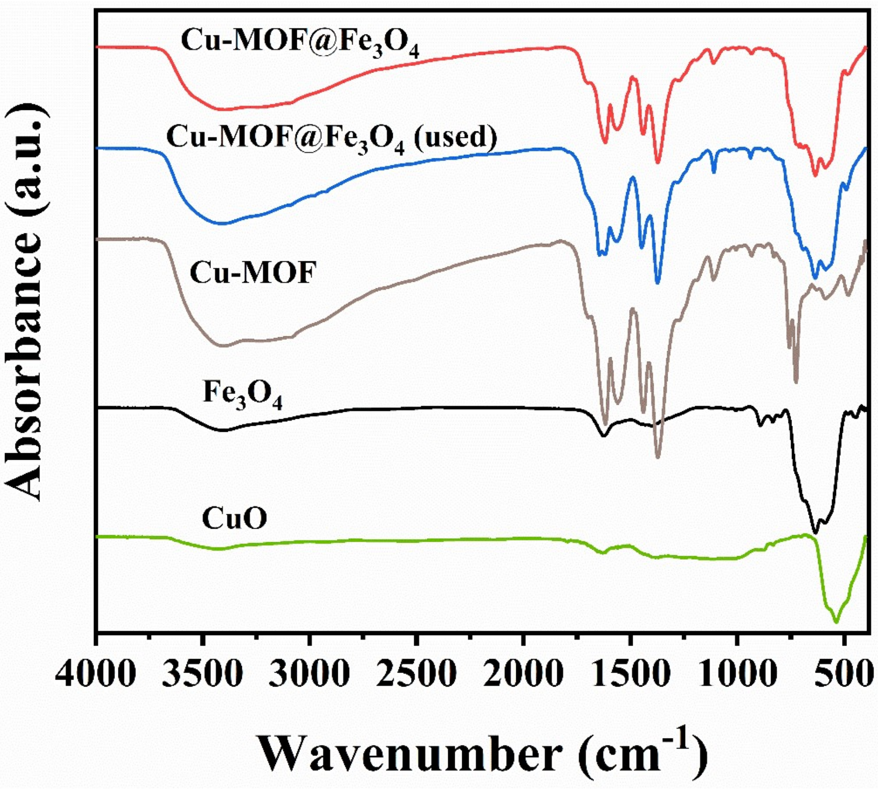

**Fig. S3.** FTIR Infrared spectra obtained from five samples: (a) Cu-MOF@Fe$_3$O$_4$ catalyst; (b) Cu-MOF@Fe$_3$O$_4$ catalyst used for the catalytic hydroxylation at 80 °C for 32 h; (c) Cu-MOF catalyst; (d) Fe$_3$O$_4$ catalyst; (e) CuO catalyst.

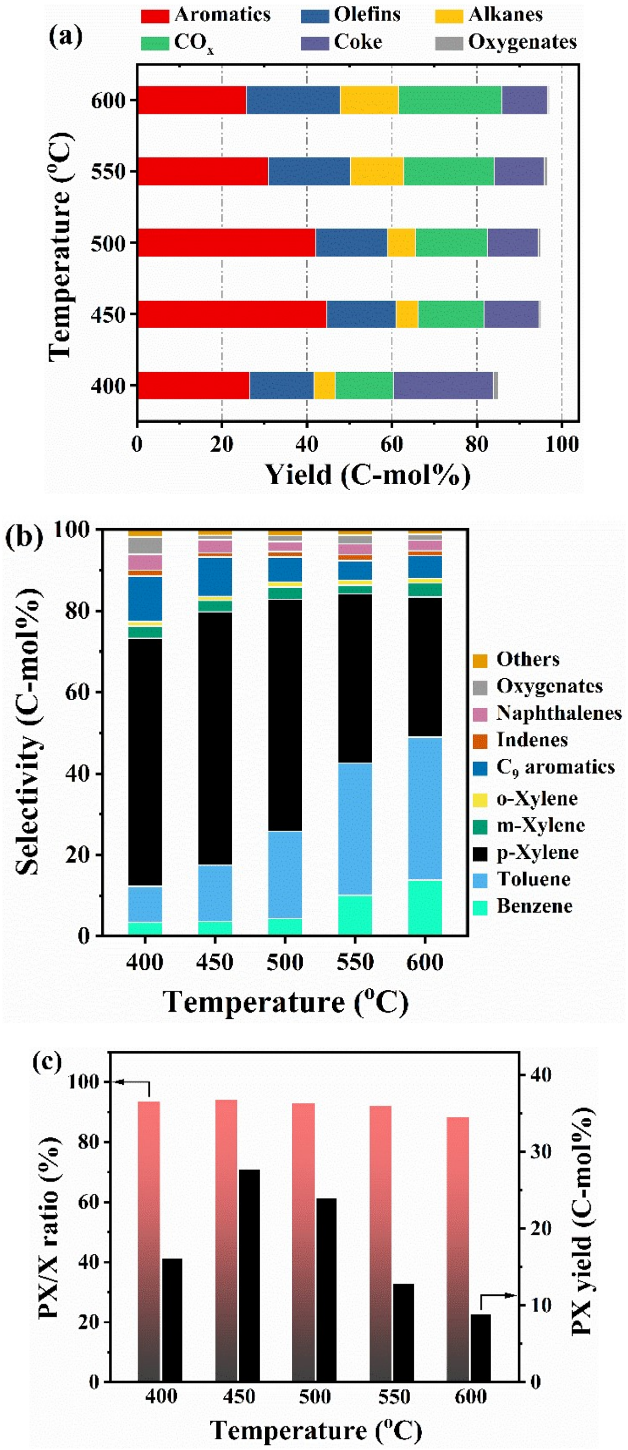

**Fig. S4.** Effect of temperature on the production of p-xylene (PX) intermediate (conditions: 5 g cellulose, 5 g methanol, 15 g $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst).

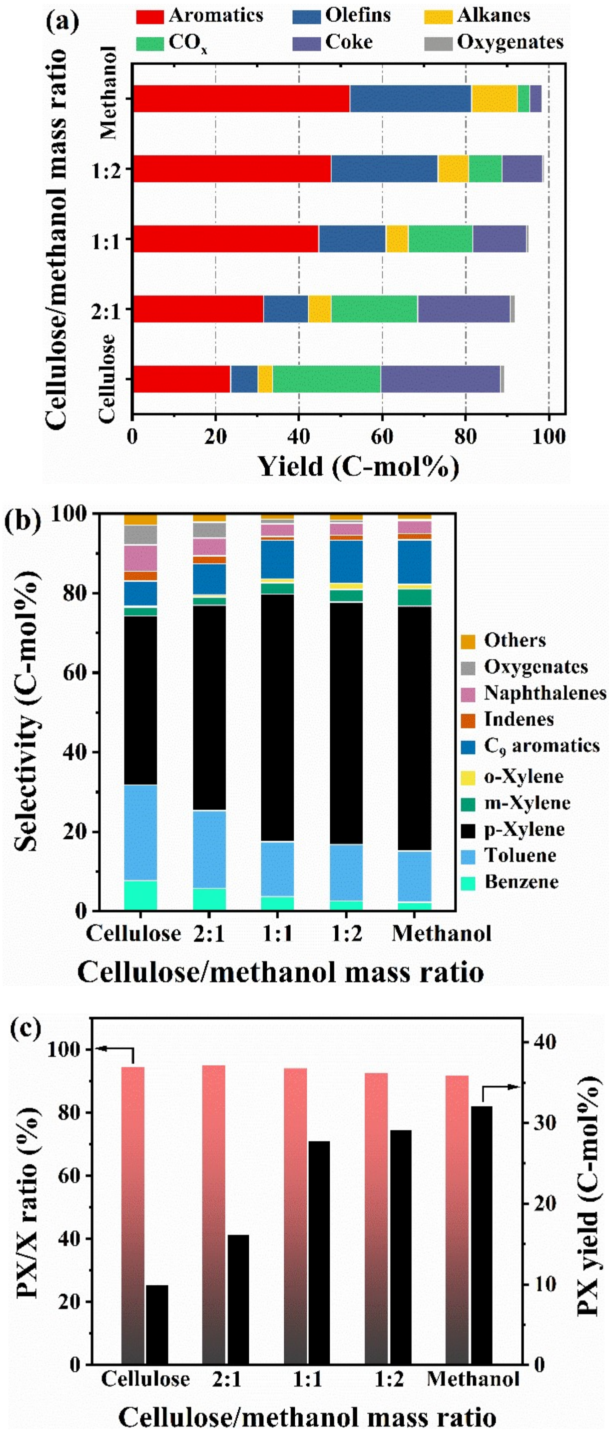

**Fig. S5.** Effect of cellulose/methanol mass ratio on the production of p-xylene (PX) intermediate (conditions: 5 g cellulose, 15 g $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst, 450 °C).

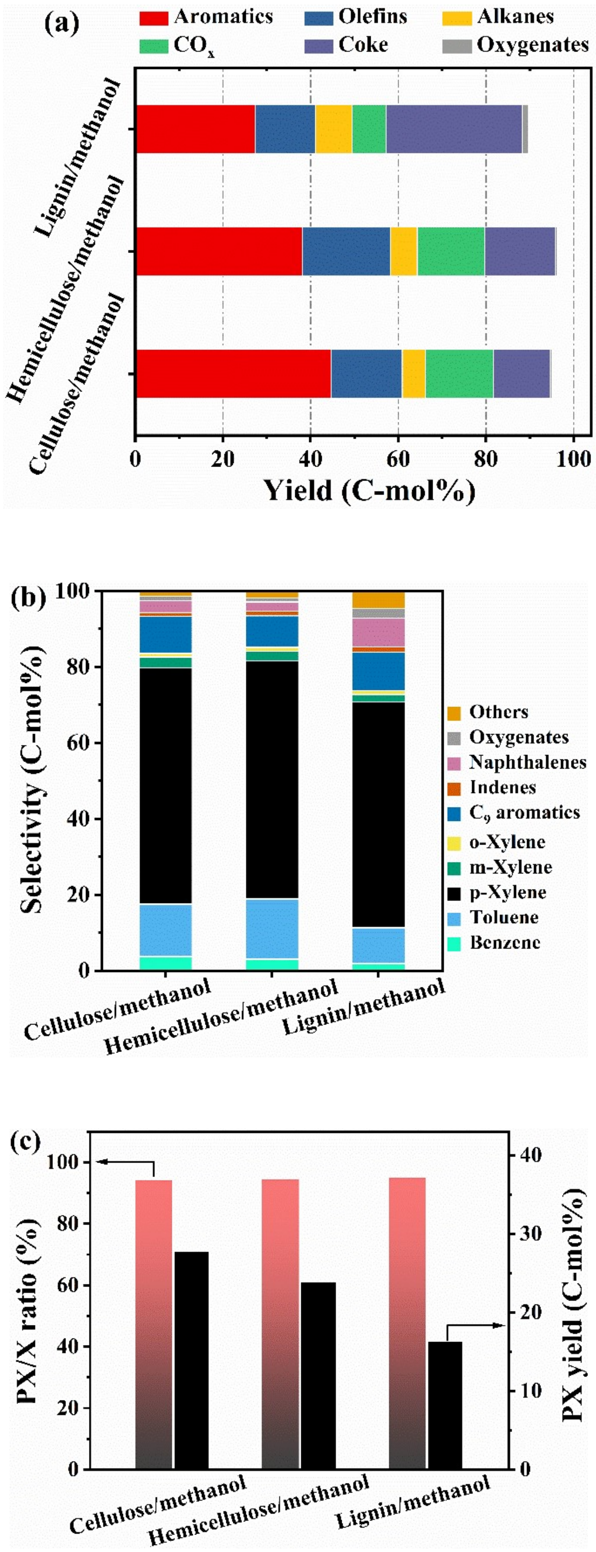

**Fig. S6.** Production of p-xylene (PX) by co-catalytic pyrolysis of different lignocellulose components (cellulose, hemicellulose, lignin) with methanol. Conditions: 5 g biomass, 5 g methanol, 15 g $Fe_3O_4$@$SiO_2$@HZSM-5 catalyst, 450 °C.

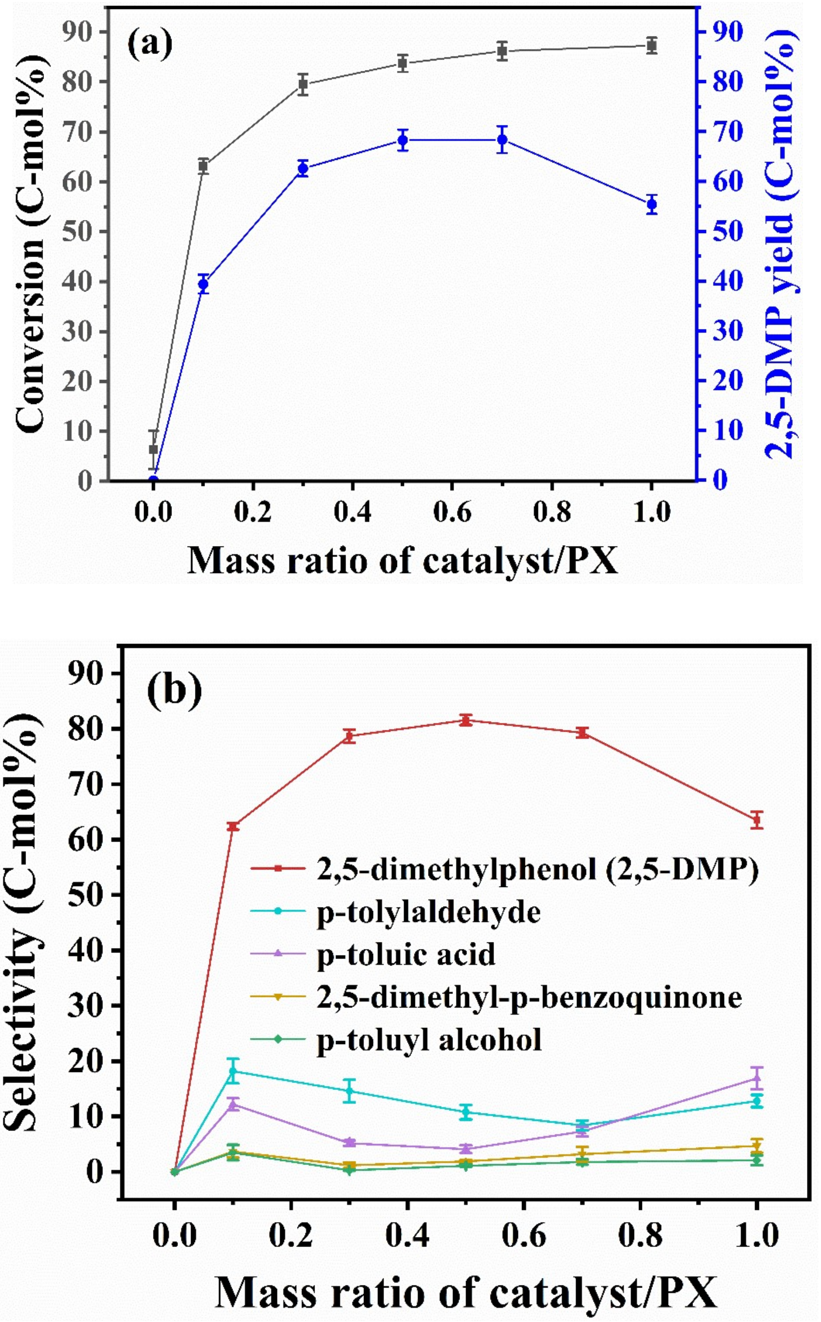

**Fig. S7.** (a-b) Influence of the mass ratio of Cu-MOF@$Fe_3O_4$ catalyst/p-xylene (PX) on the 2,5-dimethylphenol synthesis (conditions: 1.0 g p-xylene substrate, PX/$H_2O_2$ mole ratio (1:3), 4 h, 80 °C).

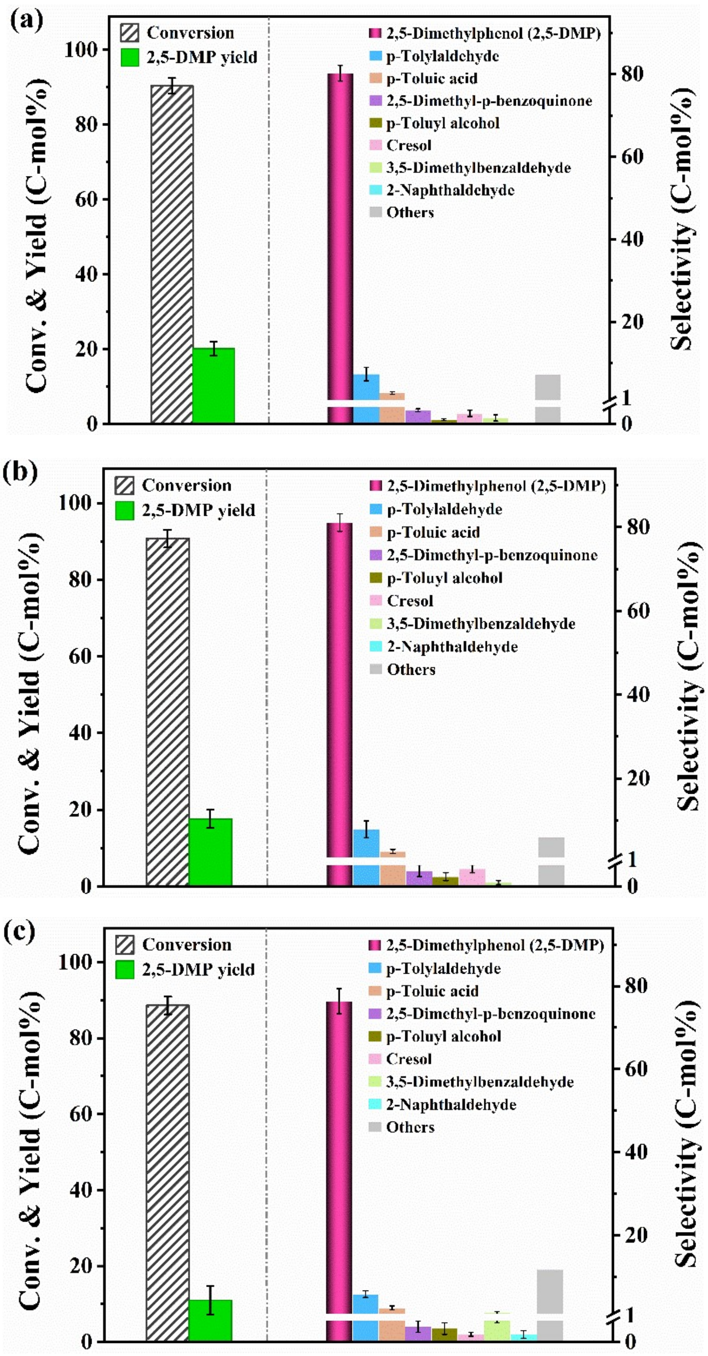

**Fig. S8.** Production of bio-based 2,5-dimethylphenol by catalytic hydroxylation of different biomass-derived intermediates with the Cu-MOF@$Fe_3O_4$ catalyst. (a) aromatic intermediate II (derived from cellulose/methanol=1:1); (b) aromatic intermediate III (derived from hemicellulose/methanol=1:1); (c) aromatic intermediate IV (derived from lignin/methanol=1:1). The absolute yield of 2,5-dimethylphenol (2,5-DMP) was evaluated by the ratio of the carbon moles of 2,5-DMP to the carbon moles of the reactants. Conditions: substrate (1.0 g), catalyst (0.5 g), substrate/$H_2O_2$ mole ratio (1:5), temperature (80 °C), reaction time (4 h).