

Supplementary Materials

Jet fuel-like production from catalytic pyrolysis of low-density polyethylene by metal-loaded activated carbon

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1 Materials

The metal precursor reagents used include chromic acetate (CAS: 1066-30-4, 99.9%), manganese (II) acetate tetrahydrate (CAS: 6156-78-1, 99.99%), iron (II) acetate (CAS: 3094-87-9, 90%), cobalt (II) acetate tetrahydrate (CAS: 6147-53-1, 99.99%), nickel (II) sulfate hexahydrate (CAS: 10101-97-0, 99.9%), copper (II) monohydrate (CAS: 6046-93-1, 99.95%), zinc phosphate tetrahydrate (CAS: 6046-93-1, 95%) and silver acetate (CAS: 563-63-3, 99.5%). Zinc phosphate tetrahydrate and silver acetate were purchased from Shanghai Meryl Chemical Technology Co. Ltd (China) and Shanghai Macklin Biochemical Co., Ltd (China), respectively. And other metal precursors were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd (China).

2 Catalyst preparation

First, the corncob particles were repeatedly rinsed with water to remove impurities on the surface. Then They were dried in an oven at 105°C to a constant weight and activated with a mixture of phosphoric acid (the mass ratio of phosphoric acid to corncob is 0.8). According to the mass ratio of phosphoric acid and corncob, weigh phosphoric acid and add it to 200g of deionized water to prepare the phosphoric acid solution. The mass of corncob is always 90g in each activation process. Pour the

phosphoric acid solution into a beaker with corncobs, stir it thoroughly, then seal the beaker and store it at 25°C for 10h, and then dry the activated corn cobs to a constant weight.

The production process of AC is completed in a tubular furnace. 30g of the mixture prepared in the above process was filled in a quartz tube, and both ends were fixed with quartz wool. The quartz tube was purged with N₂ for 15 minutes to create an oxygen-free environment. After that, AC was obtained by carbonizing in a tube furnace at 500°C for 1h. AC is washed with warm water and dried in a 105°C oven before use.

Impregnation AC obtained AC catalysts with different metal loading in the metal salt solution, and the metal loading amount was 1wt%, denoted as 1%X/AC (X represents different metals). Specifically, the metal precursors were dissolved in 80g of deionized water to prepare a precursor salt solution, and then 10g of AC was added to the solution. The impregnation process was carried out in a heated magnetic agitator in a 45°C water bath for 6h, and then the sample was dried. The mass of the required metal precursor is calculated by the formula. The catalyst is calcined in a nitrogen atmosphere at 500°C for 30min before use. Then these catalysts are used to catalyze the pyrolysis of LDPE to study their catalytic performance. The calculation method of metal loading amount is as follows:

Metal loading amount (wt%)=Mass of metal precursors/Mass of activated carbon
× Metal content in metal precursors

3 Double temperature zone tubular furnace introduction:

The Fig. S2 shows the temperature field distribution diagram of the tubular furnace with double temperature zones (The images taken from the official website of the equipment manufacturer). The length of a single heating temperature zone is 100mm, and the maximum heating temperature can reach 1200°C. The partition spacing between the two heating temperature zones is 50mm, which can ensure that the maximum temperature difference between the two temperature zones is 300°C. However, the largest temperature difference in our experiment was only 100°C, which was in line with the equipment operation regulations.

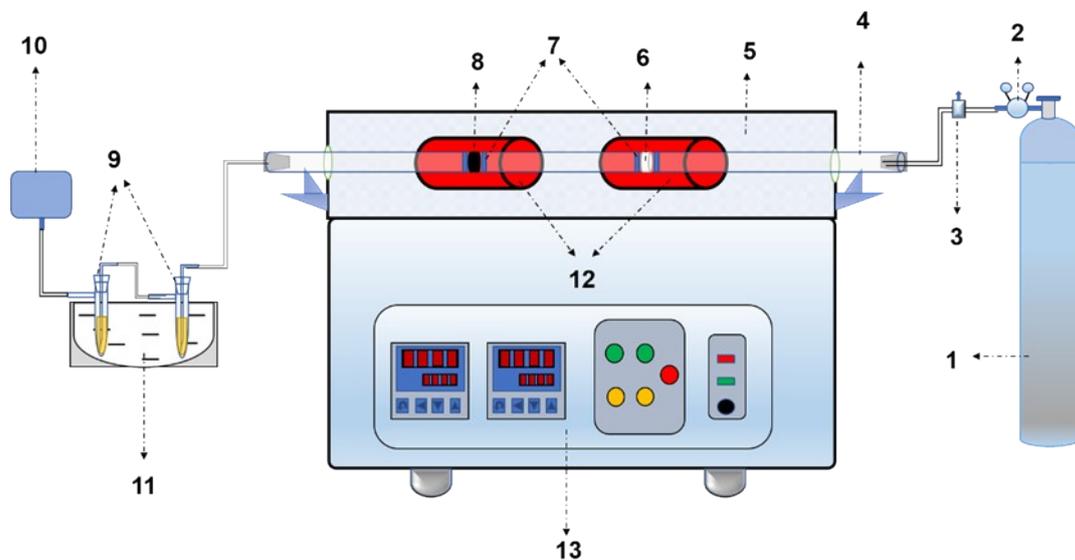


Fig. S1. The ex-situ catalytic pyrolysis system.

1, Nitrogen gas; 2, Gas pressure reducer; 3, Gas flow meter; 4, Quartz tube; 5, Double temperature zone tube furnace; 6, LDPE; 7, Quartz wool; 8, Catalyst; 9, Liquid product collector; 10, Gaseous product collection bag; 11, Liquid condenser; 12, Double temperature zone; 13, Control panel of the furnace.

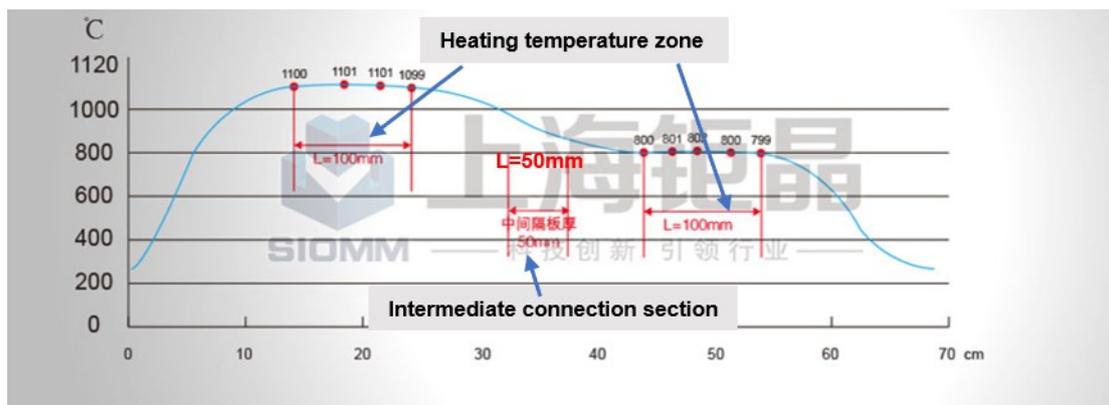


Fig. S2 The temperature field curve of tube furnace with double temperature zone.

4. TG analysis of the pyrolysis behavior of LDPE.

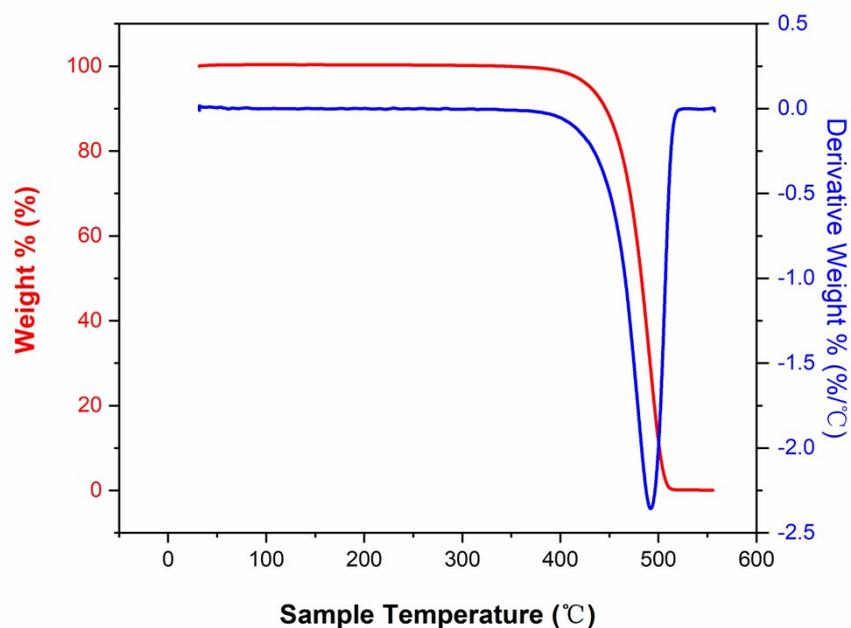


Fig.S3 Thermogravimetric analysis of the pyrolysis behavior of LDPE.

5. Distribution of liquid products from X/AC catalytic pyrolysis.

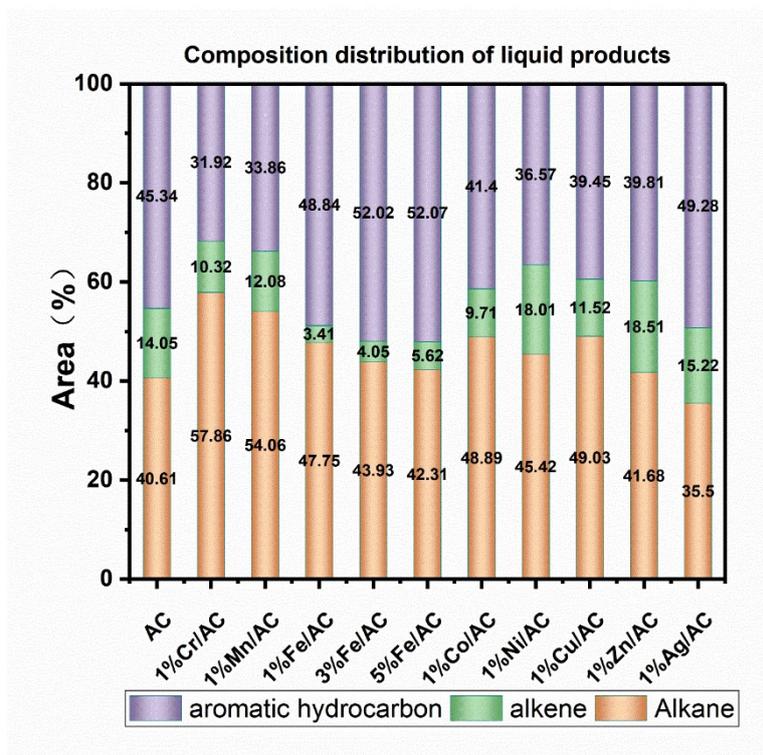


Fig.S4 Distribution of liquid products from X/AC catalytic pyrolysis.

6. Catalyst characterization of AC and Fe/AC

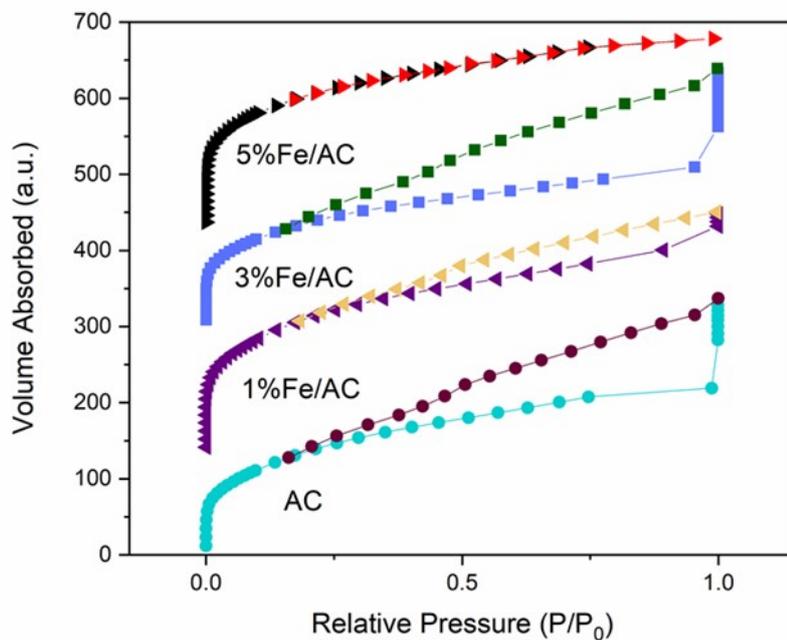


Fig. S5. The N₂ adsorption/desorption isotherm.

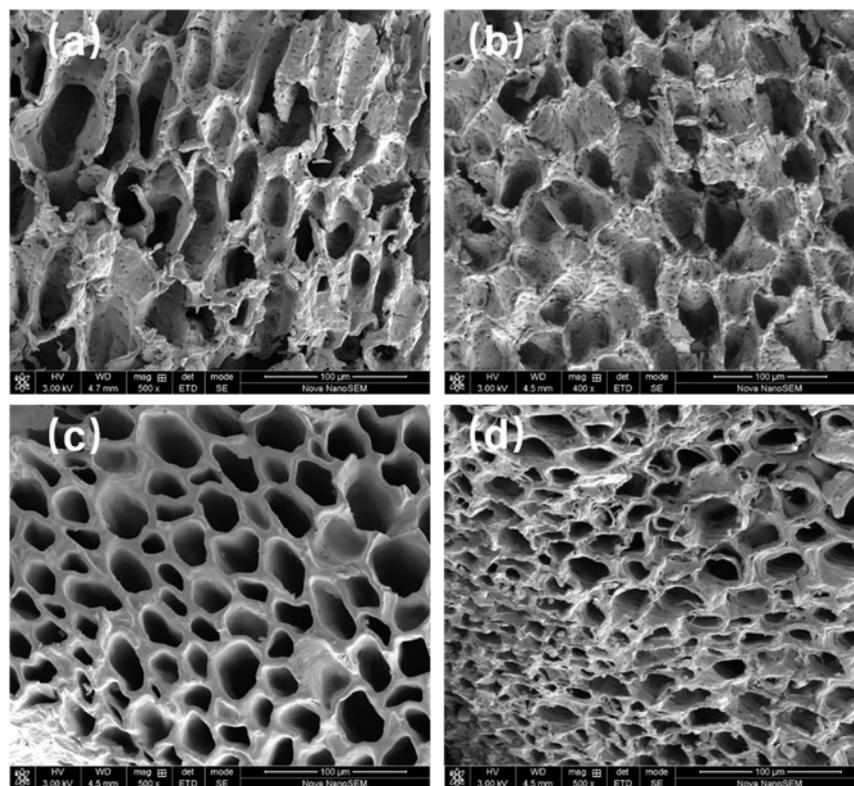


Fig.S6 SEM images of (a)AC, (b)1%Fe/AC, (c)3%Fe/AC, (d)5%Fe/AC.

Table S1 The surface area and pore structure parameters of AC and X/AC.

| Sample | S _{BET,total} (m ² /g) | S _{micro} (m ² /g) | S _{ext} (m ² /g) | V _{total} (cm ³ /g) | V _{micro} (cm ³ /g) | D _{average} (nm) |
|--------------|---|--|--------------------------------------|---|---|---------------------------|
| AC | 500.2 | 159.6 | 340.5 | 0.38 | 0.07 | 2.99 |
| AC | 570.5 | 203.1 | 367.4 | 0.40 | 0.11 | 3.05 |
| 1%Fe/AC | 719.1 | 333.9 | 385.1 | 0.54 | 0.16 | 2.93 |
| 1%Fe/AC | 670.5 | 345.1 | 325.4 | 0.49 | 0.17 | 2.79 |
| 3%Fe/AC | 514.9 | 258.8 | 256.1 | 0.42 | 0.12 | 3.26 |
| 3%Fe/AC | 576.7 | 286.9 | 289.8 | 0.46 | 0.13 | 3.29 |
| 3%Fe/AC | 656.2 | 407.1 | 249.2 | 0.48 | 0.19 | 2.94 |
| 3%Fe/AC | 700.8 | 320.5 | 380.3 | 0.42 | 0.16 | 3.03 |
| 5%Fe/AC | 776.5 | 402.7 | 373.9 | 0.50 | 0.19 | 2.57 |
| 5%Fe/AC | 694.3 | 470.1 | 224.3 | 0.42 | 0.22 | 2.42 |
| 1%Cr/AC | 626.1 | 371.4 | 254.7 | 0.39 | 0.17 | 2.48 |
| 1%Mn/AC | 788.5 | 463.8 | 324.7 | 0.48 | 0.21 | 2.46 |
| 1%Co/AC | 487.6 | 224.1 | 263.6 | 0.33 | 0.10 | 2.73 |
| 1%Co/AC-used | 400.9 | 180.5 | 220.4 | 0.23 | 0.09 | 2.33 |
| 1%Ni/AC | 439.9 | 162.4 | 277.5 | 0.30 | 0.07 | 2.74 |
| 1%Cu/AC | 821.5 | 356.9 | 464.6 | 0.56 | 0.16 | 2.72 |
| 1%Cu/AC-used | 700.8 | 300.2 | 400.6 | 0.48 | 0.10 | 2.59 |
| 1%Zn/AC | 302.0 | 182.5 | 119.5 | 0.18 | 0.08 | 2.41 |
| 1%Ag/AC | 730.6 | 452.7 | 277.9 | 0.42 | 0.21 | 2.31 |
| 1%Ag/AC-used | 688.3 | 375.8 | 312.5 | 0.40 | 0.15 | 2.21 |

EDX analysis of the catalyst particles for surface elemental analysis was performed three times for each catalyst and the results of the scans are in Table S3. The results of the elemental analysis of the catalyst powder by XPS and ICP are in Table 3 (manuscript).

Table S2 Surface elemental analysis of Fe/ AC particles by SEM/EDX

| | 1%Fe/AC | | | | | |
|----|---------|-------|-------|---------|-------|------|
| | wt% | | | Atomic% | | |
| C | 55.25 | 57.47 | 58.29 | 69.65 | 69.96 | 70.6 |
| O | 19.09 | 23.69 | 23.31 | 18.07 | 21.65 | 21.2 |
| P | 24.49 | 16.43 | 16.32 | 11.97 | 7.76 | 7.67 |
| Fe | 1.17 | 2.41 | 2.07 | 0.32 | 0.63 | 0.54 |

| | 3%Fe/AC | | | | | |
|----|---------|-------|-------|---------|-------|-------|
| | wt% | | | Atomic% | | |
| C | 42.82 | 38.27 | 45.91 | 59.22 | 54.45 | 61.5 |
| O | 25.97 | 25.02 | 26.06 | 26.96 | 26.73 | 26.21 |
| P | 19.01 | 30.86 | 18.21 | 10.2 | 17.03 | 9.46 |
| Fe | 12.2 | 5.84 | 9.83 | 3.63 | 1.79 | 2.83 |

| | 5%Fe/AC | | | | | |
|----|---------|-------|-------|---------|-------|-------|
| | wt% | | | Atomic% | | |
| C | 58.15 | 51.7 | 51.94 | 75.3 | 66.01 | 66.07 |
| O | 13.07 | 26.86 | 27.17 | 12.7 | 25.75 | 25.95 |
| P | 17.82 | 10.68 | 10.33 | 8.95 | 5.29 | 5.09 |
| Fe | 10.96 | 10.75 | 10.56 | 3.05 | 2.95 | 2.89 |

7. Effect of Fe loading and catalytic temperature on product distribution

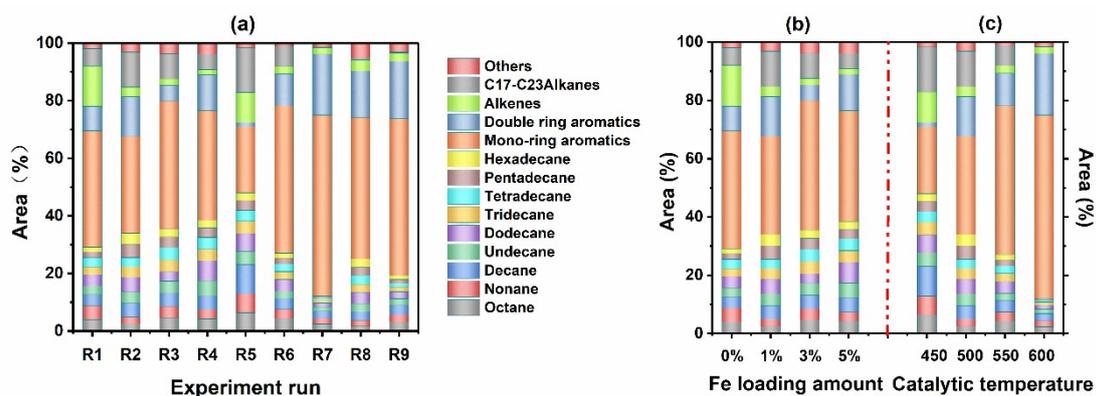


Fig.S7 The compositions of liquid product in each experiment run (a); The composition of liquid products with different Fe doping at the catalytic temperature of 500°C (b); The composition of liquid products with 1%Fe/AC at different catalytic temperatures (c).

8 Effect of nitrogen flow rate

Table S4 Product distribution at different nitrogen flow rates.

| | 30mL/min | 40mL/min | 50mL/min | 60mL/min |
|--------|----------|----------|----------|----------|
| Liquid | 67.0 wt% | 68.0 wt% | 69.5 wt% | 71.5 wt% |
| Gas | 25.6 wt% | 24.0 wt% | 24.0 wt% | 24.5 wt% |
| Coke | 7.4wt% | 8wt% | 6.5 wt% | 4.0 wt% |

9 The weight loss of 1%Fe/AC

The weight loss of 1%Fe/AC kept at 500°C and 600°C for 10min was 0.2wt% and 0.81wt%, respectively.

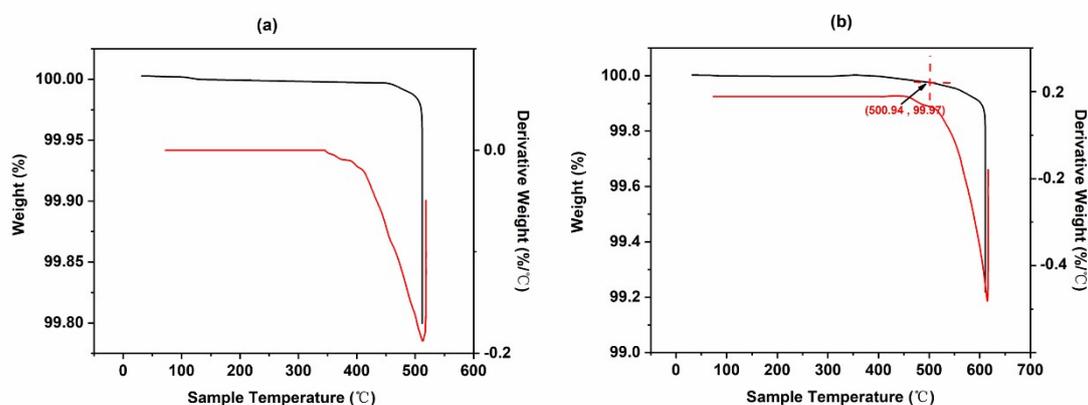


Fig. S8 Thermogravimetric analysis of 1%Fe/AC at 500°C and 600°C.

10 Characterization of used catalysts

Fe/AC catalysts undergo coking after catalytic reactions, leading to changes in catalyst pore structure parameters. In Table S4 are the parameters of surface area and pore structure of Fe/AC after the reaction. Compared with the catalyst not used to catalyze the reaction, the mesopore area and volume of the catalyst are significantly lower, indicating that the coke cannot pass through the micropores and clog in the mesopores of the catalyst. It can be observed from the SEM images (Fig.S8) that the morphology of the catalyst after the catalytic reaction was also changed; however, it can be known from the results of FTIR spectral characterization (Fig.S9) that the functional group structure of the catalyst did not occur.

Table S5 Surface area and pore structure parameters of Fe/AC after catalytic reaction.

| Sample | $S_{\text{BET, total}}(\text{m}^2/\text{g})$ | $S_{\text{micro}}(\text{m}^2/\text{g})$ | $S_{\text{ext}}(\text{m}^2/\text{g})$ | $V_{\text{total}}(\text{cm}^3/\text{g})$ | $V_{\text{micro}}(\text{cm}^3/\text{g})$ | $D_{\text{average}}(\text{nm})$ |
|--------|--|---|---------------------------------------|--|--|---------------------------------|
| 1%Fe | 519.1 | 333.9 | 185.1 | 0.23 | 0.16 | 2.33 |
| 3%Fe | 498.2 | 309.1 | 189.2 | 0.25 | 0.20 | 2.17 |
| 5%Fe | 417.0 | 328.5 | 88.6 | 0.23 | 0.16 | 2.16 |

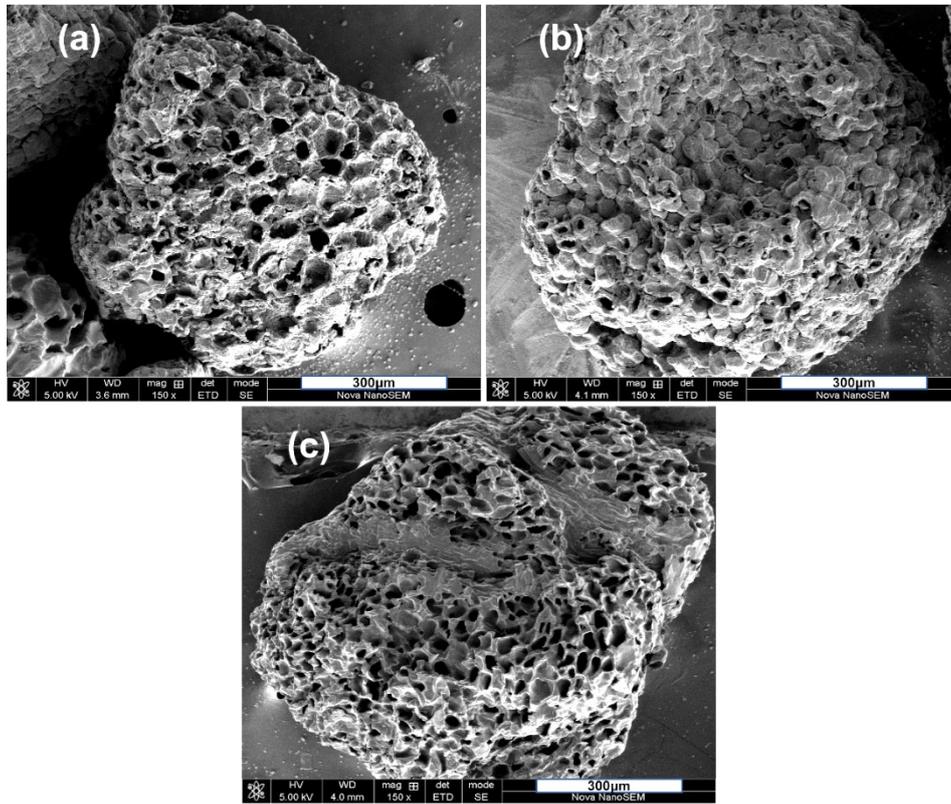


Fig. S9 SEM images of (a) 1%Fe/AC, (b)3%Fe/AC, (c)5%Fe/AC.

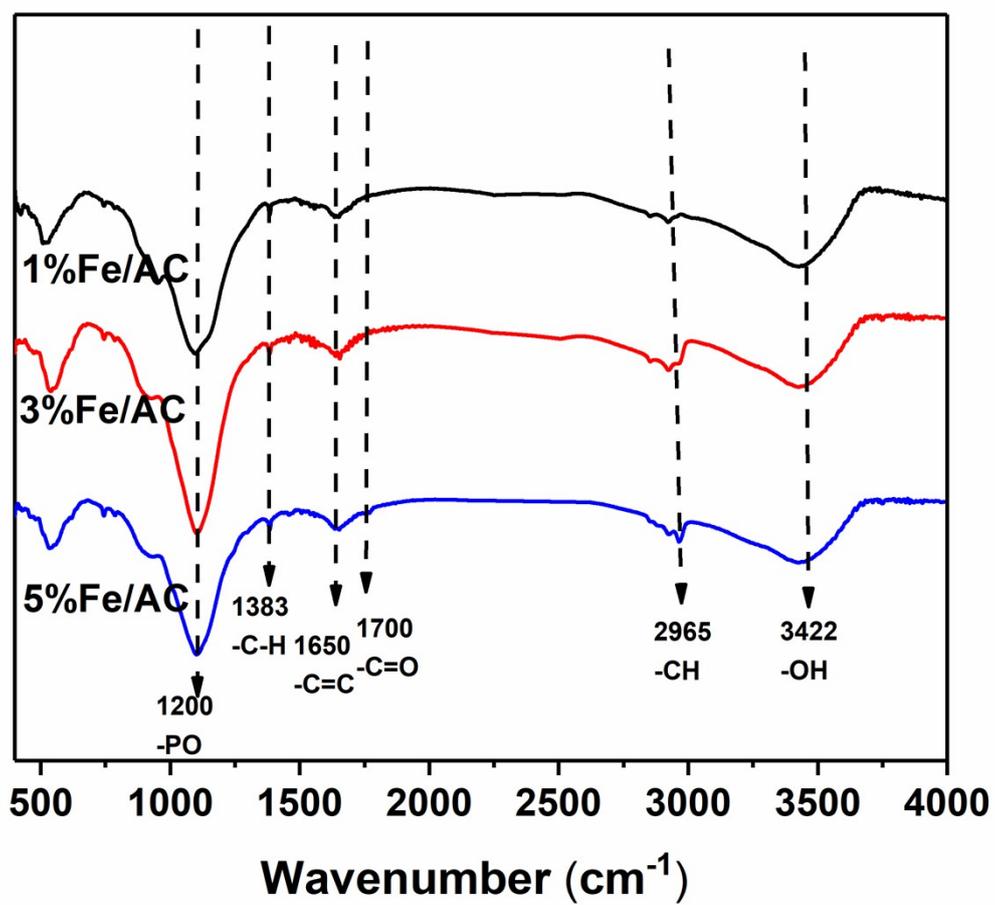


Fig.S10 The FTIR spectra of Fe/AC.

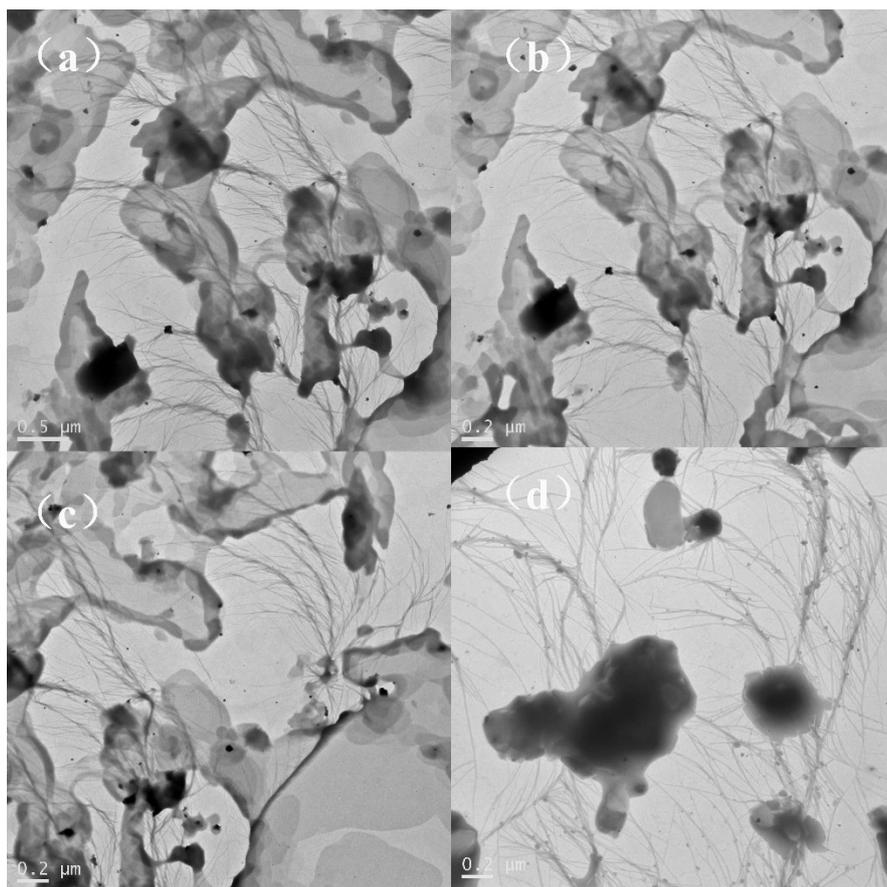


Fig. S11 The TEM image of the used catalyst.