Production of liquid fuels from Kraft lignin over bimetallic Ni-Mo supported on ZIFs-derived porous carbon catalyst

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Materials and methods

Catalyst characterization

Transmission electron microscopy (TEM) images were conducted using a JEM-2100F electron microscope with 200 kV. For TEM analysis, the catalyst was dispersed in ethanol solvent under ultrasonication and then dropped onto the copper grid for observation well.

Scanning transmission electron microscopy (STEM) images were observed using a microscope with the accelerating voltage of 5kV. For SEM analysis, the

samples prepared through dropping the ultrasonic ethanol solutions onto the glass slide and microslide for observation roundly.

Power X-ray diffraction (PXRD) patterns of the catalyst samples were analyzed on a TTR-III (Japan) powder diffractometer using the radiation of Cu Kα (λ= 1.54184 Å).

X-ray photoelectron spectroscopy (XPS) was recorded using a Thermo ESCALAB 250Xi instrument with Al Kα radiation at 15kV and 150 W. The binding energy was calibrated on basis of the C 1s peak at 285 eV.

The automatic volumetric adsorption instrument (MicroActive for ASAP 2460) analyzer was employed to conduct specific surface area of Brunauer-Emmett-Teller (S_{BET}) and pore size analysis. Firstly, the catalysts were degassed at 573K for 12h, and then measured at 77K. Finally, the surface area was calculated according to the equation of Barrett–Joyner–Halenda (BJH) method.

Thermogravimetric analysis (TG) was performed on a TGA-Q5000-V3.17-Build 265 analyzer under nitrogen atmosphere with a heating ramp of 10.00°C/min from room temperature to 873K.
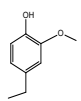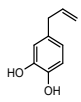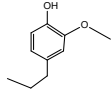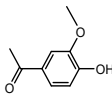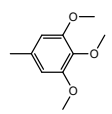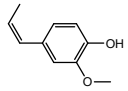
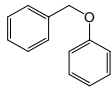NH_3-Temperature programmed desorption (NH_3-TPD) was performed on ChemStarTPx automatic chemisorption instrument equipped with a TCD. Before analysis, the sample (100 mg) was enclosed into a U-shaped quartz tube, and firstly degassed at 673K for one hour in the flow of 99.999% He gas (30 ml/min) and cooled to 373K. Meanwhile, the samples were saturated with 10% NH_3/He gas and then the

physically adsorbed ammonia was removed at desired temperature by the flow of He gas (30 ml/min).

H_2-temperature-programmed reduction (H_2-TPR) analysis was carried out on the instrument of ChemStarTPx analyzer (Quantachrome, American).The sample (100 mg) was loaded into the U-type quartz reaction, which was firstly pretreated at 673K for 1h under the flow of Argon (30 mL/min). Then it was cooled to room temperature, the catalysts were heated up to 1027K at the heating rate of $10°C.min^{-1}$ under the flow of 10% H_2/Ar gas.
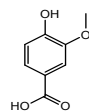
Table S1

The name and chemical structure of main products in GC-MS-FID analysis.

| Number	Name	Structural	Retention Time (min)
1	Guaiacol		9.57
2	Veratrole		10.54
3	4-Methylguaiacol		11.37
4	4-Ethylguaiacol		12.78
5	Eugenol		13.91
6	4- Propylguaiacol		14.12
7	Vanillin		14.53
8	3.4.5-Trimethoxytoluene		14.64
9	Isoeugenol		15.22
10	Acetovanillone		15.79
11	2.6-Di-tert-butyl p-phenol		16.11
12	3,4-dimethoxy acetophenone		16.80
13	Benzyl Phenyl Ether		16.92

| 14 | Homovanillic acid | | 17.83 |

Reaction condition: 0.5g Kraft lignin, 0.2g catalyst, 300°C, 2MPa H_2, 3h, 800 rpm.
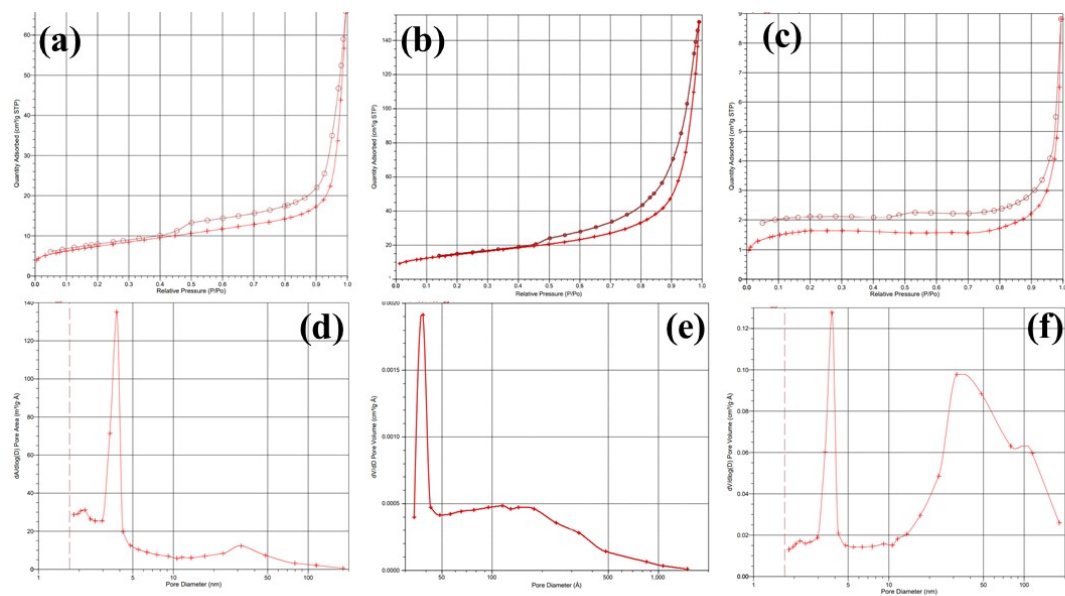
Figure S1. The isotherm and pore sized distribution curves of various catalyst. (FDC precursor (a,d); 10%NiMo@FDC-fresh catalyst (b,e); and 10%NiMo@FDC-spent catalyst (c,f).)
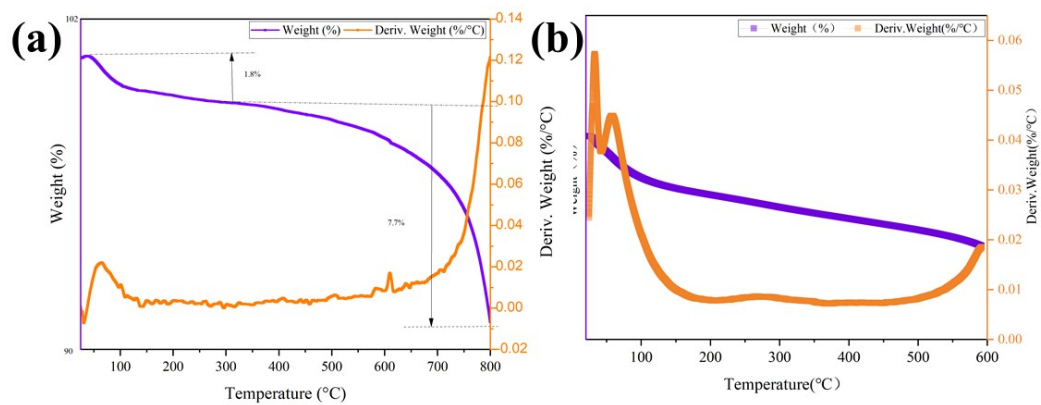
Figure S2. TG analysis of the fresh 10%NiMo@FDC catalyst and spent 10%NiMo@FDC catalyst.
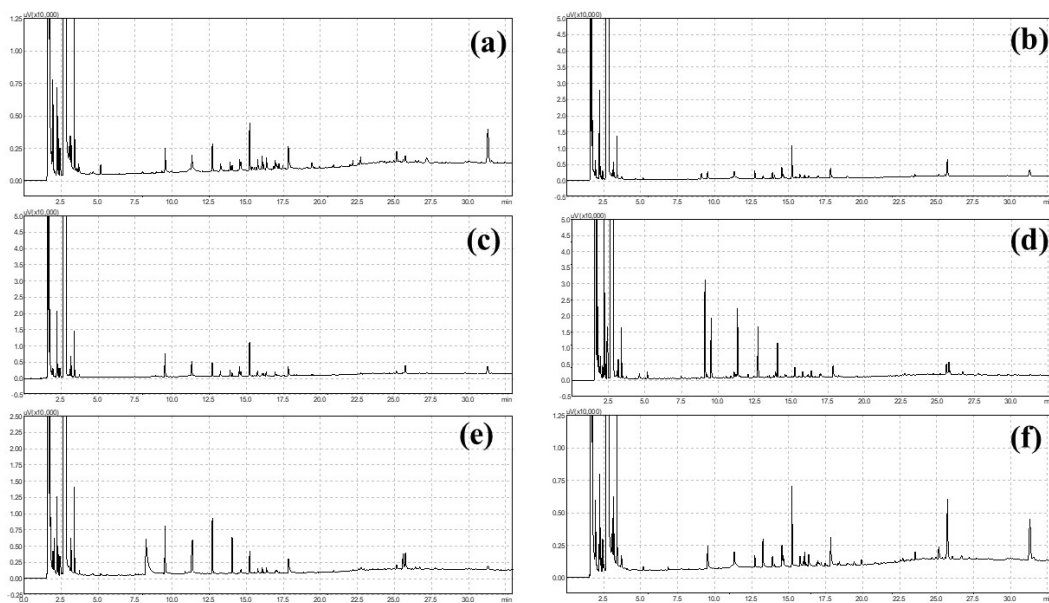
Figure S3. The representative chromatographs of GC analysis in the liquid products using various of catalysts. (Ni@FDC (a); Mo@FDC (b); 5%NiMo@FDC (c); 10%NiMo@FDC (d); 10%NiMo* (e); 10NiW@FDC (f)). NiMo* is the HKUST-derived porous carbon suppored NiMo catalyst.