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Supporting Information

A facile strategy based on metal-free design of carbon to deliver an insight into the active sites for liquid phase carbocatalysis

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Experimental section

Materials

Microcrystalline cellulose and nitrobenzene (99%) were purchased from Alfa Aesar. Hydrazine monohydrate (85%), nitric acid (GR), methanol (AR) and ethanol (AR) were supplied by China Medicine Group Shanghai Chemical Reagent Company. Styrene (99%), benzyl alcohol (99%) and sodium borohydride (98%) were bought from Aladdin Reagent Co. Ltd., Shanghai, China.

Catalyst preparation

All the chemicals that with analytical purity are commercially available. To synthesize biomass based carbon, cellulose was placed in a ceramic crucible with a cover. Then the precursor was heated to 600 ^{o}C with the heating rate of 5 ^{o}C/min in the N_2 flow, and maintained for 2 h. The obtained black powder was denoted as C_{bio}. To get the surface modified product, the C_{bio} was oxidized with concentrated nitric acid at 120 ^{o}C for 2 h. After oxidation, the obtained powder was rinsed with de-ionized water until the filtrate became neutral, followed by drying at 100 ^{o}C. The functionalized sample was labeled as OC_{bio}.

Catalyst Characterization

The morphology of samples was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM, Tecnai G2 F20). Powder X-ray diffraction (XRD) characterization was performed on a STOE STADI P transmission diffractometer equipped with a primary focusing Germanium monochromator (Cu Kα1 radiation) and Dectris MYTHEN 1K position sensitive microstrip solid-state detector. Fourier transform infrared (FT-IR) spectrum was carried out on a Thermo Scientific® Nicolet spectrophotometer. Raman spectroscopy was performed by a LabRam HR 800 using 633 nm laser. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, and the nitrogen adsorption-desorption isotherms were acquired from Micromeritics ASAP 2020 plus/2060. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) ESCALAB 250 set-up equipped with a monochromatic Al Kα X-ray source (1486.6eV; anode operating at 15kV and 20mA). Solid state nuclear magnetic resonance (NMR) experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm magic angle spinning (MAS) probe with a spinning rate of 12 kHz. ^{13}C CP-MAS NMR spectra were recorded using a cross polarization sequence.

Catalytic performance evaluation

In a typical catalytic performance evaluation, the reduction of nitrobenzene was performed in a bath mode. Unless otherwise noted, a certain amount of the catalyst, 10 mmol of nitrobenzene, 5 equivalent of hydrazine hydrate (85%), 2 mL of ethanol were added to the 50 mL bottom rounded flask with the cooling system, followed by the reaction at 100 ^{o}C for a certain period of time. After the reaction, the products were analyzed by high performance liquid chromatography (HPLC) quipped with SinoChrom ODS-BP column and ultraviolet (UV) detector. For the recycling test, the used catalyst was collected, washed with ethanol, and then dried at 60 ^{o}C before the next run. The reaction condition was the same as mentioned above except that the catalyst was the recovered sample rather than the fresh one.

For C=C bond reduction, 20 mg of catalyst, 2 mmol of styrene, 5 equivalent of hydrazine hydrate and 2 mL of ethanol were charged to a bottom rounded flask under oxygen atmosphere, and then reacted at 70 ^{o}C. The conversion of styrene was determined by gas chromatography (GC).

The methanolysis of $NaBH_4$ to produce hydrogen was performed at room temperature in a 50mL of bottom rounded flask charged with 30 mg of catalyst, 60 mg of $NaBH_4$ and 10 mL of methanol.

The selective oxidation of benzyl alcohol was carried out in a 15 mL of sealed glass reactor that charged with 50 mg of benzyl alcohol and 50 mg of catalyst. The reactor was placed in a 100 ^{o}C oven for 24 h, and the product was analyzed by GC.

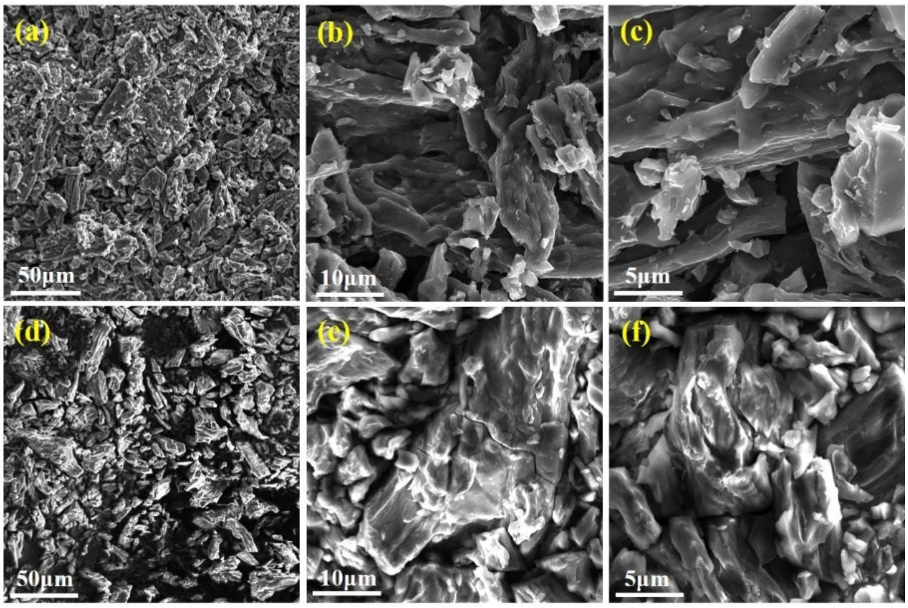

Figure S1. SEM images of C_{bio} (a-c) and OC_{bio} (d-f)

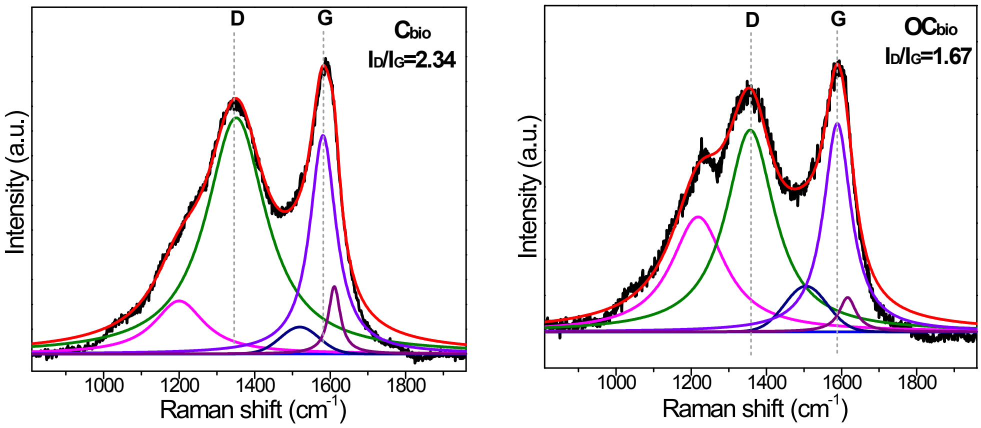

Figure S2. Raman spectra of C_{bio} and OC_{bio}

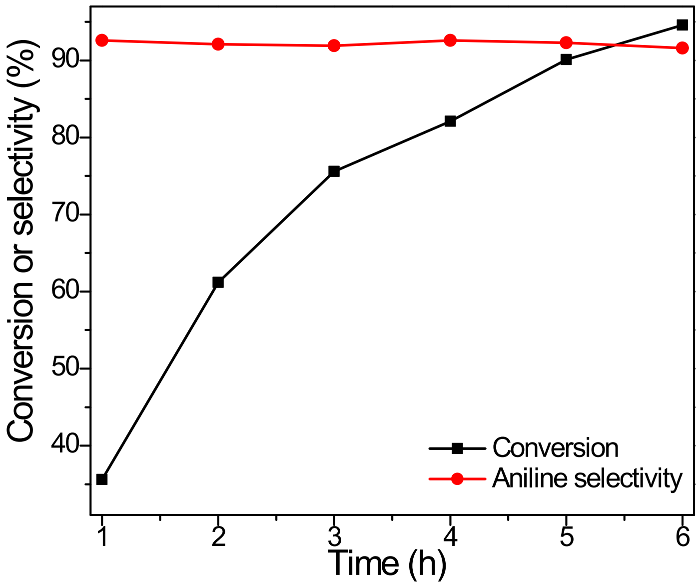

Figure S3. Nitrobenzene reduction in the presence of OC_{bio}

Table S1. Surface oxygen content for C_{bio} and OC_{bio}

Sample	Content (at %)			
	O	C=O	O=C-O	C-O (H)
C_{bio}	4.9	1.4	2.8	0.7
OC_{bio}	22.4	10.5	10.5	1.4

Table S2. The contents of metal impurities in each sample measured by ICP-OES

Sample	Content (mg/g)			
	Fe	Co	Ni	Cu
cellulose	0.03	0.02×10^{-3}	-	-
C_{bio}	0.11	0.13×10^{-3}	0.01×10^{-3}	0.05×10^{-3}
OC_{bio}	0.07	0.08×10^{-3}	-	0.03×10^{-3}