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Electronic Supplementary Information

Photo-induced reduction of biomass-derived 5-hydroxymethylfurfural using graphitic carbon nitride supported metal catalysts

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Experimental

Materials

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. 5-Hydroxymethylfurfural (HMF, 98%), dicyandiamide, cyanamide, NH_4HF_2, trimethylamine, $ZnCl_2$, $CuCl_2·2H_2O$, $NiCl_2·6H_2O$, $CoCl_2·6H_2O$, $LaCl_3·7H_2O$, $CeCl_3·7H_2O$ and ethanol were purchased from Aladdin Industrial Inc. (Shanghai, PR China) and Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). 2,5-Dihydroxymethyl-tetrahydrofuran and 2,5-dihydroxymethylfuran were obtained from J&K Scientific Ltd. (Guangdong, P. R. China) and Tengzhou Lanhai Biotechnology Development Co. Ltd. (Tengzhou, P. R. China). Ludox-HSO_4 silica was purchased from Sigma-Aldrich Chemical Reagent Co. Ltd. Potassium tetrachloropalladate (II) (K_2PdCl_4), potassium tetrachloroplatinate (II) (K_2PtCl_4) was purchased from Kunming Boren Precious Metals Co. Ltd. (Kunming, P. R. China). Hydrogen gas (>99.999%) was obtained from Huate Co. Ltd. (Foshan, P. R. China). De-ionized pure water from Millipore-MilliQPlus System was used as solvent.

Catalyst preparation

g-C_3N_4 and mpg-C_3N_4:g-C_3N_4 and mpg-C_3N_4 were prepared according to the literature method.[1]

M/g-C_3N_4 (M = Pt, Pd):In a typical experiment for Pt/g-C_3N_4 synthesis, g-C_3N_4 supported platinum was prepared by photo-deposition method.[2,3] g-C_3N_4 (100 mg) dispersion in H_2O (10 mL) was treated with K_2PtCl_4 (5.3 mg) in H_2O (40 mL) and the mixture was were stirred at room temperature overnight. Afterwards, triethylamine (TEA, 2 mL) was added to this suspension and the mixture was further stirred for 30 minutes. The suspension was then irradiated under a 210 W Xe lamp for 1 h with continuous stirring. The obtained precipitates were separated via centrifugation, washed thoroughly with distilled water and finally dried under vacuum at 60 °C overnight, yielding Pt/g-C_3N_4 (Pt 2.0wt%, based on ICP-AES). Pd/g-C_3N_4 was prepared following the same synthetic procedure as for Pt/g-C_3N_4 used.

M/g-C_3N_4 (M = Zn, Ni, Cu, Co, La, Ce):Metal-doped g-C_3N_4 was prepared following the method reported in literatures.[4,5] In a typical preparation of Zn/g-C_3N_4, dicyandiamide (1.0 g) and $ZnCl_2$ (0.1 g) mixed with deionized water (5 mL) was heated and stirred at 100 °C. The mixed solution was continually heated at 100 °C to remove water. The resulting yellow mixtures were then heated at 550 °C for 4 hours under flowing nitrogen atmosphere, followed by naturally cooling to room temperature under nitrogen gas.

Catalytic Performance

Photo-induced HMF reduction to DHMF: In a typical experiment, photo-catalyst Pt/g-C_3N_4 (30 mg, Pt 2.0wt%), HMF (13 mg, 0.1 mmol), TEA (0.5 mL) and water (4.5 mL) were added to a Pyrex reaction vessel. The mixture was irradiated under a visible light source using 210 W Xenon lamp (CEL-HXF300, Beijing Zhongjiaojinyuan Science Co. China, operated at 210 W) equipped with a 420 nm cut-off filter for four hours with continuous stirring. The temperature of the mixture was maintained at room temperature by a water bath during the reaction. The reaction was monitored by using high performance liquid chromatography (HPLC).

Analysis:HMF and the hydrogenation products were determined by HPLC (Shimadu LC-20AT) equipped with UV and refractive index (RI) detectors. The analysis was conducted with a Shodex Sugar SH-1011 column (300×8 mm) using HPLC grade H_2SO_4 (0.005 M) water solution as the eluent and a flow rate of 0.5 mL min^{-1} at a column temperature of 50 °C. The conversion of HMF was determined by a UV detector (284 nm); whereas, the concentrations of products such as DHMF, DHMTHF and hexanetriol (HT) were monitored by a RI indicator.

Characterization

The Brunauer-Emmett-Teller (BET) surface area measurements were performed with N_2 adsorption-desorption isotherms at 77 K (SI-MP-10/PoreMaster 33, Quantachrome). The samples were degassed under vacuum at 423 K for 24 hours before measurement; the specific BET surface areas were evaluated using the method in the p/p_0 range 0.05 to 0.3.

X-ray diffraction (XRD) patterns for the samples were recorded on a PANalytical X'pert Pro MPD diffractometer operated at 40 kV and 40 mA, using Ni-filtered Cu-Kα radiation.

X-ray photoelectron spectroscopy (XPS) spectra was performed with a Kratos AxisUltra (DLD) photoelectron spectrometer operated at 15 kV and 10 mA at a pressure of about 5×10^{-9} torr using Al Kα as the exciting source (1486.6 eV). C 1s photoelectron peak (BE = 284.2 eV) was used for the binding energy calibration.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed by means of a Perkin–Elmer Optima 8000 instrument.

High-resolution transmission electron microscopy (HRTEM) was recorded by using a JEM-2100HR instrument. Samples for HRTEM analysis were prepared by placing a drop of the suspension sample in ethanol onto carbon-coated Cu grids, followed by evaporating the solvent.

Room-temperature UV-vis diffuse reflectance spectroscopy (UV-vis DSR) was recorded on a Perkin Elmer Lambda 750 UV-vis spectrophotometer and $BaSO_4$ as the reference material.

References

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