

Reactivity enhancement of N-CNTs in green catalysis of C_2H_2 hydrochlorination by Cu catalyst

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Supporting Information

Experimental Sessions

CNT synthesis

The MWCNTs were produced by a fluidized bed CVD on Fe-based catalyst. The N-CNTs were synthesized on a Fe/Mo/vermiculite catalyst.²¹ The temperature of the reactor rose to 750 °C under the protection of Ar and H₂. C₂H₄ together with NH₃ was then introduced to realize the growth of CNT arrays. The typical flow rates of Ar, H₂, C₂H₄, and NH₃ were 250, 200, 100 and 100 sccm, respectively. The NCNT1 were produced with a similar procedure to NCNT, but with 60 NH₃ flow rate. The NCNT2 was obtained by treatment of MWCNTs with Azobisisobutyronitrile (abbreviated as AIBN): The mixture of 0.4 g purified MWCNTs, 8.0 g AIBN and 50 mL tetrahydrofuran were sonicated for 15 min and then transferred into the thermostatic water bath (50 °C) under stirring for 5 h. The mixture were then filtered by ethanol for 3 times and then dried for 24 h to obtain NCNT2.

All CNTs followed three purification cycles after the synthesis. Each cycle contained dispersion of CNTs in 6.0 mol·L⁻¹ HCl aqua solution for 24 h, filtration by deionized water, dispersion in 6.0 mol·L⁻¹ HF aqua solution and filtration by deionized water.

To obtain abundant oxygen functional groups, MWCNTs followed the treatment of mixing with 8 mol·L⁻¹ HNO₃ and 18 mol·L⁻¹ H₂SO₄, mild stirring at 90 °C for 4 hrs and filtration by deionized water.

The purified CNTs were dried at 120 °C over 12 h before further use.

Catalyst preparation

0.12 g CuCl₂·2H₂O was weighted and dissolved in the 100 mL deionized water; 0.30 g N-CNTs was then added into the solution under ultrasonic treatment for 2h; After good dispersion of CNTs in CuCl₂ solution, the mixture was centrifuged under 5000 r/min for 10 min. The solid in the bottom was dried under 90 °C for 8 h before evaluation or analysis.

Catalytic evaluation

The weighted 0.20 g samples were evaluated as follows: loaded into the quartz tube, dried under 10 sccm N₂ atmosphere at 120 °C for 10 min, activated under 10 sccm HCl atmosphere at 180 °C for 15 min, and reacted under the flow of C₂H₂ and HCl at 180 °C for 180 min ($Q_{\text{acetylene}} / Q_{\text{HCl}} = 1:1.1$). The GHSV was 180 h⁻¹ calculated by the value of $Q_{\text{acetylene}}$ (mL/min) / V_{CNTs} (mL), depending on the volume of the samples.

Characterization

High-resolution transmission electron microscopy (TEM, JEM 2010, at 120.0 kV) was used to determine the detailed structure of the CNTs and the tiny Cu NPs on the CNTs. The activity of catalyst was evaluated by the conversion of C₂H₂ collected at the outlet of reactor and the product was sampled per hour, with which analyzed via gas chromatography (GC, Tianmei, GC-7890T) to get the ratio of VC and residual C₂H₂. The column was selected from Beijing Analysis Instrument Co., limited with type of GDX-301. The elemental composition and

chemical state of the elements was analyzed by X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi, Al K α source). Auger Electronic Spectrom (AES, ULVAC-PHI-700) was assisted to distinguish the Cu species. Temperature Program Reduction (TPR, Quantachrome, The ChemBET PULSAR TPR / TPD) analysis was used to confirm the copper species in the catalyst in flowing of H₂ from 200 to 800 °C. X-ray Diffraction (XRD, D8 ADVANCE Diffractometer) was applied to reveal information about the crystal structure, chemical composition, and physical properties of the compositions. Fourier transform infrared spectroscopy (FTIR, Nicolet, NEXUS) was used to obtain surface functional groups with wave number ranging from 4000 cm⁻¹ to 660 cm⁻¹.

Table S1. Cu content in Cu-NCNT and Cu-MWCNT catalyst based on the XPS analysis

Sample name	Sample types	Content of Cu wt(%)
Cu-NCNT	Fresh one	5.43
	Reacted one	5.42
Cu-MWCNT	Fresh one	5.52
	Reacted one	5.50

Table S2. Cu content in Cu-NCNT1 and Cu-NCNT2 catalyst

Sample name	N content	Cu content*	Surface area (m ² ·g ⁻¹)
Cu-NCNT1	2.4	5.52	171
Cu-NCNT2	1.7	5.74	159

* The Cu content was derived from the analysis of ICP.

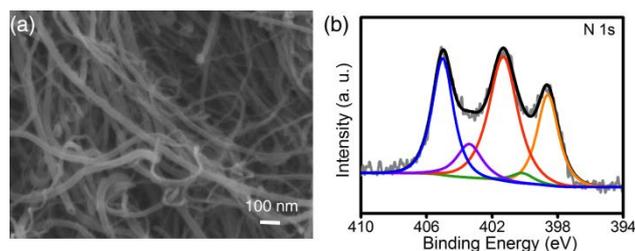


Figure S1. (a) SEM images of purified N-CNTs; (b) N 1s core-level spectrum of N-CNTs. Five N-C bond species were fitted corresponding to the pyridinic (398.3–399.8 eV), pyrrolic (400.1–400.5 eV), quaternary (401–402 eV), nitrogen oxide species (403.0–403.4 eV) and chemisorbed N (404.0–405.6 eV).

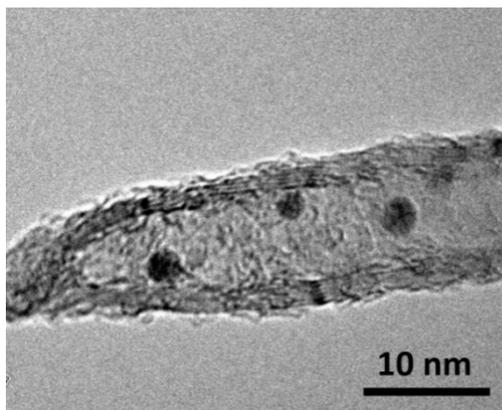


Figure S2. TEM image of the Cu-MWCNT

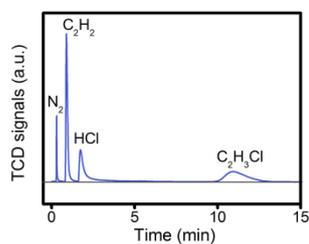


Figure S3. The typical detection curve of the gas chromatography, showing no by-product detected within the limit of detection.

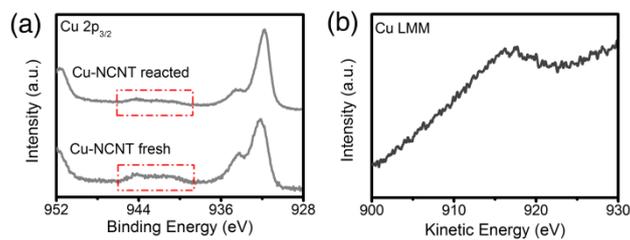


Figure S4. (a) XPS spectrum of fresh and reacted Cu-NCNT, the visible shake-up satellite peak was to distinguish the existence of Cu²⁺ but no Cu⁰ species; (b). The Cu LMM Auger transitions to distinguish the existence of Cu⁺ but no Cu⁰ species.

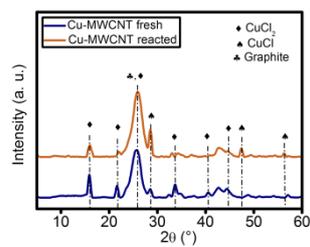


Figure S5. XRD patterns of the fresh and reacted Cu-MWCNT.

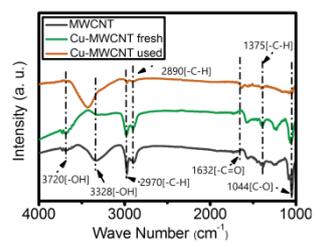


Figure S6. FTIR spectra of the MWCNTs, fresh and reacted Cu-MWCNT catalysts.

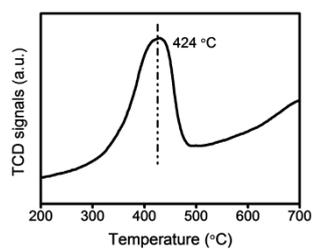


Figure S7. TPR spectrum of fresh Cu-MWCNT catalyst.

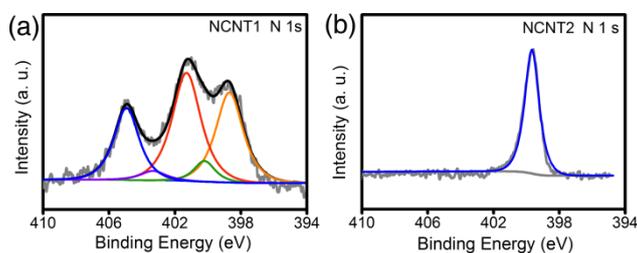


Figure S8. N 1s XPS spectra of (a) NCNT1 and (b) NCNT2.