

Ultra-low Ru-Promoted CuCl₂ as Highly Activity Catalyst for the Hydrochlorination of Acetylene

JiangtaoXu, Jia Zhao, Tongtong Zhang, Xiaoxia Di, ShanchuanGu, Xiaonian Li*

Industrial Catalysis Institute of Zhejiang University of Technology, State Key
Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Hangzhou,
310014, P.R. China

* Corresponding author. Tel: +86 571 88320002. E-mail address: xnli@zjut.edu.cn

Supporting Information

Experimental Sessions

Catalyst preparation

A commercially multiwall carbon nanotubes (MWCNTs) were purchased from Shenzhen Nanoport Company and selected for the preparation of support. The MWCNTs were first pretreated with HNO₃ (65 wt%) at room temperature for 1 h. Then the pre-treated MWCNTs were filtered, washed with deionized water until pH = 7 and then dried at 110 °C for 12 h.

Bimetallic Cu-Ru/MWCNTs catalysts were prepared using impregnation technique. The Cu and Ru precursors, RuCl₃ aqueous solution and CuCl₂·2H₂O was first dissolved in *aqua regia* and the solution was added dropwise to the pre-treated MWCNTs support under ultrasonic treatment for 2h. After good dispersion of MWCNTs in CuCl₂ and RuCl₃ solution, The solid in the bottom was dried under 90 °C for 8 h before evaluation or analysis. Cu nominal loading in all the catalysts was fixed at 6.0 wt% at various Ru loading, namely, 100, 200, 400, and 600 ppm, and were denoted as Cu100Ru/MWCNTs, Cu200Ru/MWCNTs, Cu400Ru/MWCNTs, and Cu600Ru/MWCNTs, respectively. The same procedure was also followed to prepare the corresponding Cu/MWCNTs and Ru/MWCNTs catalysts for comparison.

Catalyst characterization

The sizes of particles on samples were also observed by a scanning transmission electron microscope (STEM, Tecnai G2 F30 S-Twin, 300 kV). The solid samples were finely ground. The resultant fine powders were dispersed ultrasonically in the ethanol and were then loaded on a copper grid (Beijing Zhongjingkeyi Technology Co.,

Ltd.).

X-ray Diffraction (XRD) was applied to reveal information about the crystal structure, chemical composition, and physical properties of the compositions and were performed on a PANalytical-X'Pert PRO generator with Cu K α radiation ($\lambda = 0.1541$ nm).

Temperature-programmed reduction (TPR) experiments were performed to examine the reducibility of the catalysts on a micro-flow reactor fed with a flow of hydrogen (10% in Ar) at a rate of 45 ml min⁻¹. The weight of the tested samples was (about) 75 mg. The temperature was increased from 30 to 850 °C at a rate of 10 °C min⁻¹. The hydrogen consumption was measured using a thermal conductivity detector.

Catalytic test

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass microreactor (i.d. 10 mm). Acetylene (10 mL min⁻¹, 1 bar) and hydrogen chloride (12 mL min⁻¹, 1 bar) were fed through a mixing vessel via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), with a total GHSV (C₂H₂) of 180 h⁻¹. A reaction temperature of 180 °C was chosen, blank tests using an empty reactor filled with quartz wool did not reveal any catalytic activity, and quartz sand was used to extend the bed length, above and below the catalyst itself, separated by quartz wool. The gas phase products were passed through an absorption bottle containing NaOH solution to remove excess HCl first and then analysed on-line by GC equipped with a flame ionisation detector (FID). Chromatographic separation and

identification of the products was carried out using a Porapak N packed column. The conversion of acetylene and the selectivity to VCM were calculated by Eqs.(1)-(2), as follows:

$$\text{Acetylene conversion (\%)} = \left(1 - \frac{F_A}{F_{A0}}\right) \times 100\% \quad (1)$$

$$\text{VCM Selectivity (\%)} = \frac{F_{\text{VCM}}}{1 - F_A} \times 100\% \quad (2)$$

Where F_{A0} , F_A , and F_{VCM} represent the volume fraction of acetylene in the raw gas, the volume fraction of remaining acetylene, and the volume fraction of vinyl chloride in the product mixture gas, respectively.

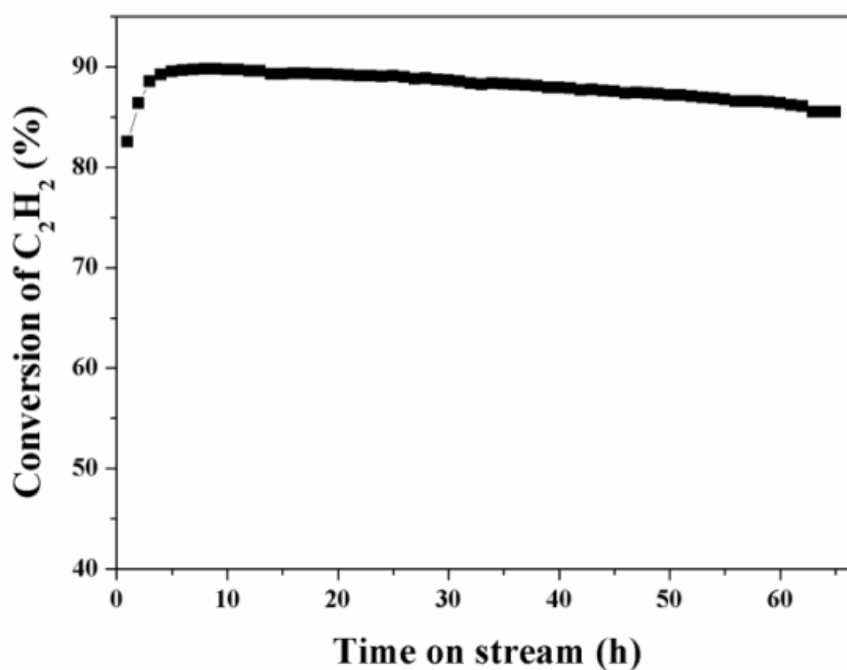


Fig. S1 Long-term stability test of Cu400Ru catalyst. Reaction conditions: temperature (T) = 180 °C; GHSV(C₂H₂) = 30 h⁻¹; feed volume ratio V(HCl)/V(C₂H₂) = 1.2.

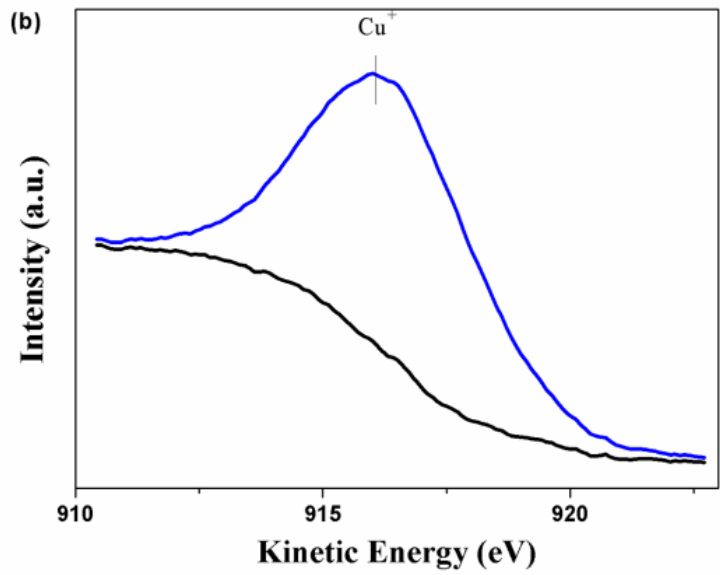
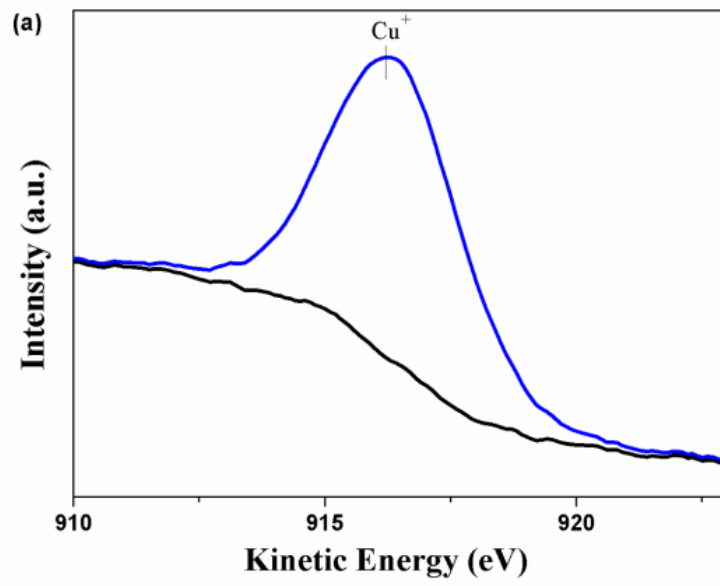


Fig. S2 The Cu LMM Auger transitions of Cu/MWCNTs(a) and Cu₄₀₀Ru/MWCNTs(b) to distinguish the existence of Cu⁺ but no Cu⁰ species.