

Reactivity enhancement of N-CNTs in green catalysis of C₂H₂ hydrochlorination by a Cu catalyst†

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We reported the prominent effect of nitrogen-doped carbon nanotubes (N-CNTs) on reactivity enhancement in catalyzing acetylene hydrochlorination, which improved the TOF of Cu to ca. 1.2 min⁻¹, proving that N-CNTs is a potential green substrate, and that the Cu-based catalyst is an alternative to the toxic conventional HgCl₂ catalyst.

Acetylene hydrochlorination is a very important reaction for polyvinylchloride (PVC) synthesis following the reaction: C₂H₂ + HCl → CH₂=CHCl, Δ*H* = -124.8 kJ mol⁻¹. Conventionally, heterogeneous catalyst HgCl₂ was used to catalyze the addition reaction of HCl to acetylene for the production of vinyl chloride monomer (VCM).^{1,2} It has over 10 million tonne production capacity annually at present in China. Unfortunately, the HgCl₂ vapor released into the environment easily accumulates in the creatures and causes chronic poisoning, which is severely harmful to human beings and environment. To meet the demand of sustainable development for the whole of society,³ increasing attention has been paid to this process. Therefore, searching promising catalysts for acetylene hydrochlorination to be environmentally friendly and low-emission process is a topic of increasing interest and importance. Hutchings' group firstly correlated the catalytic activity of metals in the form of metal chlorides, finding out the positive relationship between the reactivity and electronegativity.⁴ Accordingly, catalysts like Au-C,⁵⁻⁹ CuBi-SiO₂¹⁰ and AuCu-C¹¹ were reported as potential mercury-free catalysts. Generally, the design of novel catalysts is aiming to possess prominent reactivity and long lifespan, thus optimization of the catalysts is mainly focused on active components, such as adding copper into Au catalyst or adding oxidizing gas like NO to eliminate the inactivation.¹² However,

comparing to the comprehensive study of the active components, the understanding of the substrates' effect in reactivity promotion was scarce and not thoroughly studied.

The morphology and size of carbon nanotubes (CNTs) are an advantageous substrate since most of the metal particles are expected to be exposed and functionalized as effective catalysts, as well as reducing the mass transfer resistance in diffusion, suggesting their potential use in heterogeneous catalysis.¹⁶ Hence, employing CNTs as the substrate realizes the design to enhance the interaction with active components and allows a promoted catalytic reactivity.^{3,13-15} Considering the application in catalysis, the pristine CNTs containing purely hexagonal carbon networks are mainly inert. Fortunately, the chemical properties can be easily tailored by heteroatom functionalization on nanocarbon sheets or molecular carbon geometries at the edges or defects, *etc.* For instance, the presence of N in CNTs enhanced the immobilization of the Pt or Pt-Co alloyed nanoparticles (NPs), and the catalysts performed high catalytic activity and stability for the oxygen reduction reaction (ORR),^{17,18} or cinnamyl alcohol reaction.¹⁹ Since metal NPs play a major role to convert the reactants, the impact of appropriate substrates to promote catalytic performance shall not be ignored. For instance, acting as the gold catalyst substrates for hydrochlorination, carbon has much better activity promotion effect than silica, metal oxides and zeolites due to its good electron conductivity and high specific surface area. Likewise, the presence of N atoms in the CNTs tunes the electron affinity and improves the wetness and hydrophilicity of CNTs accordingly, supporting a new idea to employ it as one active substrate for mercury-free hydrochlorination.

Based on this consideration, we explored one novel catalyst, that was copper chlorides NPs loaded on the nitrogen-doped carbon nanotubes (N-CNTs) for acetylene hydrochlorination and named it as Cu-NCNT. Cu, featured in low toxicity, acceptable catalytic activity, easiness to obtain, low cost and good thermo-stability, was selected as the active element.⁴ Tested under the evaluation conditions of 180 h⁻¹ (gas hourly space velocity, GHSV, C₂H₂ based) and 180 °C, the catalyst

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loading 5 wt% Cu performed impressively 45.8% conversion of C_2H_2 , *i.e.* 1.2 min^{-1} of turn over frequency (TOF). The TOF value was fairly high among the Cu-based catalysts, corresponding roughly to 10 times of that supported on the N-free CNTs (TOF of 0.10 min^{-1}). The significant difference in reactivity proved the effect of N dopants in tuning the electron affinity of CNTs, enhancing the interaction between N-CNTs and Cu NPs, and further facilitating the hydrochlorination. Besides, the increasing of N content in the CNTs' sheets promoted the reactivity of Cu catalysts significantly. As a result, N-CNTs was thought to be a potential but high-effective green substrate.

N-CNTs were synthesized by chemical vapor deposition (CVD) method, and purified with HF and HCl aqueous solutions for further employment as the substrate.^{20,21} The synthesized N-CNTs showed the features of cup-stacked structure altered by doping of N atoms, the outer diameter around 20 nm in average and $174 \text{ m}^2 \text{ g}^{-1}$ of the surface area (Fig. S1a†). X-ray photoelectron spectroscopy (XPS) revealed a nitrogen content of 2.4% (Fig. S1b†). In preparation, the tiny $CuCl_2$ NPs ($d_{\text{mean}} = 2.35 \text{ nm}$, $\sigma = 0.46$, Fig. 1a and b) could be synthesized and dispersed uniformly on the N-CNTs *via* impregnation method, which was abbreviated as Cu-NCNT. The similar catalyst abbreviated as Cu-MWCNT was derived similarly by employing the oxygen-rich multi-walled carbon nanotubes (MWCNTs, $d_{\text{mean}} = 18 \text{ nm}$, $195 \text{ m}^2 \text{ g}^{-1}$ of the surface area) as the substrate. The structure of Cu-MWCNT was shown in Fig. S2.† The content of Cu in both Cu-NCNT and Cu-MWCNT was quantified to be approximately 5.8 wt% according to inductively coupled plasma (ICP) shown in Table 1. As a reference, XPS was also applied to quantify the Cu content and its data had no more than 5% error with ICP data (The content of Cu in Cu-NCNT and Cu-MWCNT was shown in Table S1†).

The activity of hydrochlorination was evaluated under the conditions of $180 \text{ }^\circ\text{C}$ and 180 h^{-1} of gas hourly space velocity (GHSV, C_2H_2 based) over 180 min. Cu-NCNT and Cu-MWCNT accompanying with pure N-CNTs and MWCNTs were all taken part in the evaluation. The conversion of C_2H_2 was defined as the volume ratio of CH_2CHCl in the outer mixture of CH_2CHCl and C_2H_2 . As shown in Fig. 2a, Cu-NCNT had best performance

Table 1 Cu content in Cu-NCNT and Cu-MWCNT based on the ICP analysis

Sample name	Sample types	Content of Cu (wt%)
Cu-NCNT	Fresh one	5.84
	Reacted one	5.63
Cu-MWCNT	Fresh one	5.86
	Reacted one	5.83

among the tested samples with an initial conversion of 45.8% and stabilized around 43.5%, while Cu-MWCNT only had about 4.0% conversion. The selectivity of CH_2CHCl in Cu-NCNT was over 98% according to the spectrum of thermal conductivity detector (TCD) shown in Fig. S3.† VCM was detected as the main product and only minor 1, 1-dichloroethane, *trans*-1, 2-dichloroethylene less than 0.5% was measured. The test method of the selectivity was the same as that in the former work, which was abbreviated here.¹⁰ Interestingly, N-CNTs had the similar reactivity with the Cu-MWCNT, while no conversion was detected in MWCNTs. The reactivity analysis indicated two roles the N-CNTs played in the reaction, one providing anchoring sites for Cu NPs and the other catalyzing the reaction themselves as active components, and the former one was dominant. Therefore, we speculated that the acetylene hydrochlorination preferred to take place in the binding sites of Cu and N, and the schematic diagram was shown in Fig. 2c, more details of which would be stated subsequently. To compare the capacity of chlorinating C_2H_2 into VCM, the reactivity of the metal-based catalysts (including Au, Hg, Zn and Ba) and the Cu-based catalysts on the different substrates (C, MWCNTs), as well as the Cu-NCNT catalyst was drawn in Fig. 2b. The TOF of Cu-NCNT was approximately 5 and 10 times higher than that of Cu-C and Cu-MWCNT, and the value was very close to that of the Hg-C and Au-C catalysts though the Cu had far lower electronegativity than the Hg and Au.⁴ Being especially more active than

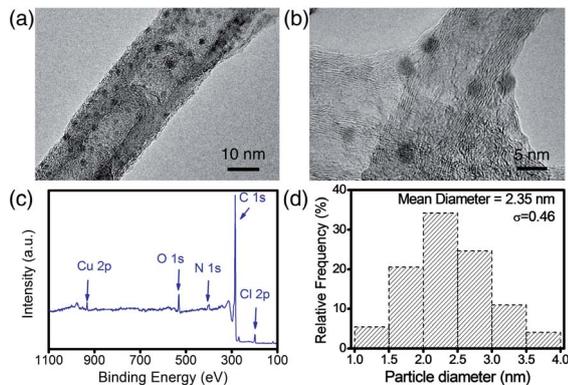


Fig. 1 (a) and (b) TEM images of the fresh Cu-NCNT; (c) XPS spectrum of Cu-NCNT: The catalyst contains elements of C, N, O, Cu and Cl. (d) The statistics of nanoparticles diameter: the average diameter is 2.35 nm.

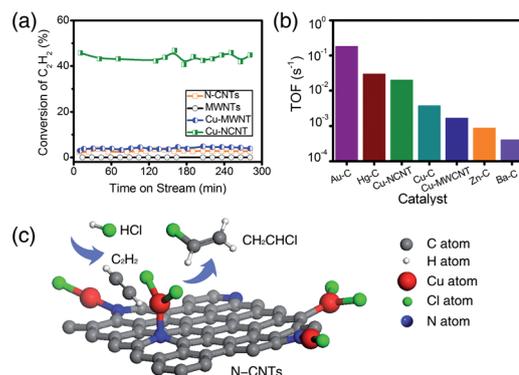


Fig. 2 (a) The reactivity evaluation of the catalysts: Cu-NCNT, Cu-MWCNT, N-CNTs and MWCNTs ($T = 180 \text{ }^\circ\text{C}$, $GHSV = 180 \text{ h}^{-1}$, $Q(HCl)/Q(C_2H_2) = 1.1 : 1.0$); (b) the TOF value for the different catalysts: Au-C,⁷ Hg-C,²² Cu-NCNT, Cu-C,²³ Cu-MWCNT, Zn-C and Ba-C. (c) The schematic diagram of acetylene hydrochlorination catalyzed by Cu-NCNT.

Zn or Ba, greener than Hg, and cheaper than Au, Cu-NCNT realized the significant advantages in green catalysis as an alternative route to produce vinyl chloride. The employment of N-CNTs in the hydrochlorination improved our understanding to the substrate role, which was, C substrate supplied a place to promote the metal NPs dispersion and loading, and accelerated the reactivity of the metal NPs.

To understand the active species in Cu-NCNT and the promoting effect of the N-CNTs, XPS and Fourier transform infrared spectroscopy (FTIR) were applied. The oxidation states of Cu species were determined by the analysis of Cu $2p_{3/2}$ electronic transitions and the Cu LMM Auger transitions. A shake-up satellite peak located higher than the Cu $2p_{3/2}$ transition was used to differentiate Cu^{2+} species and reduced copper.²⁴ The distinction between the Cu^+ and Cu^0 species was characterized through examination of the Auger kinetic energy (KE) (see in Fig. S4†). According to the data, the Cu-NCNT had peak at 917.0 eV with no visible one around 918.0 eV, suggesting the presence of Cu^+ but no metallic copper species.^{25,26} As Fig. 3a shows, both fresh and reacted catalyst possessed two peaks at around 932.0–932.2 eV and 934.4–934.5 eV, which was thought to be the existence of mixed valence state of copper with different ratio. The binding energy of Cu species was slightly lower than the standard values, assumed to be the electron transfer between the Cu and substrate. XRD patterns also demonstrated that the catalyst only had two Cu-related substances of CuCl and CuCl₂, which were illustrated in Fig. 3b. The conversion preserved stable while the valence of copper transformed easily during the evaluation, suggesting the similar reactivity of the two species. That coincided with the reported conclusions previously.⁴ As a reference, the Cu-MWCNT had similar XRD patterns (see in Fig. S5†), but showing entirely different catalytic behavior, which pointed the confusion to the features of the substrate. To explain the difference, FTIR spectrums were well studied shown in Fig. 3c and S6.† The absorbance at 3720 cm^{-1} and 1044 cm^{-1} was attributed to the –OH and –CO respectively, while the one at 2327 cm^{-1} was thought to be –CN. As the FTIR spectrums shown, the CNTs surface had abundant oxygen functional groups, proving the hydrophilic

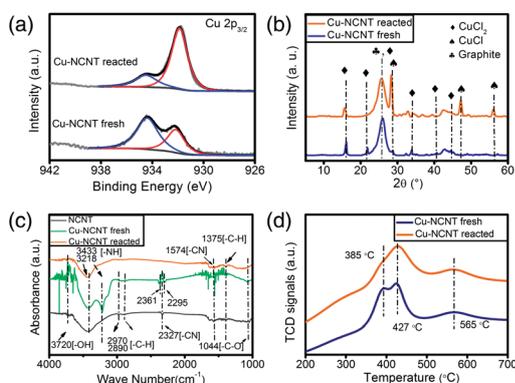


Fig. 3 (a) XPS spectrums of the Cu $2p_{3/2}$ in fresh and reacted Cu-NCNT catalyst; (b) XRD patterns of the fresh and reacted Cu-NCNT; (c) FTIR spectrums of the N-CNTs, fresh and reacted Cu-NCNT catalyst; (d) TPR spectrums of fresh and reacted Cu-NCNT catalyst.

surface and convenience for NPs anchoring; differently, the absorbance of –CN in Cu-NCNT was strongly enhanced and split into two peaks while no notable enhancement occurred in Cu-MWCNT, indicating the enhanced interaction of Cu with –CN rather than oxygen-containing functional groups. It should be noted that the disappearance of the enhancement in the FTIR spectrums of the reacted Cu-NCNT should be attributed to the coverage of reactant and products adsorbed on the related functional groups. The temperature program reduction (TPR) analysis also proved the speculation for the interaction. As shown in Fig. 3d, the strong peak of H₂ consumption attributed to Cu^{2+} and Cu^+ (389 and 427 °C) was 4 °C and 7 °C higher than the standard consumption peaks (385 °C and 420 °C)²⁷ respectively, while the peak indicated to Cu^+ in Cu-MWCNT had weaker shift shown in Fig. S7,† suggesting the stronger interaction of Cu and N-CNTs than the Cu and MWCNTs.

Overall, it was proved that the presence of N species could improve the reactivity of the copper significantly due to the enhanced interaction of the Cu and N-CNTs. However, the N-poor MWCNTs had no such role in this reaction.

To gain new insights on the correlation between N content in N-CNTs and the reactivity, another two Cu-NCNT samples were synthesized as control samples in the name of Cu-NCNT1 and Cu-NCNT2. NCNT1 was synthesized following the same procedure of NCNT, but had lower N content (1.7%). NCNT2 were available by self-decomposition of azodiisobutyronitrile on MWCNTs to form cyano-like groups. Two samples' related information can be found in the Table S2 and Fig. S8.† The reactivity test shown in Fig. 4a indicated that the conversion (from ca. 43% to ca. 30%) decreased as the N content (from ca. 2.4% to ca. 1.7%) decreased. Interestingly, increasing the N content on the CNTs' surface functional groups had no clear reactivity promotion, which had nearly the same conversion of the Cu-MWCNT. The fact revealed that the dopants of N in the carbon sheets were effective for the reactivity enhancement, while the surface modification of N-related functional groups had little positive effect. That might rely on the different tuning ability of electron conductivity between doping and surface modification. Correlating the conversion of C₂H₂ and N content in 3 catalysts (Cu-MWCNT, Cu-NCNT1 and Cu-NCNT), we found that the two had a positive correlation. As the N content in the carbon sheets of CNTs increased, the reactivity of Cu catalysts increased as shown in Fig. 4b. The increasing of N content promoted the reactivity of Cu-NCNT catalysts.

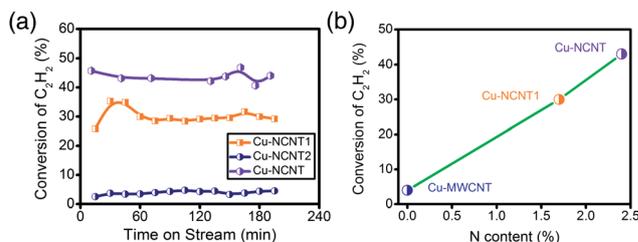


Fig. 4 (a) The reactivity evaluation of the catalysts: Cu-NCNT, Cu-NCNT1 and Cu-NCNT2 ($T = 180$ °C, $GHSV = 180$ h^{-1} , $Q(HCl)/Q(C_2H_2) = 1.1 : 1.0$); (b) the relationship between the conversion of C₂H₂ and N content in 3 catalysts (Cu-MWCNT, Cu-NCNT1 and Cu-NCNT).

Conclusions

In summary, the N-CNTs has been successfully applied as green catalyst substrate for sustainable hydrochlorination, and performs prominent reactivity promotion in Cu-NCNT catalyst. The doping of N in N-CNTs significantly improves electron conductivity ability of the carbon sheets, interaction between Cu and N-CNTs and further adsorption of C₂H₂ on the catalyst surface, contributing to high activity and excellent CH₂CHCl selectivity. The increasing of N content in the CNTs' sheets promoted the reactivity of Cu catalysts significantly. The active components were thought to be the mixture of Cu⁺ and Cu²⁺, which had the similar reactivity, supporting the good and stable conversion during the reaction. Corresponding to the commonly used Hg-based catalysts, the Cu-NCNT catalyst (2.4% N) offers promoted reactivity for sustainable hydrochlorination with a TOF value of 1.2 min⁻¹ based on Cu. Such a system offers opportunities for efficient mercury-free catalysis.

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