

Nitrogen-Modified Activated Carbon Supported Cu(II)Cu(I)/NAC Catalysts for Gas–Solid Acetylene Dimerization

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Abstract

Improving dispersibility and stability of Cu(II)Cu(I)/activated carbon (AC) is a crucial aspect for enhancing its catalytic performance in the process of gas–solid acetylene dimerization. The Cu(II)Cu(I)/NAC-500 catalyst using nitrogen-modified AC (NAC) as a support, delivered excellent catalytic performance and stability *vs* undoped Cu(II)Cu(I)/AC at 100 °C and 120 h⁻¹ of C₂H₂ gas hourly space velocity. Under the optimal conditions, the Cu(II)Cu(I)/NAC-500 catalyst exhibited a stable catalytic performance during a 10 h test with 65% C₂H₂ conversion; and the selectivity to monovinylacetylene (MVA) reached 86%. The existence of nitrogen species can increase the interaction between copper and the support, and increase dispersion of the copper species on the support, which were benefit for the catalytic performance.

Graphic Abstract



Keywords Nitrogen-modified \cdot Urea \cdot Gas-solid reaction \cdot Acetylene dimerization \cdot Cu(II)Cu(I)/AC \cdot Activated carbon

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1 Introduction

Monovinylacetylene (MVA) is produced as a starting material for chloroprene rubber synthesis and can be used as a raw material in producing other important chemical products such as butanedione through hydration [1] and benzene via polymerization with acetylene [2]. The representative catalyst in acetylene dimerization is Nieuwland catalyst (NC), which is comprised of CuCl and KCl or NH_4Cl in acid solution [3]. Studies include the solvent effect [4], mechanism [5], the NC structure [6], ligand modification [7, 8], kinetics [9], and metal additives on gas–liquid C_2H_2 dimerization with NC [10, 11] have been reported. However, the short-comings of these processes, such as low acetylene conversion and MVA selectivity, more polymers produced and difficult to separate and recycle, still exist in gas–liquid C_2H_2 dimerization.

Recently, we have reported the synthesis of a Cu/AC catalyst and evaluated it for gas-solid reaction for C2H2 dimerization [12]. Compared with the traditional C₂H₂ dimerization reaction, the Cu/AC catalyst has better activity with 48.3% C₂H₂ conversion and 87.4% selectivity to MVA. This prior work solved several drawbacks of traditional gas-liquid NC-catalyzed C₂H₂ dimerization reactions. However, the main reason for catalyst deactivation is the loss of copper active species. In order to increase the catalyst's activity and overcome the loss of copper active species on Cu(I)/AC catalysts for gas-solid C₂H₂ dimerization reactions, we then prepared Cu(II)Cu(I)/AC with different Cu⁺/Cu²⁺ ratios and analyzed the synergistic effects of both Cu^{2+} and Cu^{+} [13]. As expected, the results achieved the desired effect, which showed that the addition of Cu(II) could inhibit Cu loss in the catalysts. However, the dispersibility and stability of the Cu(II)Cu(I)/AC require further improvements. For example, the acetylene conversion of Cu(II)Cu(I)/AC decreases from 79 to 58% after running for 10 h.

It is well known that the interactions between the support and catalyst play an important role in governing the catalyst's particle size. In general, nitrogen-modified supports strategy are often used for this purpose. The literature reports that nitrogen introduced into the AC support affects catalyst activity at least three aspects [14]. First, it can increase catalyst particle dispersion and decrease catalyst particle size during the nucleation and growth process of catalyst nanoparticles. Then, the nitrogen atoms in the AC supports are believed to provide improvement of the nucleation rate of active species particles [15, 16] and higher nucleation rates increase the surface defects [17]. Third, increasing chemical binding between the support and catalyst results in enhanced stability of the catalysts. The nitrogen functionalities act as chemical binding sites and increase the bonding strength of the active ingredient and the carrier, which, in turn, increases the catalytic activity by increasing the dispersion of active species by providing resistance to particle agglomeration [15].

Zhou et al. [18] reported Cu-based catalysts supported on N-doped carbon nanotubes significantly improved the electron conductivity ability of the carbon sheets. The N1s spectra of N-doped activated carbon-containing materials usually indicate the existence of multiple nitrogen-containing species [19]. These N species usually stabilize catalyst nanoparticles [20] and generate favorable nucleation sites for reaction [21]. Doping ways and/or preparation conditions may affect the composition and distribution of N substances [22], and thus we wondered if N modification of AC can also enhance the activity and dispersibility of the gas–solid acetylene dimerization.

In this work, we incorporate nitrogen into the AC support via post-treatment method with urea to introduce nitrogen functional groups in AC that yield the corresponding nitrogen-modified activated carbon (NAC) supports. These materials were heaved at different temperatures, and then the gas–solid acetylene dimerization was studied over these Cu(II)Cu(I)/NAC catalysts.

2 Experimental

2.1 Preparation of N-Doped AC Catalyst

A coconut-shell-activated carbon was used as the starting material. This material was initially washed with 1 mol L^{-1} HCl at the temperature of 70 °C for 5 h, filtered, washed with distilled water, and dried at 150 °C for 12 h (labeled AC).

A mixture of AC (5 g), glacial acetic acid (3 mL 37%), and distilled water (20 mL) was stirred for 2 h. Urea (3 g) was then added to the solution and stirred for another 2 h at room temperature in the dark. The solution was evaporated to dryness at 100 °C and calcined at 500 °C (heating rate: $5 °C min^{-1}$) under a N₂ atmosphere for 1 h. The resulting sample was labeled as NAC-500. Samples with other calcination temperatures were named NAC-300 and NAC-700. The preparation of the Cu(II)Cu(I)/NAC catalyst is shown in Supplementary Fig. S1.

EtNH₂·HCl (3.83 g) was dissolved in mixed solvent containing 1,4-dioxane (3 mL) and DMF (7 mL) at 80 °C water bath. CuCl was then added to the solution with stirring under N₂ atmosphere. The NAC-500 was added into the above mixture until the CuCl was completely dissolved. The mixture was then stirred for 2 h, cooled to 25 °C and stirred for another 12 h, filtered, and dried in vacuum oven at the temperature of 80 °C for 12 h to produce Cu(I)/NAC-500. The CuCl₂ aqueous solution (3.24 g CuCl₂ in 10 mL distilled water) as an addition was added to the Cu(I)/NAC-500 powder with stirring for 12 h at 25 °C. Subsequently, the mixture was filtered and dried in vacuum oven for 12 h at 80 °C to obtain the Cu(II)Cu(I)/NAC-500 catalyst with a Cu⁺/Cu²⁺ molar ratio of 1:0.3. The copper loading of all catalysts was based on metallic copper.

2.2 Description of Analytical Methods and Catalytic Tests

A fixed-bed micro reactor (i.d., 10 mm) was used to evaluate the activity of the catalysts. N₂ was used to pass into the pipeline to clear away air before starting the reaction. C_2H_2 (4.0 mL min⁻¹) was pumped into the fixed-bed micro reactor filled with 2 mL of catalyst to achieve a C_2H_2 gas hourly space velocity (GHSV) of 120 h⁻¹, and the reaction temperature was increased to 100 °C. A gas chromatograph (Shimadzu, GC-2014C) was used to analyze the composition of the reaction products. The evaluation criteria of the catalytic performance was the acetylene conversion (X) and selectivity to MVA (S). The following equation was used to calculate the X and S:

$$X = [(\alpha_2 + 2\alpha_3 + 2\alpha_4 + 3\alpha_5)/(\alpha_1 + \alpha_2 + 2\alpha_3 + 2\alpha_4 + 3\alpha_5)] \times 100\%$$

 $S = [2\alpha_3/(\alpha_2 + 2\alpha_3 + 2\alpha_4 + 3\alpha_5)] \times 100\%$

The α_1 , α_2 , α_3 , α_4 , and α_5 are respectively represented volume fractions of acetylene, acetaldehyde, MVA, 2-chloro-1,3-butadiene, and 1,5-hexadien-3-yne (DVA) in the gas products.

2.3 Catalyst Characterization

X-ray diffraction (XRD) was tested by X-ray diffractometer (Bruker D8 ADVANCE) with a Cu Ka radiation (0.1542 nm) in the 2 θ scanning range 10° – 90° . Transmission electron microscopy (TEM) images were carried out a JEM2100F (FEI, Hillsboro, OR, USA) instrument. Temperature-programmed reduction (TPR) tests were recorded a Micromeritics ASAP 2720 instrument. The temperature was increased from 25 to 900 °C with 80 mL min⁻¹ 10% H₂/Ar. The thermogravimetric analysis (TG) of the catalysts used a NETZSCH STA 449F3 Jupiter instrument, and the temperature increased from 25 to 900 °C in an air atmosphere. The specific surface areas of the samples were determined by Brunauer-Emmett-Teller (BET) analysis. X-ray photoelectron spectroscopy (XPS) were collected using a Kratos AMICUS spectrometer (Shimadzu, JP). Raman spectra was recorded using a Horiba Jobin Yvon LabRAM HR800 (633 nm laser excitation).

3 Results and Discussion

3.1 Catalytic Performance of the Catalysts for Acetylene Dimerization

Supplementary Fig. S2a, b shows the activity of catalysts on NAC-300, NAC-500, and NAC-700. Supplementary Fig. S2c, d presents the catalytic performance of the undoped Cu(II)Cu(I)/AC and N-doped Cu(II)Cu(I)/NAC-500. As we can see, Supplementary Fig. S2a, b shows that Cu(II)Cu(I)/ NAC-500 (with 14.17% of Cu in total measured by ICP-AES) had the best performance among the tested catalysts with a conversion that stabilized around 65%; the selectivity to MVA was 86%. In comparison, the acetylene conversion of Cu(II)Cu(I)/AC decreases from 79 to 58% after running for 10 h. The selectivity to MVA was 77% indicating that Cu(II)Cu(I)/AC is rapidly deactivated under these reaction conditions. This reveals that nitrogen-modified AC supports obviously affect the activity and stability of the catalysts.

3.2 Raman Spectroscopy

Raman spectroscopy characterized the ordered and disordered structures of the prepared nitrogen-modified AC. The Raman spectra (Fig. 1) of AC, NAC-300, NAC-500, and NAC-700 had two distinct peaks near 1590 and 1350 cm⁻¹, which are ascribed to the G-band and the D-band, respectively [23]. The D band corresponds to the carbon disorder and defective structures, and the G band refers to the graphitic structure. The I_D/I_G ratios increases as the calcination temperature increases. This result indicates that nitrogenmodified AC can increase the degree of disorder and the number of surface defects [24]. Physical surface defects often increase the nucleation rate [25], which increase the catalyst's particle dispersion.

3.3 Dispersion and Sintering of Cu Species

Narrower size distributions and smaller Cu particles have been observed on nitrogen-modified AC even with relatively high copper loadings suggesting that surface defects can nucleate Cu particles more uniformly (Supplementary Fig. S3). During catalyst nanoparticle deposition, nitrogenmodified AC can be modify the nucleation and growth [14]. This results in smaller catalyst particles and increased catalyst particle dispersibility.

Supplementary Fig. S4 displays the obtained XRD of AC, NAC-500, Cu(II)Cu(I)/AC, and Cu(II)Cu(I)/NAC-500. XRD patterns show that there is no obvious Cu characteristic



Fig. 1 Raman spectra of AC, NAC-300, NAC-500, and NAC-700

peaks in the catalysts except for amorphous diffraction peaks of activated carbon (JCPDS 75-1621) [26]. This is ascribed to the high dispersibility of the Cu species or that content of Cu is too low to be detected in XRD [27].

The H₂-TPR profiles of undoped Cu(II)Cu(I)/AC and N-doped Cu(II)Cu(I)/NAC-500 catalysts are shown in Fig. 2. The Cu(II)Cu(I)/AC showed three peaks with lower temperature peaks appearing at 361 and 456 °C, respectively; a high temperature peak appeared at 784 °C (the H₂-TPR data of Cu(II)Cu(I)/AC was from our previous work [13]). The reduction of Cu(II)Cu(I)/NAC-500 showed three peaks with higher temperature peaks appearing at 379 and 496 °C, respectively, and a high temperature peak appearing 806 °C. The TCD signal at 700–850 °C may be the combustion gas from activated carbon [28, 29]. The Cu(II)Cu(I)/NAC-500 catalyst showed reduction peaks at the highest temperature indicating a relatively stronger interaction between active components and carrier [30].

3.4 Valence Changes of the Active Species

The XPS results detail the elemental compositions (Fig. 3a). The peaks near 284.8, 399.5, and 531.7 eV are ascribed to the binding energy of C1s, N1s, and O1s, respectively [31]. Supplementary Table S1 indicates the presence of nitrogen species and nitrogen content of 3.0 wt% for Cu(II)Cu(I)/NAC-500 sample. Figure 3a shows that nitrogen was successfully doped into AC. There were three kinds of nitrogen, binding energies of pyridinic nitrogen, pyrrolic nitrogen and quaternary nitrogen were at 398.6, 400.4, and 401.2 eV, respectively (Fig. 3b) [32, 33]. Supplementary Fig. S5 shows the relative contents of nitrogen species of the N-doped samples. The NAC-300 has the least pyridinic nitrogen (10.4%). It is clear that the pyridinic nitrogen is the dominant nitrogen



Fig.2 $H_2\text{-}TPR$ profiles of undoped Cu(II)Cu(I)/AC and N-doped Cu(II)Cu(I)/NAC-500 catalysts

species in NAC-500 and NAC-700. The NAC-500 sample has the highest amount of pyridine nitrogen (58.9%), which indicates that the N species is dependent on the calcination temperature [34]. Pyridinic nitrogen is the main nitrogen species on NAC samples (Fig. 3c). Figure 3d showed the XPS spectra (the Cu 2p data of Cu(II)Cu(I)/AC was from our previous work [13]) of nitrogen-doping Cu(II)Cu(I)/ NAC-500 and undoped Cu(II)Cu(I)/AC catalyst. The peak at 934.2–934.6 eV is attributed to Cu²⁺, while 931.9–932.1 eV is attributed to Cu⁺ species [35, 36], and the result shows that nitrogen doping has little effect on the electronic structure of the active component.

3.5 Coking Deposition During the Reaction

TG was used to study the carbon deposition on the catalysts (Supplementary Fig. S6). Before 100 °C, the slight weight loss is ascribed to the adsorbed water in the fresh Cu(II) Cu(I)/AC and Cu(II)Cu(I)/NAC-500 catalysts. The obvious weight loss at 100-200 °C is associated with the decomposition of residual solvent and cosolvent and urea in the fresh catalyst. In the temperature range of 200-320 °C, the weight losses of the used Cu(II)Cu(I)/AC and Cu(II)Cu(I)/NAC-500 catalyst is 14.99 and 27.27%, respectively, while the fresh Cu(II)Cu(I)/AC and Cu(II)Cu(I)/NAC-500 catalysts have a loss of 23.10 and 21.89%, respectively. When the temperature exceeds 320 °C, the weight decreases rapidly due to the combustion of AC. From 200 to 320 °C, carbon deposition with Cu(II)Cu(I)/AC and Cu(II)Cu(I)/NAC catalysts were 8.11 and 5.38%, respectively (Table 1). This result indicated that the carbon deposition of N-doped catalysts can be improved.

3.6 Textural Properties of Catalysts

The BET data of AC, NAC-300, NAC-500 and NAC-700 had little change before and after the nitrogen modification of AC (Supplementary Table S2). Therefore, the modification has only a small effect on the textural properties of the support. When AC loaded CuCl₂ and CuCl, the surface areas (S_{BET}) of support AC decreased from 1036.00 to 184.30 m² g⁻¹, which is likely due to the heavy load. Compared to S_{BET} and total pore volumes (V) in the fresh catalysts, the S_{BET} and V in used catalysts were smaller. This is due to carbon deposition in the reaction process, which is consistent with the TG data.

4 Conclusion

We demonstrated that the nitrogen-doped AC can enhance the catalytic performance of Cu(II)Cu(I)/AC. The nitrogen-doped Cu(II)Cu(I)/NAC-500 catalysts with a nitrogen



Fig. 3 XPS survey spectra **a** of AC, N-doped samples, and **b** N1s spectrum for the N-doped samples, **c** N1s spectrum Cu(II)Cu(I)/NAC-500 and **d** Cu 2p in Cu(II)Cu(I)/NAC-500 and Cu(II)Cu(I)/AC catalyst

Table 1	Amount	of	coke	deposition	on	the	Cu(II)Cu(I)/AC	and
Cu(II)C	u(I)/NAC	-50	0					

Samples	Amount of coke deposition (%)
Cu(II)Cu(I)/AC [13]	8.11
Cu(II)Cu(I)/NAC-500	5.38

content of 3.0 wt% are quite stable and more active for the gas-solid acetylene dimerization. The enhanced catalytic performance was ascribed to the relatively strong interaction with the support from the AC surface by urea pretreatment. In addition, nitrogen species can increase the dispersion of the copper species. The excellent catalytic performance of the Cu(II)Cu(I)/NAC-500 catalyst demonstrated its potential for gas-solid acetylene dimerization.

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Compliance with Ethical Standards

Conflict of Interest There are no conflicts of interest to declare.

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