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Article

Effect of Cu^+/Cu^{2+} Ratio on the Catalytic Behavior of Anhydrous Nieuwland Catalyst during Dimerization of Acetylene

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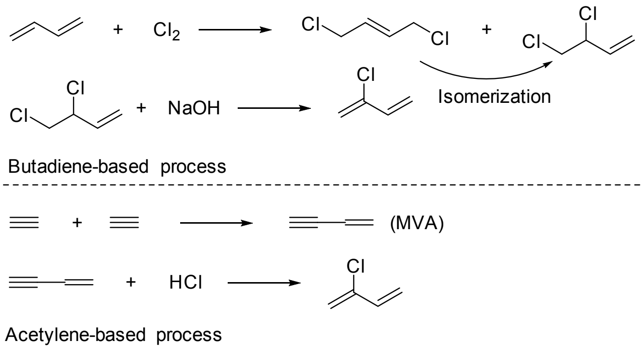
Abstract: The relative contents of Cu^+ and Cu^{2+} in solutions of anhydrous Nieuwland catalyst and $CuCl_2$-added anhydrous Nieuwland catalyst were detected by X-ray photoelectron spectroscopy (XPS). Results indicated that Cu^+ could be transformed into Cu^{2+} during the process of acetylene dimerization into monovinylacetylene, leading to deactivation of the catalyst. Moreover, the addition of Cu^{2+} inhibited the oxidation of Cu^+ into Cu^{2+} and enhanced the performance and lifetime of the catalyst. The optimum molar ratio of Cu^+ to Cu^{2+} was approximately 2:1; at this ratio, up to 40% acetylene conversion may be achieved.

Keywords: monovinylacetylene; acetylene dimerization; anhydrous Nieuwland catalyst; Cu^+-Cu^{2+} cooperative catalysis

1. Introduction

Monovinylacetylene (MVA), an acetylene downstream product, is extensively used to synthesize chloroprene (CR), styrene, butanedione, and other important chemical products. CR is the monomer of polychloroprene, which is one of seven synthetic rubbers used worldwide because of its overall physical properties, including excellent mechanical strength and high resistance to burning, light, and oxidation [1]. CR is generally used in the production of auto parts, machinery, industrial products, and adhesives [2,3]. Although largely superseded in many developed countries by butadiene-based processes for CR production [4,5], the acetylene method [6] remains an important process in countries where coal-based economies remain active, such as in China (Scheme 1).



Scheme 1. Two methods for 2-chloro-1,3-butadiene synthesis.

MVA, the key precursor in acetylene-based methods to produce CR [7], is traditionally obtained by the dimerization of acetylene, promoted by Nieuwland catalyst [8]. This catalyst is composed of CuCl and KCl or NH_4Cl in an acid aqueous solution. Aqueous catalytic systems are advantageous in acetylene-conversion reactions because they are environmentally friendly, convenient to prepare, and promote facile reactions. However, their major drawbacks include low acetylene conversion rates because of the low solubility of acetylene in the aqueous catalyst, which reduces contact opportunities between the alkyne and the catalytic system. In addition, the reaction of acetylene in aqueous catalyst systems yields not only MVA ($CH{\equiv}CH + CH{\equiv}CH \rightarrow CH{\equiv}C{-}CH{=}CH_2$) but also other by-products, such as acetaldehyde [9] by hydration of acetylene ($CH{\equiv}CH + H_2O \rightarrow CH_3CHO$), and divinylacetylene (DVA) by trimerization of acetylene ($CH{\equiv}C{-}CH{=}CH_2 + C_2H_2 \rightarrow CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$), respectively, which could lead to lower MVA selectivity. Therefore, the activity, selectivity, and stability of Nieuwland catalyst should be further improved for acetylene dimerization.

Nieuwland catalyst has recently attracted increased attention, and several reports focusing on its reaction mechanism, structure, and modification have been published [10]. For example, Fukuzumi et al. demonstrated the dimerization mechanism of the catalyst by detecting copper–acetylene and copper–monovinylacetylene π-complexes using in situ NMR measurements; the results of this work indicated that eliminating MVA in the gas phase is important to avoid further reaction of the copper(I)–MVA π-complex with the acetylene π-complex, which leads to DVA formation [11–13]. Han et al. [14] investigated the precipitate composition, formation process, and effect of pH and showed that loss of the active component (i.e., CuCl) in Nieuwland catalyst was caused by the formation of a dark red precipitate ($CuCl{\cdot}2C_2H_2{\cdot}1/5NH_3$). In addition, to balance acetylene conversion with the loss rate of CuCl, the system pH should be in the range of 5.80–5.97. Tao et al. reported that urea [15], $LaCl_3$ [16], and $CeCl_3$ [17] can efficiently improve acetylene conversion or MVA selectivity when added to aqueous Nieuwland catalytic systems. We also previously found that the addition of $SrCl_2$ [18], $ZnCl_2$ [19], or PEGs [20] to aqueous Nieuwland catalyst could improve its MVA selectivity and lifetime.

The use of polar organic solvents (such as DMF or DMSO) instead of water and a non-aromatic amine hydrochloride instead of KCl or NH_4Cl as a solubilizer has been reported to enhance catalytic activity to overcome the low solubility of acetylene in water and decrease by-product formation [21–27]. Han et al. obtained acetylene conversion rates of 20% in anhydrous DMF and 7% in aqueous solution under the same acetylene space velocity and reaction temperature. CuCl loss could also be reduced by continuous application of HCl gas to the system [28,29].

The short lifetime of Nieuwland catalyst, whether in aqueous solution or an anhydrous organic solvent, has been reported to be caused by the formation of a dark red precipitate containing the active CuCl component [14,29]. Catalyst stability could be improved by the addition of HCl to the catalyst solution. Recently, we found that addition of $CuCl_2$ to the anhydrous Nieuwland catalyst can improve acetylene conversion; however, the reasons are unclear. As an extension, this study investigates the effect of Cu^+/Cu^{2+} ratio on acetylene conversion through an anhydrous catalyst and the relationship between copper valence and catalyst stability.

2. Results and Discussion

2.1. Effect of Cu^+/Cu^{2+} Ratio on the Dimerization Reaction of C_2H_2 by an Anhydrous Catalyst

Our previous works found that the addition of $CuCl_2$ to the anhydrous catalyst enhanced acetylene conversion (reaction condition: temperature, 80 °C; space velocity of C_2H_2, 200 h^{-1}), and the results are shown in Figure 1 [27]. The acetylene conversion can reach above 45% and last 150 min when 10 mol % $CuCl_2$ is added to the catalyst, and the integral molar quantity of Cu^+ and Cu^{2+} was 0.088 mol; by comparison, the acetylene conversion of pure anhydrous Nieuwland catalyst can only reach 36% and declines rapidly. Thus, it is assumed that the addition of an appropriate amount of Cu^{2+}

to Nieuwland catalyst improves acetylene dimerization, although CuCl has always been considered the key active component of the catalyst.

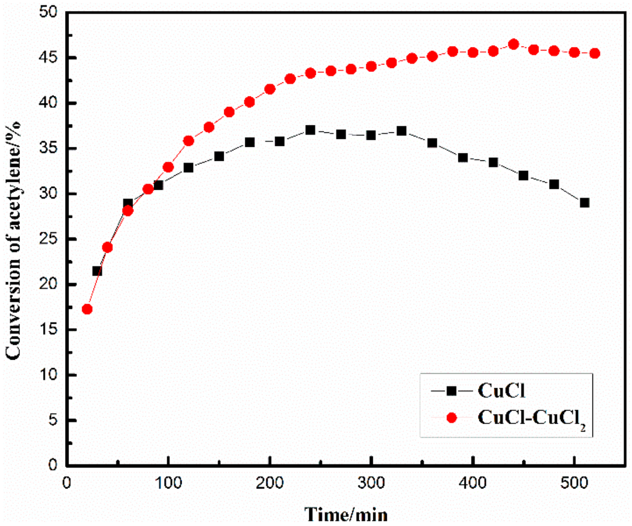


Figure 1. Effect of Cu^{2+} on conversion of acetylene.

The effect of different molar ratios of Cu^+ to Cu^{2+} under a constant total copper amount (The integral molar quantity of Cu^+ and Cu^{2+} was 0.08 mol) on the dimerization reaction of acetylene (reaction condition: temperature, 80 °C; space velocity of C_2H_2, 200 h^{-1}) were investigated. The results are summarized in Figure 2 and Table 1. As shown in Figure 2, when the integral molar quantity of Cu^+ and Cu^{2+} was 0.08 mol, the highest acetylene conversion was obtained with a 2:1 molar ratio of Cu^+ to Cu^{2+} (39% C_2H_2 conversion and 28% yield). Because the integral molar quantity of Cu^+ and Cu^{2+} has reduced, the acetylene conversion is lower than the catalyst with 10 mol % $CuCl_2$ added. Increasing the concentration of Cu^+ or Cu^{2+} resulted in lower acetylene conversion rates, which indicated that an appropriate concentration of Cu^{2+} could be used as a co-catalyst to enhance catalytic activity. A dark red precipitate was generated after acetylene was flowed for approximately 10 min at a 5.6:1 molar ratio of Cu^+ to Cu^{2+}. The conversions of C_2H_2 and selectivities of product under the different molar ratios of Cu^+ and Cu^{2+} are shown in Table 1. The results indicate that DVA—which can be used to prepare *n*-hexane by catalytic hydrogenation [30]—is a primary by-product in the process of dimerization, and higher acetylene conversion leads to relatively lower MVA selectivity.

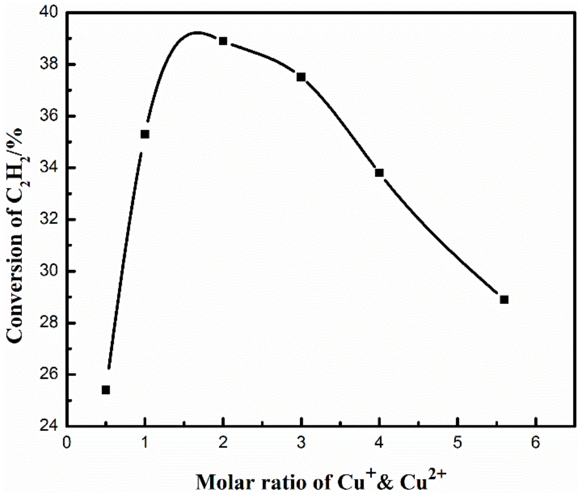


Figure 2. The conversion of C_2H_2 under different molar ratios of Cu^+ and Cu^{2+}.

Table 1. The composition of outlet gas under different molar ratios of Cu^{+}/Cu^{2+}. DVA: divinylacetylene; MVA: monovinylacetylene.

Mole Ratio of Cu^{+}/Cu^{2+}	**Composition of Outlet Gas (%)**				**C_2H_2 Conversion (%)**	**MVA Selectivity (%)**
	MVA	**DVA**	**Acetaldehyde**	**C_2H_2 (Recovered)**		
5.6:1	12.72	2.88	0.12	84.28	28.9	74.4
4:1	15.15	3.58	0.12	81.15	33.7	73.6
3:1	16.95	4.33	0.16	78.56	37.5	72.1
2:1	17.94	4.42	0.18	77.46	38.9	72.7
1:1	16.27	3.51	0.30	79.92	35.2	75.0
1:2	11.07	2.43	0.10	86.40	25.5	75.0

As mentioned above, the formation of precipitates causes a short Nieuwland catalyst lifetime, whether in aqueous solution or in an anhydrous organic solvent. Therefore, we analyzed the composition of the precipitates by using TGA (Thermogravimetric Analysis), FT-IR (Fourier transform infrared spectroscop), and XPS to investigate the reasons why increasing mole ratio of Cu^{+} leads to precipitate formation. The TGA results show three weight loss temperatures of 223 °C, 481 °C, and 841 °C, corresponding to weight losses of 25%, 50%, and 25%, respectively (Figure 3). The FI-IR spectra of the precipitates obtained at different drying temperatures are shown in Figure 4 (Figure 4a, 100 °C; Figure 4b, 450 °C). Strong, sharp peaks observed at 3343 and 2309 cm^{-1} could be attributed to C≡C−H and C≡C stretching vibrations, respectively. No peaks were observed within the ranges of 3100–3010 cm^{-1} and 1610–1690 cm^{-1}, thus confirming the absence of =CH and C=C stretching vibrations in the precipitate. The alkyne present in the precipitate was C_2H_2. Bands located at 3447 cm^{-1} indicated N−H stretching vibrations, while bands at 1546 and 957 cm^{-1} were attributed to N–H bending vibration. Bands located at 1490 and 1380 cm^{-1} were attributed to CH_2 and CH_3 bending vibrations, respectively. The FT-IR data obtained when the precipitate was heated at 450 °C in a tube furnace for 1 h with nitrogen is illustrated in Figure 4b. Specific peaks indicating N−H and C−N disappeared, and only the characteristic peaks of C≡C−H and C≡C bonds remained. This result indicates that the first and second weight losses of the precipitate correspond to the losses of $CH_3CH_2NH_2$ and C_2H_2, respectively.

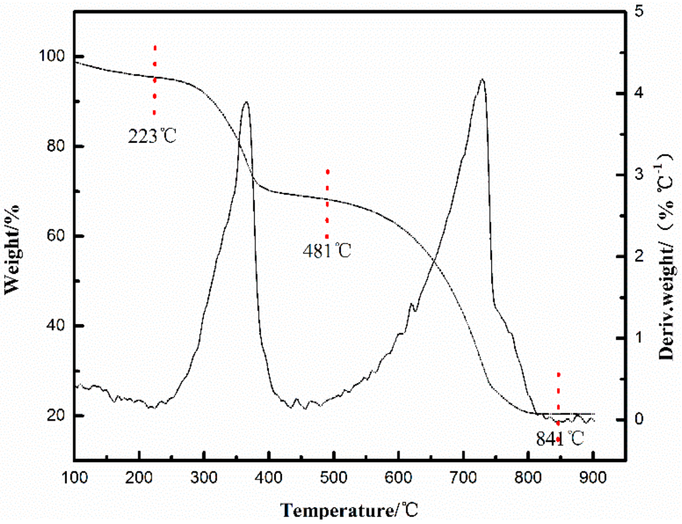


Figure 3. Thermogravimetry-differential thermal analysis (TG/DTG) thermograms for the dark red precipitate.

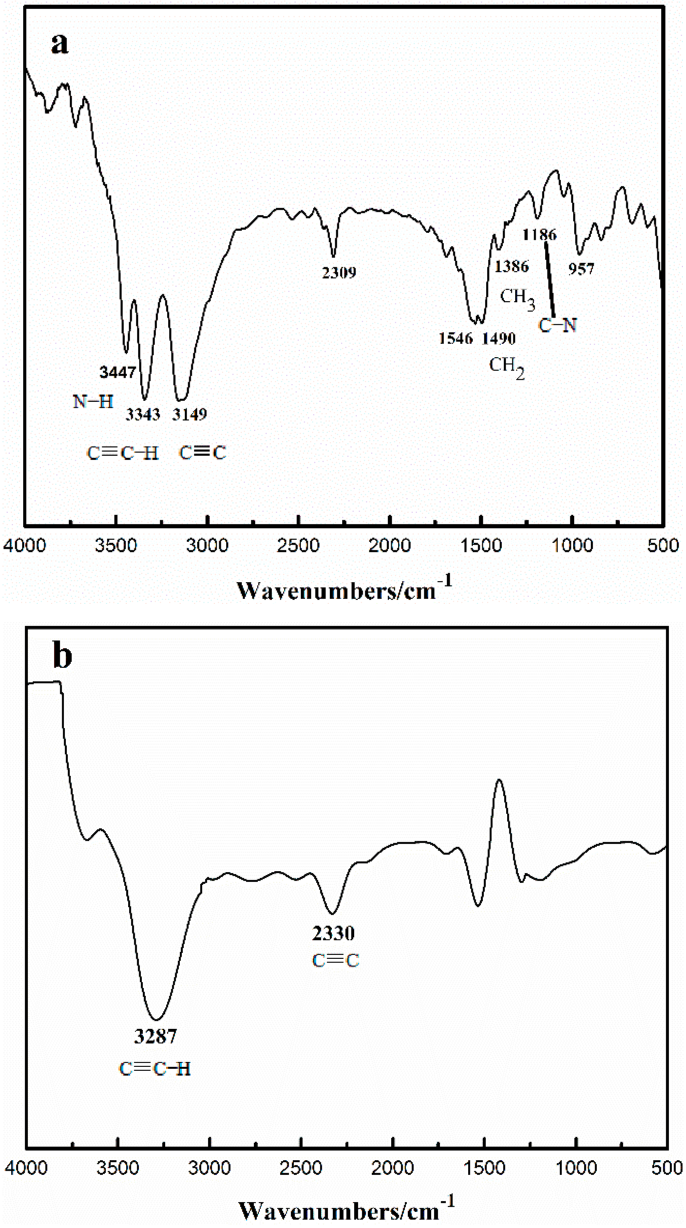


Figure 4. FT-IR (Fourier transform infrared spectroscop) study of thermally decomposed product of the precipitate at different temperatures, (**a**) at 100 °C and (**b**) at 450 °C.

Relevant information on the distribution of copper valence states was obtained by XPS after calcination of the precipitate at 840 °C in the tube furnace for 1 h with nitrogen. The XPS survey spectrum of Cu is shown in Figure 5a; the peak of Cu^+ can be clearly seen at 932.48 eV. Figure 5b shows the high-resolution spectrum of Cu, which indicates distinct distributions of two Cu valence states; that is, the signals observed at 932.48 and 934.87 eV correspond to Cu^+ and Cu^{2+}, respectively. The relative atomic percentages of Cu^+ and Cu^{2+} were determined by XPS to be 66% and 34%, respectively. Thus, the composition of the precipitate was $2C_2H_2{\cdot}CH_3CH_2NH_2{\cdot}(2/3CuCl{\cdot}1/3CuCl_2)$; this precipitate was formed by the coordination of C_2H_2 and $CH_3CH_2NH_2$ with Cu(I) and Cu(II) in the anhydrous catalyst. As a result, a certain amount of Cu^{2+} in this catalytic system is vital for this reaction, and higher mole ratio of Cu^+ will lead to precipitate formation, followed by short lifetime.

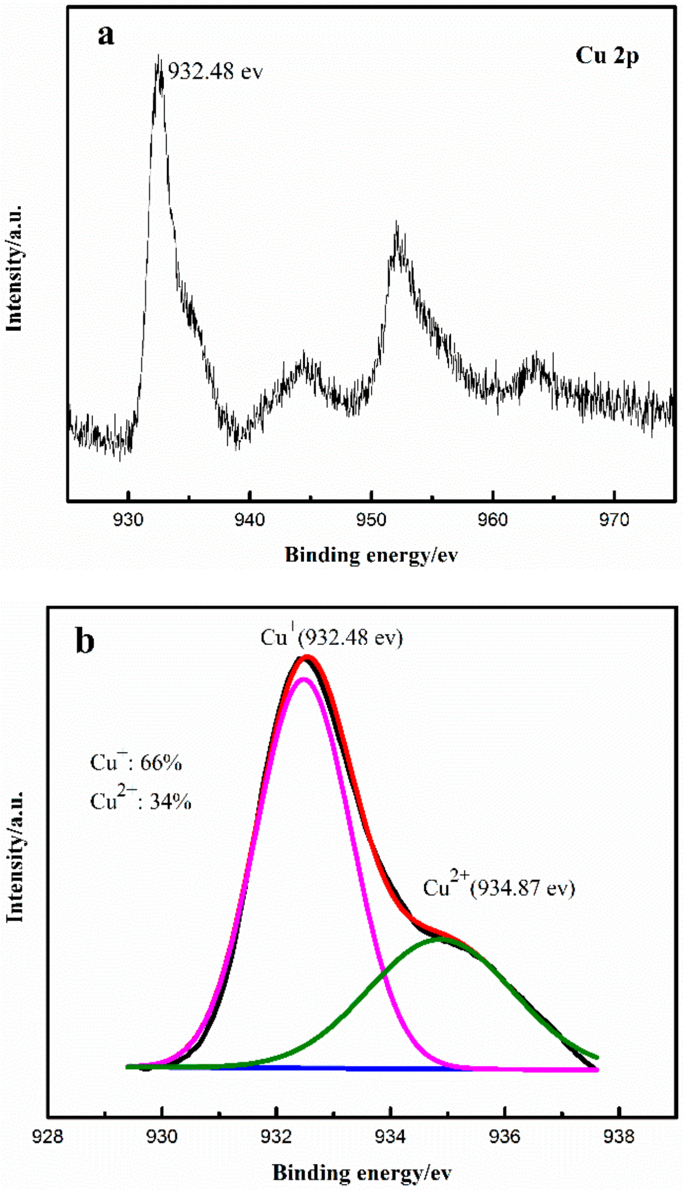


Figure 5. (**a**) XPS (X-ray photoelectron spectroscopy) survey spectrum of precipitate and (**b**) high-resolution XPS of Cu^{2+} and Cu^{+} spectra.

2.2. Relationship between the Deactivation Mechanism and Concentration of Cu^{2+} during Acetylene Dimerization

While the Cu^{+} ion is generally believed to be the primary active component in Nieuwland catalyst, addition of a certain amount of Cu^{2+} to the reaction system has also been shown to be beneficial to the dimerization reaction of C_2H_2 in the anhydrous catalyst. The result of the addition of a certain amount of Cu^{2+} on the basis of the original experiment is shown in Figure 1. Addition of Cu^{2+} not only improved C_2H_2 conversion but also increased the catalyst lifetime. Thus, we performed the following experiment to explore the reasons behind these phenomena.

Curve-fitting of the high-resolution XPS spectra was performed to investigate the valence states and relative amount of copper species in cat-a, cat-b, cat-c, and cat-d, and the results are shown in Figure 6. In cat-a, peaks at 932.40 and 934.69 eV represent Cu^{+} and Cu^{2+}, which showed relative contents of 58% and 42%, respectively. The molar percentages of Cu^{+} and Cu^{2+} in cat-b—which was obtained from the catalyst solution after dimerization for 6 h were calculated to be 22% and 78%, respectively. Thus, the content of Cu^{2+} in cat-b increased from 42% to 78%, compared with that in cat-a.

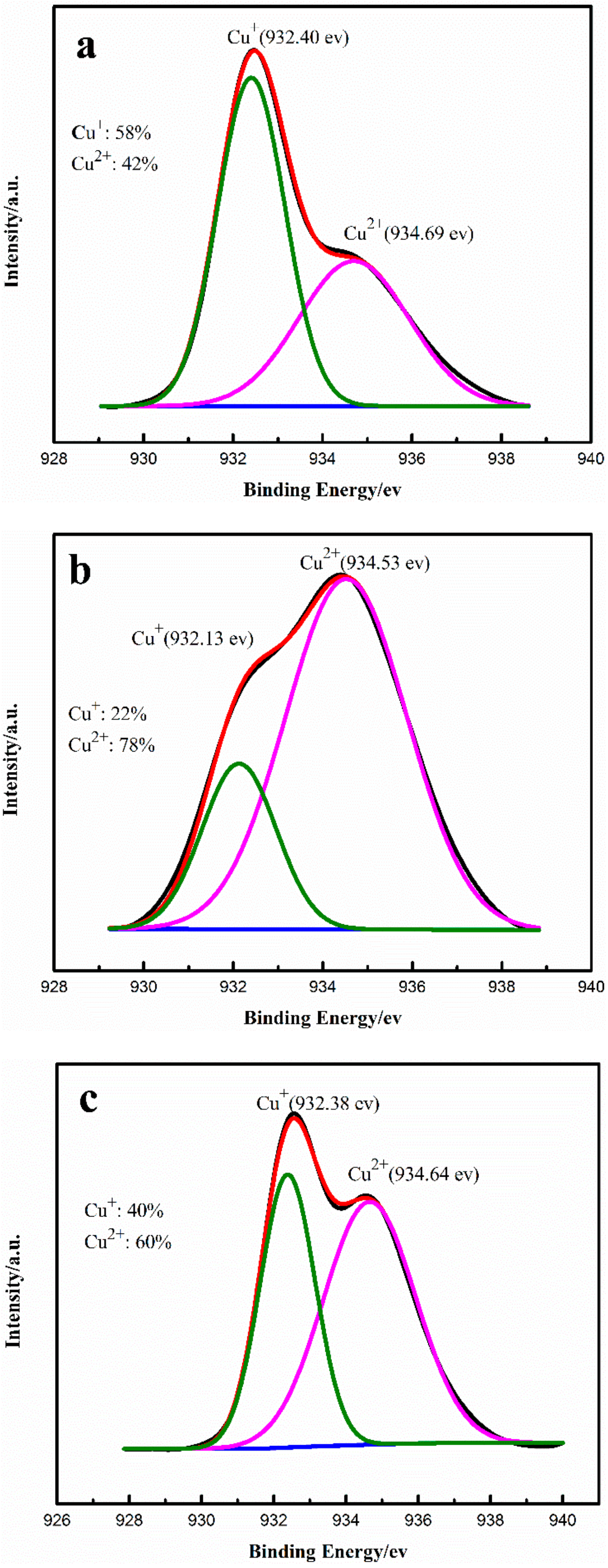


Figure 6. *Cont.*

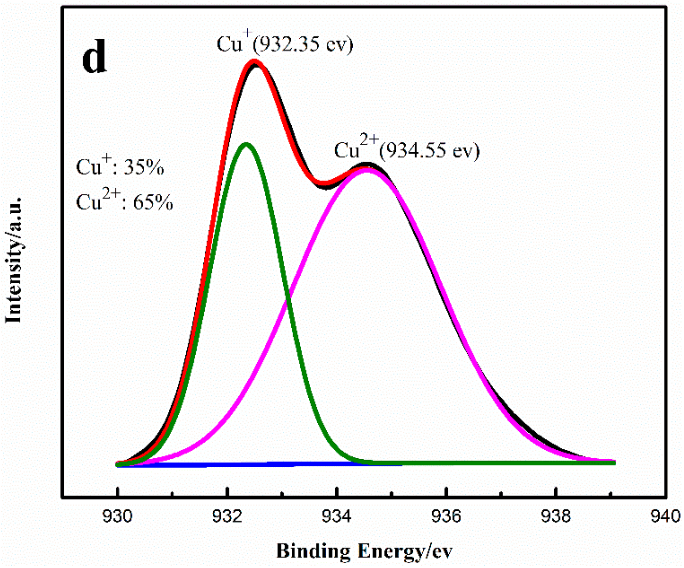


Figure 6. High-resolution XPS spectra of (**a**) cat-a; (**b**) cat-b; (**c**) cat-c; (**d**) cat-d. Red line: fitting curve; Black line: original data line ; Blue line: original data ; Green line: the characteristic peak of Cu^+; Pink line: the characteristic peak of Cu^{2+}.

The same results were observed in cat-c and cat-d. Fresh $CuCl_2$-added anhydrous Nieuwland catalyst (cat-c) contained 40% Cu^+ and 60% Cu^{2+}, while the used catalyst (cat-d) contained 35% Cu^+ and 65% Cu^{2+}. Only 5% yield of Cu^{2+} proportion increased under this reaction condition. Thus, addition of Cu^{2+} may be inferred to inhibit the transformation of Cu^+ into Cu^{2+}.

In combination with the catalytic performance and the XPS spectra results, it is reasonable to conclude that, aside from the formation of a dark red precipitate containing the active CuCl component, the transformation of Cu^+ into Cu^{2+} could also explain the deactivation of the anhydrous Nieuwland catalyst. The addition of a certain amount of Cu^{2+} can effectively inhibit Cu^+ oxidation into Cu^{2+} during dimerization and enhance the performance and lifetime of the catalyst.

3. Materials and Methods

3.1. Reaction Equipment

Gas–liquid dimerization of acetylene was performed in a self-designed glass reaction vessel consisting of two cylindrical casings with different radii, the glass reaction equipment with 240 mm length, 40 mm inner diameter and 10 mm outer diameter. The catalytic reaction proceeded in the internal casing. A sand core baffle was inserted into the internal casing to increase contact between acetylene and the catalyst solution. The reaction temperature was controlled by circulating water in the outer casing.

3.2. Materials, Catalyst Preparation, and Acetylene Dimerization

Reagent-grade CuCl (99%), $CH_3CH_2NH_2{\cdot}HCl$ (98%), *N*,*N*-dimethylformamide (DMF, 99.5%), and 1,4-dioxane (98%) were purchased from Adamas (Shanghai, china). DMF and 1,4-dioxane were dried with $MgSO_4$ and distilled under reduced pressure.

Based on our previous research results [28], CuCl (7.92 g, 0.08 mol) and $CH_3CH_2NH_2{\cdot}HCl$ (3.83 g, 0.047 mol) were added to a mixture of DMF (7 mL) and 1,4-dioxane (3 mL) at 80 °C for at least 30 min under nitrogen until complete dissolution of CuCl to obtain anhydrous Nieuwland catalyst ([CuCl] = 5.0 M, 17 mL).

As shown in Figure 7, the pipeline was purged with nitrogen for 30 min before the reaction to remove air in the system. C_2H_2 was successively passed through a calibrated mass flow controller to limit the C_2H_2 flow, a $K_2Cr_2O_7$ solution to eradicate H_2S and PH_3, a NaOH solution to eradicate the acidic gas, and a drying tube to remove trace water, and then it flowed into a pre-heated glass reaction vessel, which contained the catalyst. The exit gas mixture passed through an absorption bottle containing NaOH solution, and then into a Shimadzu GC-2014C chromatogram (Shimadzu, Japan) equipped with a GDX-301 chromatography column and flame ionization detector for analysis.

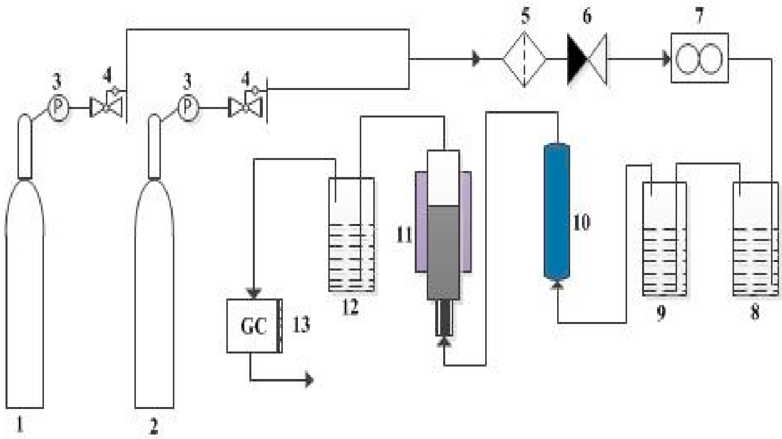


Figure 7. Schematic diagram of the C_2H_2 dimerization system. (**1**: C_2H_2; **2**: N_2; **3**: gas pressure gage; **4**: value; **5**: gas filter; **6**: check valve; **7**: mass flow controller; **8**: $K_2Cr_2O_7$ solution; **9** and **12**: NaOH solution; **10**: drying tube; **11**: reactor; **13**: Gas Chromatograph (GC-2014C)).

3.3. Dark Red Precipitate Separation and cat-a, cat-b, cat-c, and cat-d Preparation

The dark red precipitate was separated from the catalyst solution by filtration, washed several times with the mixed solvent, and dried in a vacuum at 60 °C.

Fresh and used anhydrous Nieuwland catalyst solutions were dried in a tube furnace at 100 °C for 1000 min under a N_2 atmosphere to remove the solvent; the solids obtained were denoted as cat-a and cat-b, respectively. Replacement of the anhydrous Nieuwland catalyst solution with 10 mol % of $CuCl_2$-added anhydrous Nieuwland catalyst solution yielded solids via the same procedure; these solids were denoted as cat-c and cat-d.

3.4. Analysis

The gas sample at the outlet of the acetylene dimerization reaction was analyzed every 20 min by GC (Shimadzu GC-2014C chromatograph equipped with a GDX-301 chromatography column and flame ionization detector). Thermogravimetry-differential thermal analysis (TG-DTG) of the catalyst was performed from 50 °C to 900 °C at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet AVATAR 360 (Nicolet, Green Bay, WI, USA) over the wavenumber range of 500–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD spectrometer (Kratos, Manchester, UK) with a monochromatized Al-Kα X-ray source (225 W).

4. Conclusions

$CuCl_2$-added anhydrous Nieuwland catalyst was prepared and evaluated in terms of its catalytic performance during acetylene dimerization. Addition of Cu^{2+} enhanced the performance and lifetime of the catalyst by inhibiting Cu^{+} oxidation into Cu^{2+} during dimerization. The optimal molar ratio of Cu^{+} to Cu^{2+} was approximately 2:1; at this ratio, acetylene conversion rates of up to 40% were achieved.

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Conflicts of Interest: The authors declare no conflict of interest.

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