Effect of Iminodiacetic Acid-Modified Nieuwland Catalyst on the Acetylene Dimerization Reaction

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Abstract: The iminodiacetic acid-modified Nieuwland catalyst not only improves the conversion of acetylene but also increases the selectivity of monovinylacetylene (MVA). A catalyst system containing 4.5% iminodiacetic acid exhibited excellent performance, and the yield of MVA was maintained at 32% after 24 h, producing an increase in the yield by 12% relative to the Nieuwland catalyst system. Based on a variety of characterization methods analysis of the crystal precipitated from the catalyst solution, it can be inferred that the outstanding performance and lifetime of the catalyst system was due to the presence of iminodiacetic acid, which increases the electron density of Cu^+ and adjusts the acidity of the catalytic solution.

1. Introduction

As one of the seven main synthetic rubber materials, chloroprene (CR) possesses good mechanical properties and chemical stability [1] and is widely used in the adhesive and automobile industries and also in other fields [2,3]. Acetylene dimerization facilitated by the Nieuwland catalyst to produce monovinylacetylene (MVA) is the key step in the acetylene-based process for CR synthesis [4]. The main process of this reaction is shown in the Scheme 1. CuCl, NH_4Cl (or KCl) and water constitute the traditional Nieuwland catalyst, which has several advantages, such as being environmentally friendly, convenient to prepare, and low reaction temperature [5,6]. However, the drawbacks of this catalytic system include low acetylene conversion rates and low MVA selectivity. Thus, much effort is still needed to develop a more stable and efficient Nieuwland catalytic system to further improve the activity and selectivity of the acetylene dimerization reaction.
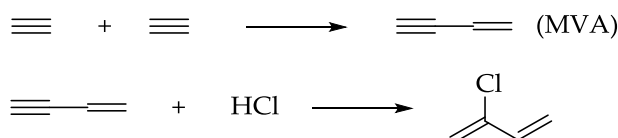
Scheme 1. Acetylene-based process for 2-chloro-1,3-butadiene production.

Because of the practical importance and the long history of the Nieuwland catalyst, recent studies on the reaction mechanism [1,6–9], catalyst structure [10,11], and factors affecting the catalytic performance [11–19] have attracted significant attention. In general, it catalyzes a homogenous transition metal-catalyzed organic transformation; the addition of a second metal and ligand/additive

results in changes in the electronic structure of the active metal, thus causing change in the performance of the catalyst; the change in the electronic structure of the active metal may be due to an electron transfer between the active metal and second metal or ligand/additive. In the catalytic recycling of acetylene dimerization, the electron transfer from Cu in $Cu_nCl_{n+1}^-$ (the active component in the Nieuwland catalyst) to the π^* orbital of the C≡C bond is an important step, which acts as an activating C≡C bond. Additionally, when the electron density of Cu(I) is higher, a higher catalytic activity is obtained. Consequently, several groups have successfully improved the acetylene dimerization reaction using this strategy. For example, Tao et al. reported that the addition of urea [20], phosphine ligands [21], LaCl$_3$ [22,23], and CeCl$_3$ [24] to a Nieuwland catalyst solution can effectively enhance the acetylene conversion or MVA selectivity. Han et al. reported that the addition of DL-alanine to the Nieuwland catalyst can reduce the activity of acetylene dimerization and improve the MVA selectivity [25]. We also found that the addition of SrCl$_2$ [26], ZnCl$_2$ [27], PEGs [28], and CuCl$_2$ [9] can improve the selectivity of MVA or the lifetime of the catalyst. However, these modified catalysts can only improve either the acetylene conversion or MVA selectivity, and simultaneous improvements in conversion and selectivity have not been reported in the literature.

In this paper, we report iminodiacetic acid as an efficient ligand, which can simultaneously improve acetylene conversion and MVA selectivity, for acetylene dimerization catalyzed using the Nieuwland catalyst. With the iminodiacetic acid-modified Nieuwland catalyst, a 38.0% yield for acetylene conversion and 84.2% yield for MVA selectivity were obtained; the yields are comparatively higher than that obtained with the traditional Nieuwland catalyst. Moreover, the structures and reaction mechanism of the catalysts are also discussed. These results provided a new idea for improving the performance of Nieuwland catalyst, and this method is viable for use in both laboratory research and large industrial scales for acetylene-based CR production in the future.

2. Results and Discussion

2.1. Catalytic Activities of NC and L-NC

Initially, the catalytic performances of NC and **L**-NC were tested under fixed reaction conditions (space velocity of acetylene = 105 h^{-1}, reaction temperature = 80 °C, **L**: CuCl = 0.03:1), and the results are shown in Figure 1 and Table 1. For acetylene conversion, all five ligands promoted the initial catalytic activity of NC and enhanced the catalyst stability for acetylene dimerization. The order of the catalyst activity is **L$_4$**-NC > **L$_1$**-NC > **L$_3$**-NC > **L$_2$**-NC > **L$_5$**-NC ≈ NC. For MVA selectivity, all the **L**-NCs exhibited good selectivity in the range of 76–87%, whereas there was only 76% MVA selectivity for NC. This was surprising given the previous findings that a higher acetylene conversion resulted in lower MVA selectivity. Taken together, **L$_1$** is the most efficient ligand in this reaction with 29.3% acetylene conversion and 84.6% MVA selectivity. Subsequently, the results of the effect of the amount of **L$_1$** showed that an optimal catalytic performance for acetylene dimerization was achieved when 4.5% of **L$_1$** was used, which is shown in Figure 2 and Table 2. The acetylene conversion and MVA selectivity were 38% and 84.2%, respectively, with a 12% increase in yield in comparison with the NC system.
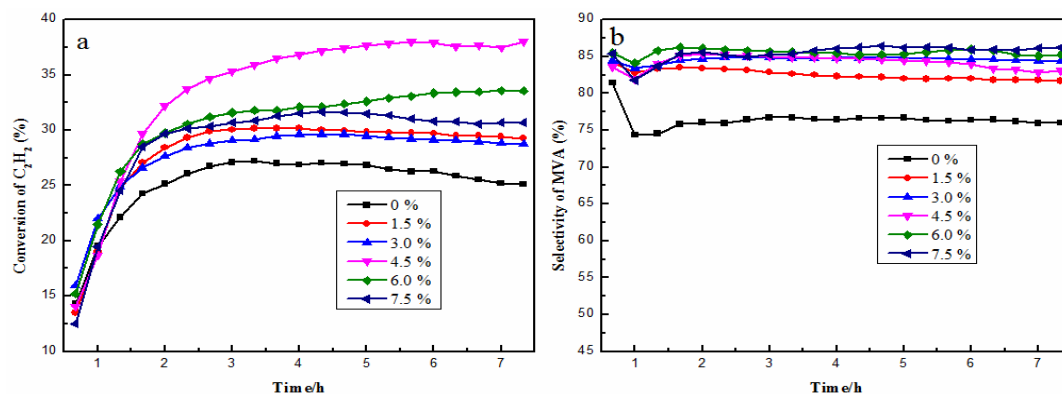
Table 1. Effect of **L$_1$**–**L$_5$** (3%) for acetylene dimerization.

Catalysts	Acetylene Conversion (%)	MVA Selectivity (%)	Yield (%)
NC	26.4	76.4	20.1
L$_1$-NC	29.3	84.6	24.8
L$_2$-NC	27.3	87.5	23.8
L$_3$-NC	28.8	79.4	22.9
L$_4$-NC	29.7	78.5	23.3
L$_5$-NC	26.3	87.1	22.9

Note: Space velocity of acetylene was 105 h^{-1} and reaction temperature was 80 °C. The data is the average of three independent runs.
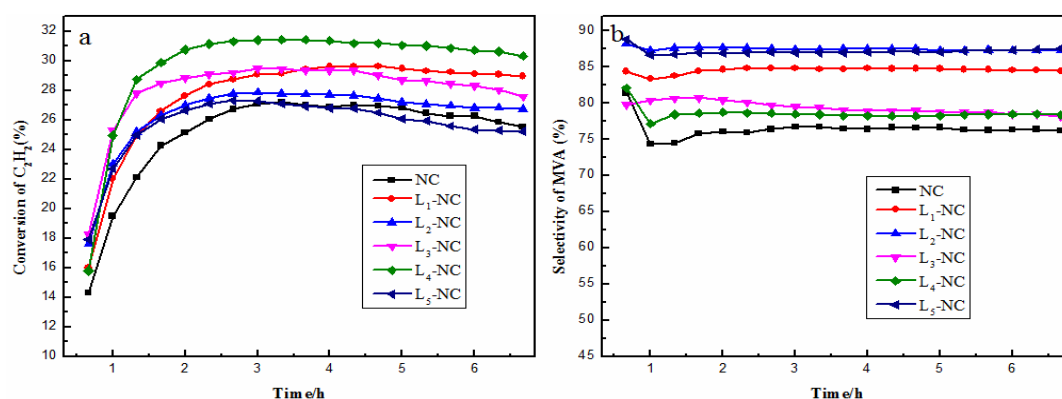
Figure 1. (**a**) Conversion of C_2H_2 and (**b**) selectivity to monovinylacetylene (MVA) in acetylene dimerization over NC and **L**-NC. (Reaction conditions: Space velocity of acetylene 105 h^{-1}, reaction temperature 80 °C, 3% of **L$_1$**–**L$_5$**).

Figure 2. (**a**) Conversion of C_2H_2 and (**b**) selectivity to MVA in acetylene dimerization over 0–7.5% of **L$_1$**. (Reaction conditions: Space velocity of acetylene 105 h^{-1}, reaction temperature 80 °C).

Table 2. Effect of the amount of **L$_1$** for acetylene dimerization.

L$_1$ (%)	Acetylene Conversion (%)	MVA Selectivity (%)	Yield (%)
0	26.4	76.4	20.1
1.5	29.7	82.3	24.4
3.0	29.2	84.7	24.7
4.5	38.0	84.2	32.0
6.0	32.5	85.5	27.8
7.5	31.0	86.0	26.7

Note: Space velocity of acetylene was 105 h^{-1} and reaction temperature was 80 °C. The data is average of independent three runs.

2.2. Stability Tests

Long-term stability experiments were conducted to compare the catalytic stabilities and performances of NC, **L$_1$**-NC, and HCl-NC (Figure 3 and Table 3). **L$_1$**-NC exhibited an excellent catalytic performance and stability, and the acetylene conversion and MVA selectivity remained stable with no obvious decline observed within 24 h. In contrast, NC and HCl–NC exhibited distinctly lower catalytic performances and stabilities.
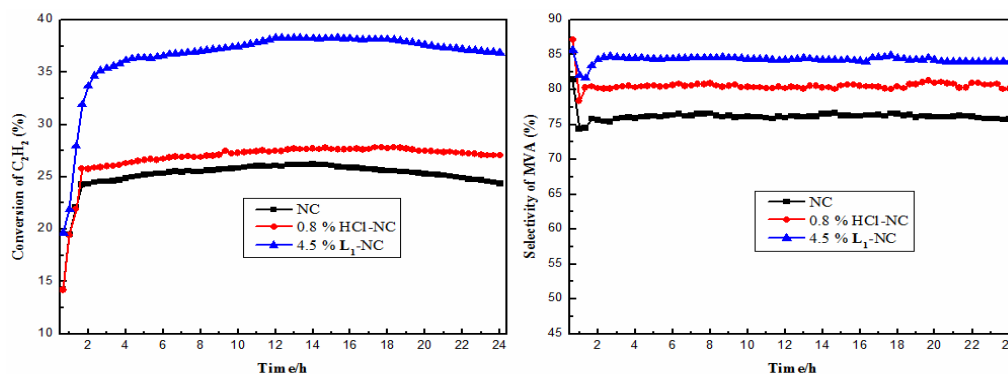
Figure 3. Catalytic performance of NC, 4.5% **L$_1$**-NC and 0.8% HCl–NC. (Reaction conditions: Space velocity of acetylene 105 h^{-1}, reaction temperature 80 °C).

Table 3. Lifetime testing for three catalysts of NC, 4.5% **L$_1$**-NC and 0.8% HCl–NC.

Catalysts	Acetylene Conversion (%)	MVA Selectivity (%)	Yield (%)
NC	25.5	76.1	19.4
HCl-NC	27.2	80.5	21.9
L$_1$-NC	37.5	84.4	31.7

Note: Space velocity of acetylene was 105 h^{-1} and reaction temperature was 80 °C. The data is average of independent three runs.

2.3. Structures of Crystals A and B

Considering the high efficiency of **L$_1$**, we investigated the relationship between the structure of NC/**L$_1$**-NC and the catalytic activity. Then, we separated crystals A and B from solutions of NC and **L$_1$**-NC via a freezing crystallization method, and we identified the composition of the crystals using FT-IR, TG, TPD-MS, XRD, XRF, and XPS analysis.

The FT-IR spectrum of crystal A is shown in Figure 4a. The peaks at 3169 cm^{-1} and 1393 cm^{-1} are characteristic peaks of O–H, and peaks representing N–H appeared at 3445 cm^{-1} and 1643 cm^{-1} [18]. In the catalyst solution, NH_4^+ was hydrolyzed to produce NH_3 ($NH_4^+ + 2H_2O = NH_3 \cdot H_2O + H_3^+O$); thus, we concluded that the crystal A contains H_2O and NH_3. As shown in Figure 4b, compared with **L$_1$**, the N–H stretching absorption peak blue-shifted by approximately 70 cm^{-1}, which indicated that N–H was likely coordinated with Cu(I) in the copper complex. The peaks at 3161 cm^{-1}, 1400 cm^{-1}, and 904 cm^{-1} were identified as the characteristic peaks of O–H in the carboxyl group. The peak at 1718 cm^{-1} is due to the C=O stretching vibration. The band located at 1064 cm^{-1} can be assigned to the C–N stretching vibration. Therefore, crystal B may contain H_2O, NH_3, and **L$_1$**. These results were also confirmed by the TPD-MS spectrum (Figure 5) because a peak for the $m/z = 17$ curve in the temperature range of 200 °C–350 °C was obtained, which suggested that the weight loss corresponded to NH_3.

To further determine the composition of the catalyst, we performed thermal analysis (TG) on crystals A and B (Figure 6). There were three weight losses for crystal A during the heating process. The first weight loss began at 100 °C, which was mainly due to the loss of crystal water [10]. Obviously, the second weight loss was due to the loss of NH_3 [18]. We calcined crystal A and crystal B in a tube furnace with nitrogen for 1 h at 450 °C; XRD studies of the residues showed that they contained CuCl and $CuCl_2$ (Figure 7). According to the TGA study for crystal A, three parts of the lost mass percentages were 0.28%, 30.04%, and 69.68%. However, there was one additional part of the weight loss between 375 °C and 405 °C for crystal B, and for crystal B, the four parts of the lost mass percentages were 1.42%, 30.40%, 3.58%, and 64.6%. XRF examination of crystals A and B showed that their Cu/Cl atomic ratios were both 2:3. Consequently, we can conclude that the compositions of crystal A and B are $Cu_2Cl_3 \cdot 6NH_3 \cdot 1/20H_2O$ and $Cu_2Cl_3 \cdot 1/10C_4H_7NO_4 \cdot 13/2NH_3 \cdot 3/10H_2O$, respectively.
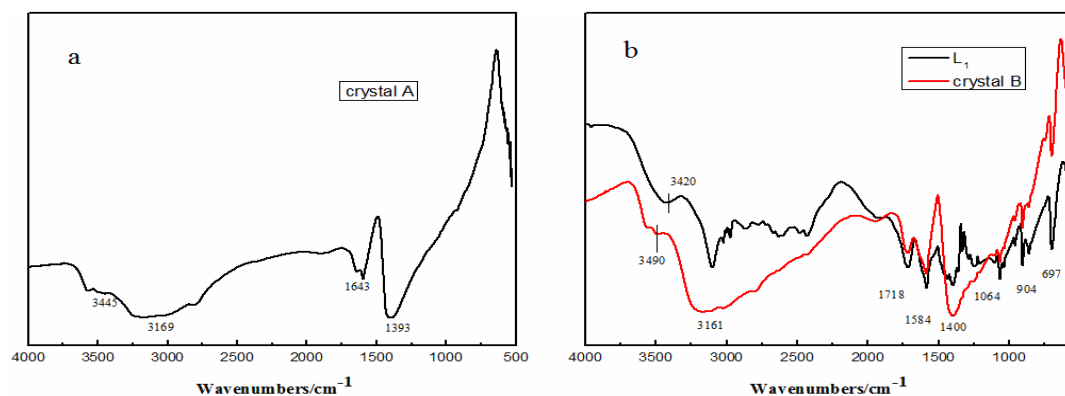
Figure 4. IR spectra of the crystal A (**a**), crystal B and **L₁** (**b**).
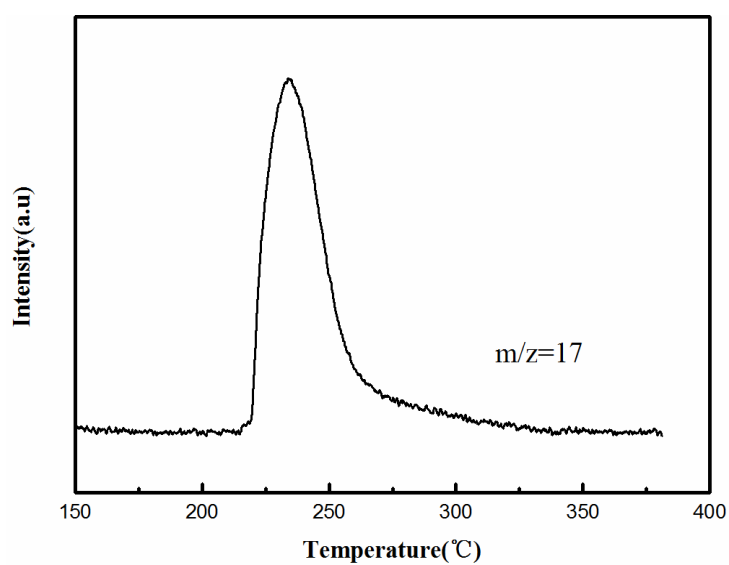

Figure 5. TPD-MS spectra of desorption of crystal A and B.
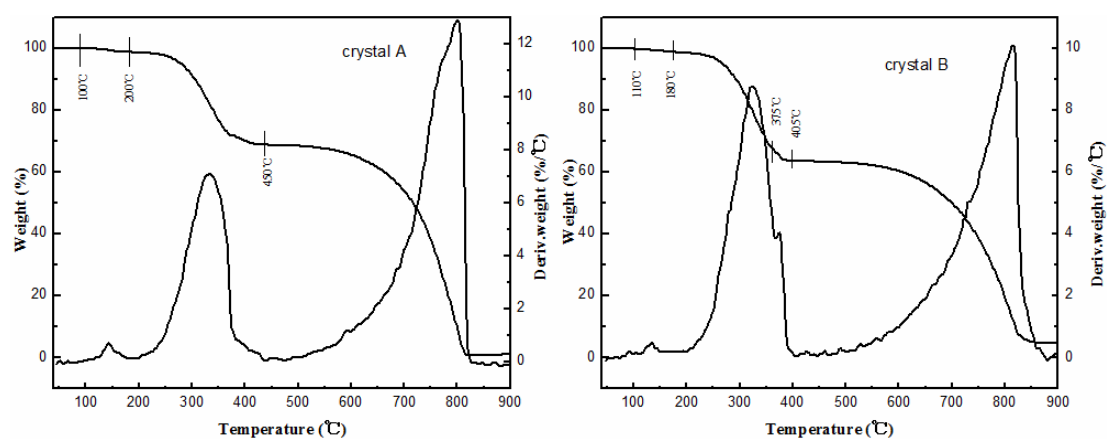

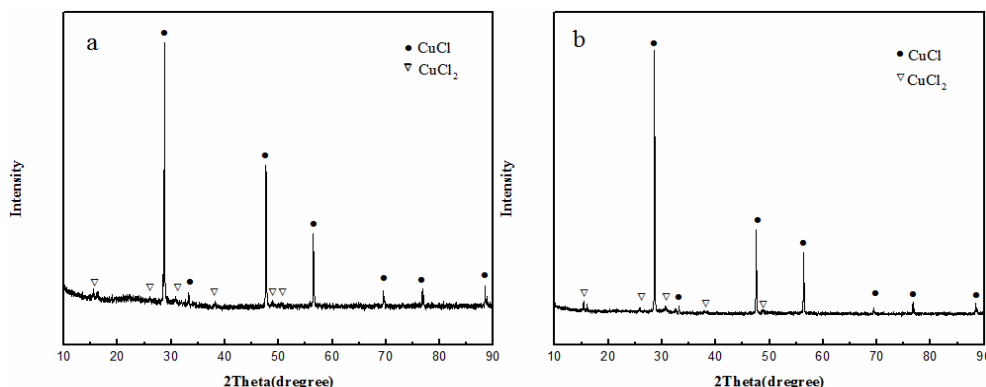**Figure 6.** TG/DTG thermograms for the crystal A and crystal B.

Figure 7. XRD pattern of heating product of the crystals A (**a**), B (**b**).

2.4. Action of the Ligand

As shown in Figure 8, the XPS results revealed that the binding energy of Cu $2p_{3/2}$ for crystal B exhibited a 0.26 eV higher negative shift compared with crystal A. This negative shift is attributed to the interaction between L_1 and copper ions, which increases the electron density of Cu^+ due to the transfer of electrons from L_1 to the Cu^+ center. This result was also supported by the TG analysis results of crystal B, whereas a higher desorption temperature for L_1 in crystal B was required.
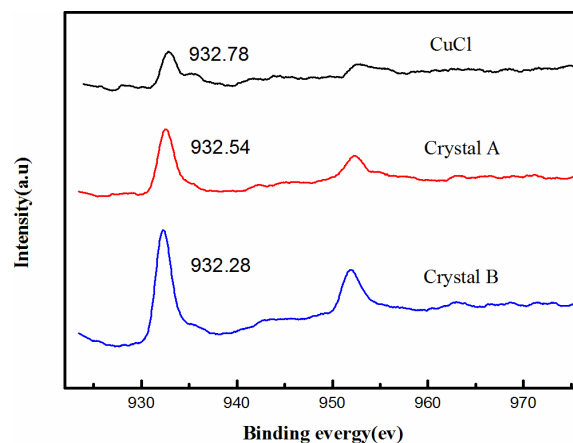

Figure 8. XPS spectra of Crystals A, B and CuCl for Cu 2p.

As mentioned above, the higher electron density of Cu(I) lead to a higher catalytic performance in acetylene dimerization. Therefore, L_1-NC exhibited the best catalytic performance (higher acetylene conversion and MVA selectivity) and stability as described in Figures 1 and 3, which was due to the strongest electronic donating and coordination capability of L_1 with Cu(I) among the five tested ligands [11]. Recently, Han et al. reported that the addition of a certain amount of hydrochloric acid to the Nieuwland catalyst can inhibit the formation of the polymer and improve the catalyst lifetime and acetylene conversion [18]. Fukuzumi et al. also reported that the addition of 2.86 mol % diethylenetriaminepentaacetic acid (DTPA) can increase the maximum yield of MVA and improve the product ratio of MVA to DVA, which may be due to the coordination of DTPA to the copper(I) active species affected the stability of the copper(I)-MVA and copper(I)-DVA complexes [1]. However, the present used additive L_1, which has a similar structure to DTPA but with more weak chelating ability and acidity, demonstrated higher catalytic performance. Therefore, both appropriate coordinate ability and acidity are important factors for an additive to enhance the catalytic activity and catalyst lifetime. At this point, L_1 is more suitable than DTPA for acetylene dimerization in large-scale application in industry.

2.5. Relationship between the Valence of Copper and Catalytic Activity

The Cu^+ ion is generally considered to be the main active component in the NC system. However, our previous studies found that Cu^{2+} also plays an important role in the acetylene dimerization reaction, and the deactivation of the anhydrous NC was caused by the transformation of Cu^+ to Cu^{2+} [9]. Hence, valence changes for copper species in fresh and used NC and **L$_1$**-NC were evaluated via high-resolution XPS, and the results are shown in Figure 9 and Table 4.
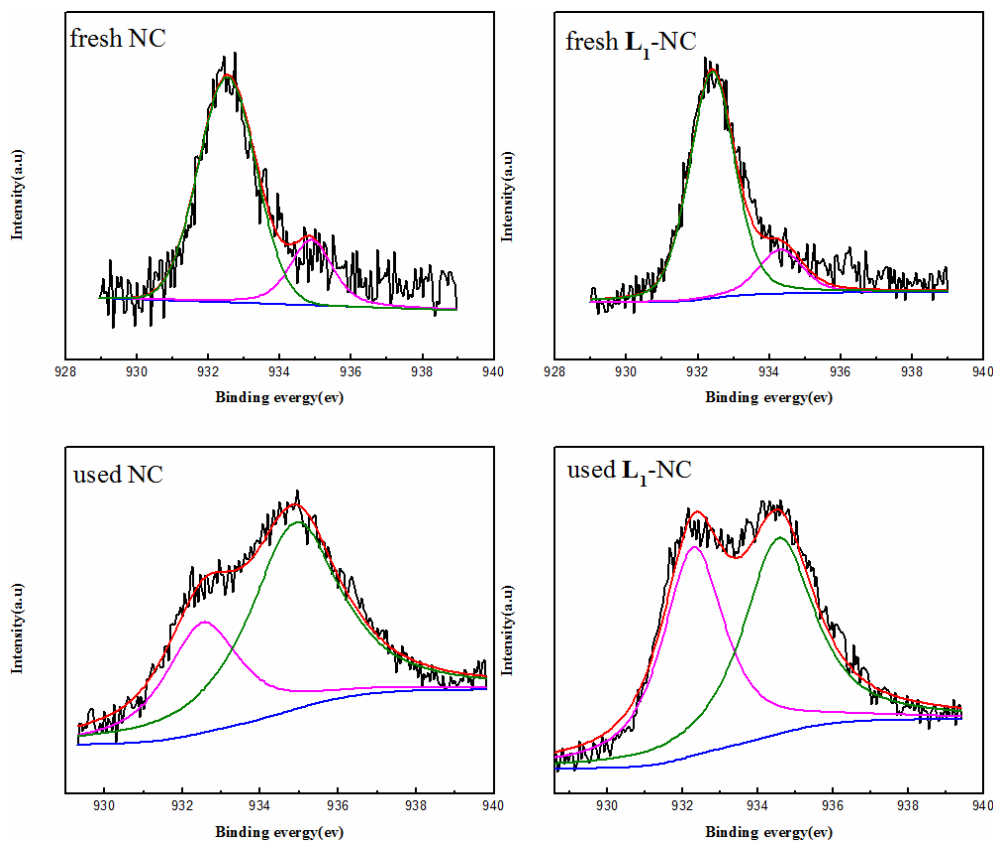

Figure 9. High-resolution XPS spectra of fresh NC, **L$_1$**-NC and used NC, **L$_1$**-NC.

Table 4. Relative content and binding energy of Cu^+ and Cu^{2+} in fresh catalyst.

Catalyst	Area%, Binding Energy (eV)			
	Cu^+		Cu^{2+}	
	Fresh	**Used**	**Fresh**	**Used**
NC	79.09 (932.53)	32.85 (932.51)	20.91 (934.87)	67.15 (934.88)
L$_1$-NC	83.14 (932.31)	48.50 (932.30)	16.86 (934.51)	51.50 (934.56)

In fresh NC, peaks at 932.53 and 934.87 eV represented Cu^+ and Cu^{2+}, which had relative contents of 79.09% and 20.91%, respectively, whereas the peak positions of Cu^+ and Cu^{2+} were at 932.31 and 934.51 eV, respectively, with relative contents of 83.14% and 16.86% for fresh **L$_1$**-NC. However, the contents of Cu^+ in the used NC and **L$_1$**-NC were 32.85% and 48.50%, respectively. The higher content of Cu^+ in used **L$_1$**-NC in comparison with that in the NC may be because **L$_1$** inhibited the reduction of Cu^{2+} to Cu^+. These results explain why **L$_1$**-NC possesses a higher initial catalytic activity and has a longer long-term lifetime than NC.

3. Experimental

3.1. Materials and Catalyst Preparation

Reagent-grade CuCl (99%), NH_4Cl (purity $\geq$ 99.5%), iminodiacetic acid (**L$_1$**), 2-(1*H*-pyrazol-1-yl)acetic acid (**L$_2$**), 1*H*-tetrazole-1-acetic acid (**L$_3$**), diglycolic acid (**L$_4$**), and guanidineacetic acid (**L$_5$**) were purchased from Adamas (Shanghai, China).

The traditional Nieuwland catalyst was labeled as NC. The Nieuwland catalysts containing **L$_1$**, **L$_2$**, **L$_3$**, **L$_4$**, and **L$_5$** were denoted as **L$_1$**-NC, **L$_2$**-NC, **L$_3$**-NC, **L$_4$**-NC, and **L$_5$**-NC, respectively. The initial amounts of **L$_1$**–**L$_5$** are 3.0 mol % based on cuprous chloride (0.60 g, 0.56 g, 0.57 g, 0.60 g and 0.53 g, respectively). The structure of the five ligands was shown in Figure 10.
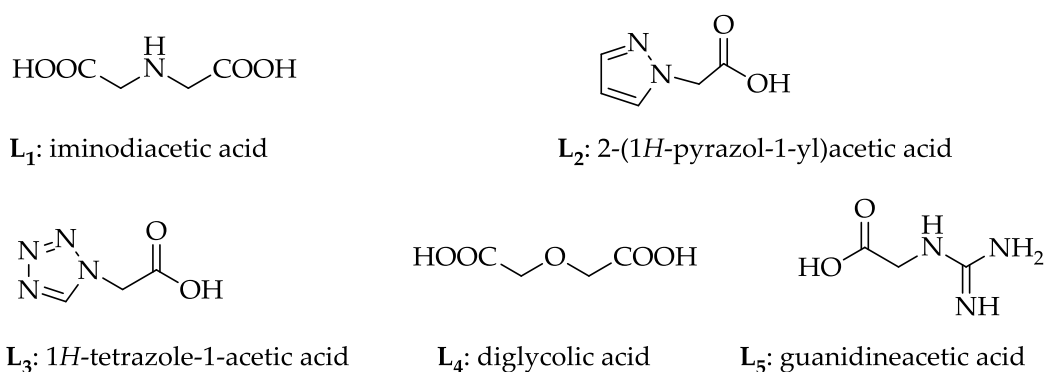

L$_1$: iminodiacetic acid

L$_2$: 2-(1*H*-pyrazol-1-yl)acetic acid

L$_3$: 1*H*-tetrazole-1-acetic acid

L$_4$: diglycolic acid

L$_5$: guanidineacetic acid

Figure 10. The structure of the five ligands.

3.2. The Structure of the Reactor

The reaction was performed in a self-designed glass reactor with a length of 400 mm, an outer diameter of 40 mm, an inner diameter of 20 mm. The reactor inner diameter contains the catalyst solution. A sand core baffle was used at the lower end of the reactor to increase the contact area between acetylene and the catalyst solution. The outer diameter was filled with circulating water to control the temperature of the reactor.

3.3. Catalyst Preparation and the Dimerization Reaction of Acetylene

The flow diagram of acetylene dimerization device is shown in Figure 11. Before the start of the reaction, the air in the pipe was removed by nitrogen during 30 min of continuous nitrogen flow. Then, 8 g of NH_4Cl and 15 mL of deionized water were added to the bubbled bed reactor at 80 °C under nitrogen atmosphere. After the mixture bubbled for approximately 10 min, 14.81 g of CuCl and a quantity of **L$_1$**–**L$_5$** was added to the reactor under nitrogen atmosphere for at least 15 min until these solids got completely dissolved; then, the catalyst was obtained. The flow of C_2H_2 was regulated by a mass flowmeter. The gases in C_2H_2, such as H_2S, PH_3, and O_2, were destroyed by $K_2Cr_2O_7$ and $Na_2S_2O_4$ solutions. The acid gas and water were eliminated using a NaOH solution and a drying tube, respectively. Then, the purified C_2H_2 flowed into a preheated catalyst-containing glass reaction vessel. The gas mixture at the outlet of the reactor was analyzed via chromatography using a Shimadzu (Suzhou, China) GC-2014C equipped with a GDX-301 chromatography column and a flame ionization detector.
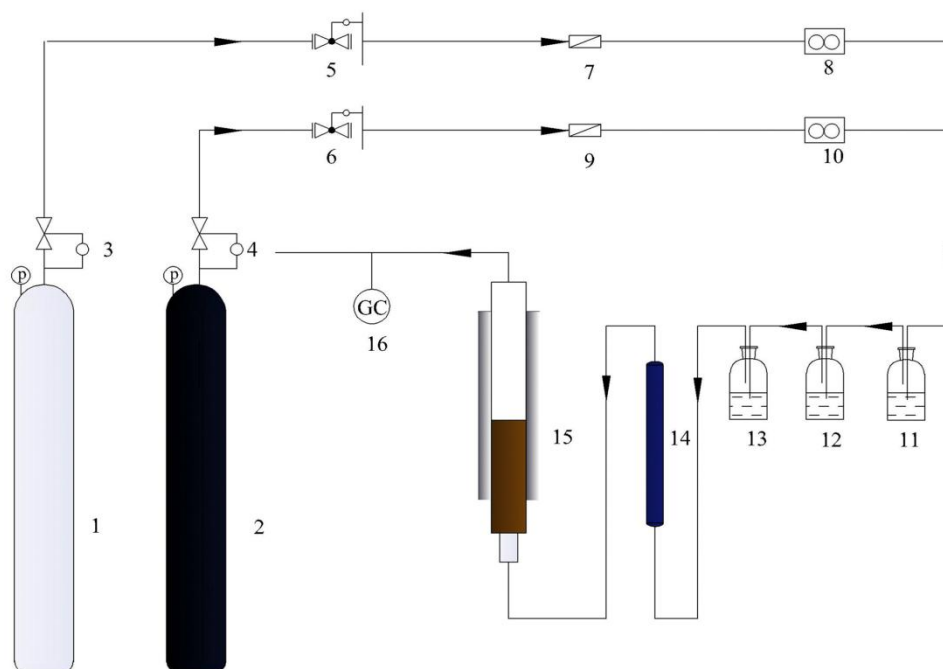
Figure 11. Schematic diagram of the C_2H_2 dimerization system: **1** C_2H_2; **2** N_2; **3, 4** partial pressure valve; **5, 6** check valve; **7, 9** gas filter; **8, 10** mass flow controller; **11** $K_2Cr_2O_7$ solution; **12** $Na_2S_2O_4$ solution; **13** NaOH solution; **14** drying tube; **15** reactor; **16** Gas Chromatograph (GC-2014C).

3.4. Analytical Methods

The conversion of C_2H_2 (*X*) and the selectivity to MVA (*S*) as the criteria of catalytic performance were defined as following equations, respectively.

$$X = [(\lambda_2 + 2\lambda_3 + 2\lambda_4 + 3\lambda_5)/(\lambda_1 + \lambda_2 + 2\lambda_3 + 2\lambda_4 + 3\lambda_5)] \times 100\%$$

$$S = [2\lambda_3/(\lambda_2 + 2\lambda_3 + 2\lambda_4 + 3\lambda_5)] \times 100\%$$

where, λ_1, λ_2, λ_3, λ_4 and λ_5 are considered as the volume fraction of acetylene, acetaldehyde, MVA, 2-chloro-1,3-butadiene and 1,5-hexadien-3-yne (DVA) in the gas product.

3.5. Separation of Crystals A and B from the NC and L_1-NC Solutions

Crystal A was obtained by gradually cooling the NC at 3 °C. It was filtrated and was washed thrice with deionized water, and then, it was dried in a vacuum oven at 55 °C. The **L_1**-NC was treated using the same method to obtain crystal B.

3.6. Treatment of the Used Catalyst Solutions

After the acetylene dimerization reaction occurred, the polymer in the catalyst solution containing NC or **L_1**-NC was filtered, and the catalyst solution was dried in a vacuum oven at 55 °C.

3.7. Catalyst Characterization

FT-IR spectra of the samples in the range of 500 to 4000 cm^{-1} were obtained using a Bruker (Karlsruhe, Gemany) Vertex70.

TG-DTG of the samples was carried out using a NETZSCH (Bavaria, Germany) STA 449 F3 Jupiter under a nitrogen atmosphere. The temperature was increased from 50 °C to 900 °C at a rate of 10 °C min^{-1}.

X-ray diffraction (XRD) patterns were collected using a Bruker (Karlsruhe, Germany) D8 Advanced X-ray diffractometer with Cu–Kα irradiation (λ = 1.5406 Å) at 40 kV and 40 mA at wide angles (10°–90° in 2θ).

A Kratos AXIS Ultra DLD spectrometer (Manchester, UK) with a monochromatized, Al–Kα X-ray source (225 W) was used to record the XPS data.

Elemental analysis of the crystals was carried out via X-ray fluorescence (XRF) using a Shimadzu (Tokyo, Japan) XRF-1800 system (Rh target) at 40 kV and 1 mA with HS Easy software.

TPD-MS experiments were carried out using a Micromeritic (Atlanta, GA, USA) ASAP 2720 apparatus equipped with a TCD detector.

4. Conclusions

We demonstrated an iminodiacetic acid-assisted aqueous Nieuwland catalyst for the acetylene dimerization reaction that can achieve a 38.0% yield for acetylene conversion and an 85% yield for MVA selectivity with an increase in yield of 12% relative to the Nieuwland catalyst system. In this transformation, iminodiacetic acid not only provides proper acidity of the catalyst solution but also prevents Cu^+ oxidation to Cu^{2+}, which are beneficial for the catalytic activity and stability. Further investigations on acetylene dimerization using this strategy are ongoing in our laboratory and will be reported in the future.

Author Contributions: Jianwei Xie and Bin Dai received the project. Yanhe You and Juan Luo performed the experiments and analyzed the spectra data. Yanhe You, Jianwei Xie and Bin Dai wrote the paper.

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

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