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# Strontium Chloride Modified Nieuwland Catalyst in the Dimerization of Acetylene to Monovinylacetylene

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$SrCl_2$ was used as a co-catalyst of CuCl in Nieuwland catalyst and CuCl as the main catalyst, $NH_4Cl$ as the solubilizer, water as the solvent and a certain amount of hydrochloric acid, thereby forming Sr-Cu bimetallic cooperative catalysis reaction systems for $C_2H_2$ dimerization. Under the optimum condition, the acetylene conversion is 13 % and monovinylacetylene selectivity can reach to 94 %.

**Keywords: Strontium chloride, Nieuwland catalyst, Acetylene dimerization, Monovinylacetylene.**

## INTRODUCTION

The dimerization of $C_2H_2$ is an important industrial process for the production of monovinylacetylene (MVA), a starting material used in $C_2H_2$-based processes for chloroprene rubber production[1]. Although largely being superseded in many developed countries by butadiene-based processes, $C_2H_2$ dimerization is still an important process for chloroprene production in locations where coal-based economies remain active, such as in China. In addition, monovinylacetylene can also be used to produce other important chemical products, such as 4-chlorophthalic anhydride, benzene, styrene and butanedione[2]. A Nieuwland catalyst composed of CuCl and KCl or $NH_4Cl$ in acidic aqueous solution has long been used for $C_2H_2$ dimerization on an industrial scales[3]. Crystallographic studies of the solid products recovered from Nieuwland aqueous solutions of CuCl and $NH_4Cl$ have revealed that the active components in Nieuwland catalyst are chlorocuprates $(Cu_mCl_n^{-(n-m)})$[4].

Dimerization of $C_2H_2$ with Nieuwland catalyst is usually conducted in a bubbling bed reactor. Acetylene gas is continuously introduced into a liquid catalyst solution and the unreacted $C_2H_2$, monovinylacetylene and other by-products flow out of the reactor together. All of the possible reactions are shown in Table-1. Monovinylacetylene is the dimerization product of $C_2H_2$, and $C_2H_2$ or monovinylacetylene can also react with $H_2O$ and HCl to yield several by-products, such as vinyl chloride, acetaldehyde, 2-chloro-1,3-butadiene and 1,5-hexadien-3-yne. The main side reaction is $C_2H_2$ trimerization, which can be considered as the further reaction of monovinylacetylene with $C_2H_2$[5].

In recent years, studies related to $C_2H_2$ dimerization have attracted significant attention. Osakada and co-workers[3] investigated the structure of Nieuwland catalyst in solid state and in solution and their results revealed that the Cu compounds are CuCl and $K_2CuCl_3$ in solid state and $KCuCl_2$ is the dominant component in solution. Han and co-workers reported the composition of the precipitate which is often formed in the $C_2H_2$ dimerization reaction. Their results indicated that the precipitate is composed of $CuCl{\cdot}2C_2H_2{\cdot}1/5NH_3$ obtained from the aqueous Nieuwland catalyst[6] and $2CuCl{\cdot}3C_2H_2{\cdot}1/3CH_3CH_2NH_2{\cdot}1/7C_3H_7NO$ in anhydrous N,N-dimethylformamide (DMF)[7]. They also studied the effect of solvent on catalytic performance and the highest yield of monovinylacetylene have been obtained when DMF was used as solvent, which contribute to its strong coordination ability to Cu(I)[8]. Tao and co-workers reported that urea[9], $LaCl_3$[10], or $CeCl_3$[11] can improve monovinylacetylene selectivity, when they were used as co-catalyst to the Nieuwland catalyst. Mechanistic studies on dimerization of $C_2H_2$ with Nieuwland catalyst were conducted by Fukuzumi and co-workers[12-14]. The results indicated that deprotonation of the $C_2H_2$ π-complex to form the σ-complex with the Nieuwland catalyst was the rate-determining step and it was important to avoid any further reaction of Cu(I)-monovinylacetylene π-complex with the $C_2H_2$ π-complex, which leads to the formation of the trimeri-zation product.

Although significant improvements have been achieved in $C_2H_2$ dimerization reaction, the drawbacks such as low $C_2H_2$ conversion and low monovinylacetylene selectivity also exist[7]. Herein, we report our efforts in finding Sr-Cu bimetallic cooperative catalysis reaction systems for $C_2H_2$ dimerization. In the catalyst system, CuCl was used as the main catalyst, $SrCl_2$

TABLE-1
REACTIONS IN THE DIMERIZATION OF $C_2H_2$ CATALYSED BY NIEUWLAND CATALYST

| Formula | Number |
|---|---|
| HC≡CH + HC≡CH → $CH_2$=CHC≡CH | (1) |
| HC≡CH + HCl → $CH_2$=CHCl | (2) |
| HC≡CH + $H_2O$ → $CH_3CHO$ | (3) |
| $CH_2$=CHC≡CH + HCl → $CH_2$=CHCCl=$CH_2$ | (4) |
| HC≡CH + $CH_2$=CHC≡CH → $CH_2$=CHC≡CCH=$CH_2$ | (5) |

as co-catalyst, $NH_4Cl$ as the solubilizer and a certain amount of hydrochloric acid was added to the catalyst solution to achieve an acidic aqueous environment.

## EXPERIMENTAL

**Reaction vessel:** The gas-liquid $C_2H_2$ dimerization was performed in a self-designed glass reaction vessel, which is similar to a straight cool condenser, contained a cylindrical gas distributor and a coaxial glass tubes with various diameter. The gas distributor caused the gas to scatter into small bubbles, thus increasing the gas-liquid contact area. The thermostatically controlled water flowed through the interspaces of the internal and external tubes to achieve the desired reaction temperature and to remove excess heat as a result of the exothermic reaction of the $C_2H_2$ dimerization.

**Catalyst preparation and catalytic reaction:** A schematic diagram of the $C_2H_2$ dimerization system is shown in Fig. 1. The pipeline was purged with nitrogen for 0.5 h before the reaction to remove air in the system. An equivalent mole of $NH_4Cl$ (based on CuCl) and 15 mL distilled water were added to the reaction vessel at 80 °C under nitrogen. After the mixture bubbled for about 10 min, $SrCl_2$ was added and then CuCl and HCl (0.3 wt. %) were added under nitrogen for at least 20 min until it dissolved, then the catalyst was obtained. Acetylene was successively passing through a filter to remove trace impurities, a calibrated mass flow controller to limit the $C_2H_2$ flow, a $K_2Cr_2O_7$ solution to eradicate $H_2S$ and $PH_3$ and a NaOH solution to eradicate the acidic gas and then it flowed into a pre-heated glass reaction vessel, which contained the catalyst. The exit gas mixture passed through an

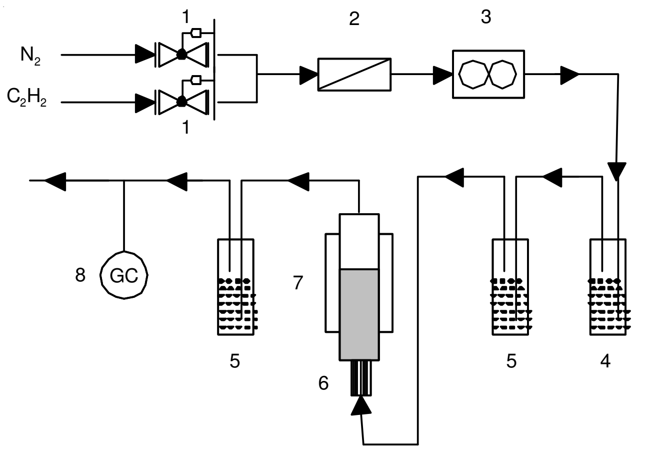


Fig. 1. Schematic diagram of the $C_2H_2$ dimerization system. 1 = valve, 2 = gas filter, 3 = mass flow controller, 4 = $K_2Cr_2O_7$ solution, 5 = NaOH solution, 6 = gas distributor, 7 = reactor, 8 = gas chromatography

absorption bottle containing NaOH solution and then into a Shimadzu GC-2014C chromatogram equipped with GDX-301 chromatography column and flame ionization detector for analysis.

**Analytical methods:** The conversion of $C_2H_2$ ($X_A$) and the selectivity to monovinylacetylene ($S_{MVA}$), which are the criteria of catalytic performance, are obtained using the following equations:

$$X_A = [(\varphi_2 + \varphi_3 + 2\varphi_4 + 2\varphi_5 + 3\varphi_6)/(\varphi_1 + \varphi_2 + \varphi_3 + 2\varphi_4 + 2\varphi_5 + 3\varphi_6)] \times 100\ \% \quad (1)$$

$$S_{MVA} = [2\varphi_4/(\varphi_2 + \varphi_3 + 2\varphi_4 + 2\varphi_5 + 3\varphi_6)] \times 100\ \% \quad (2)$$

where, $\varphi_1$, $\varphi_2$, $\varphi_3$, $\varphi_4$, $\varphi_5$ and $\varphi_6$ are considered as the volume fraction of acetylene, vinyl chloride, acetaldehyde, monovinylacetylene, 2-chloro-1,3-butadiene and 1,5-hexadien-3-yne (DVA) in the gas product.

## RESULTS AND DISCUSSION

$SrCl_2$ (10 mol %, based on CuCl), a low-cost and water-soluble salt, was initially added to the Nieuwland catalyst solution for $C_2H_2$ dimerization and the results were shown in Fig. 2. When $SrCl_2$ was employed as additive, the Nieuwland catalyst remained as a homogeneous solution without forming precipitates and the $C_2H_2$ conversion and monovinylacet-ylene selectivity are kept at 15 and 92 %, respectively. Compared with traditional Nieuwland catalyst, there was slight decrease in $C_2H_2$ conversion, but significant increase in monovinylacetylene selectivity. This could be contributed to the $SrCl_2$-Nieuwland catalyst increased the reaction energy barrier of monovinylacetylene and $C_2H_2$ to form DVA, which enhanced the monovinylacetylene selectivity[15].

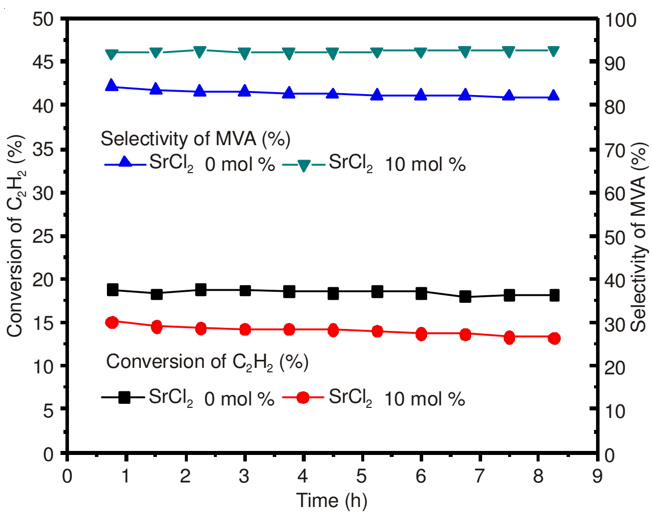


Fig. 2. Influence of Nieuwland catalyst modified with $SrCl_2$ to $C_2H_2$ dimerization

Considering that the addition of $SrCl_2$ had an obvious catalytic effect on the Nieuwland catalyst, the loading of $SrCl_2$ was then investigated. As shown in Fig. 3, increasing the amount of $SrCl_2$ from 0 to 15 mol % led to a lower $C_2H_2$ conversion from 21 to 12 %. Meanwhile, the monovinylacetylene selectivity increased from 83 to 92 % when the molar percentage of $SrCl_2$ from 0 to 10 mol %. However, the selectivity decreased to 88 % when the molar percentage of $SrCl_2$ increased to 15 %. With regard to $C_2H_2$ conversion, monovinyl-

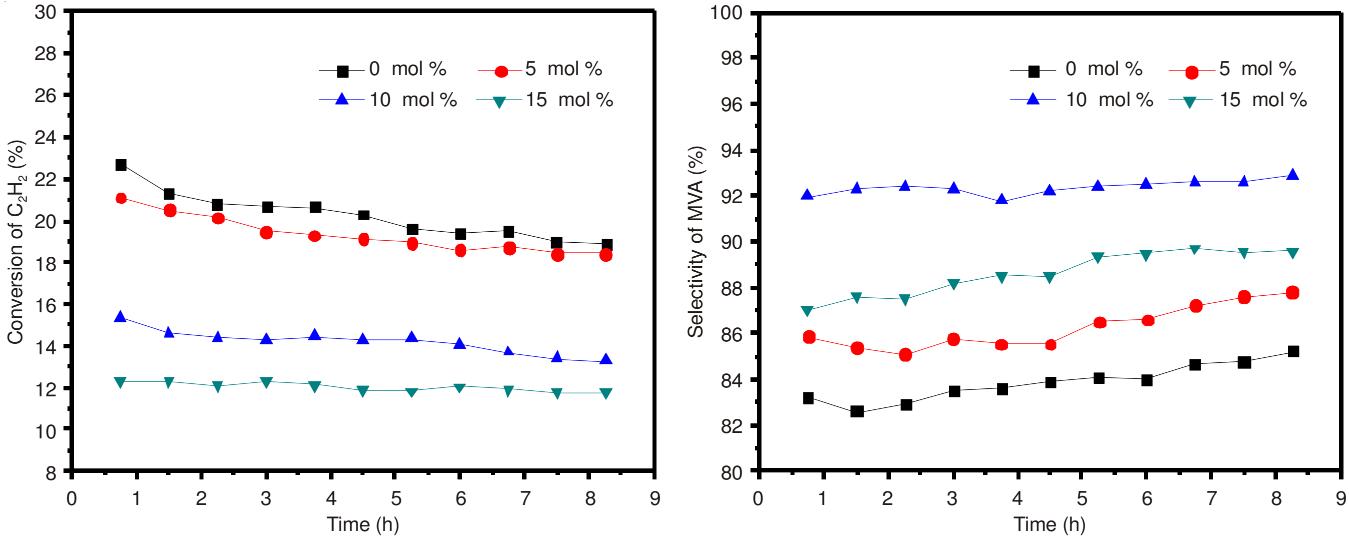


Fig. 3. Effect of $SrCl_2$ mole percentage to $C_2H_2$ dimerization

acetylene selectivity and the separation by-product of industrial production, we adopted the $SrCl_2$ molar percentage of 10 mol % in the subsequent experiment to achieve higher monovinylacetylene selectivity.

We subsequently tested the effect of CuCl mass percentage of $SrCl_2$-Nieuwland catalyst (25, 30, 35 and 37 wt. %) and the results are illustrated in Fig. 4. Given that 40 wt. % CuCl concentration of the catalyst solution was not prepared because of the insolubility of CuCl, we employed the 37 wt. % concentration instead. The results indicate that $C_2H_2$ conversion increased with the increasing CuCl concentration from 25 to 37 wt. %. However, there was a slight increase of monovinylacetylene selectivity from 25 wt. % CuCl to 30 wt. % CuCl and an obviously decrease from 30 wt. % CuCl to 37 wt. % CuCl. The optimal CuCl mass percentage of the total catalyst is 30 wt. %, with 13 % $C_2H_2$ conversion and 94 % monovinylacetylene selectivity.

Fig. 5 showed the effect of temperature on $SrCl_2$-Nieuwland catalyst catalyzing $C_2H_2$ dimerization reaction. The increasing temperature is beneficial to the $C_2H_2$ conversion and monovinylacetylene selectivity in reaction temperature from 70 to 80 °C. However, both $C_2H_2$ conversion and monovinylacetylene selectivity decreased when the temperature increased to 85 °C, which may be probably due to the catalyst deactivation.

The effect of $C_2H_2$ space velocity was investigated in the range between 120 and 240 $h^{-1}$ and the results were summarized in Fig. 6. The increase of space velocity of acetylene led to a decrease of $C_2H_2$ conversion and the conversion was similar to those at space velocities of 160 and 200 $h^{-1}$. An obvious decrease in $C_2H_2$ conversion was found at the space velocity of 240 $h^{-1}$, which is probably due to the incomplete reaction caused by the shorter residence time in the catalyst solution at higher gas space velocity. Moreover, monovinylacetylene selectivity increased with the increase of space velocity from 120 to 200 $h^{-1}$ and then decreased when the space velocity increased to 240 $h^{-1}$. At a space velocity of 200 $h^{-1}$, the highest selectivity and good $C_2H_2$ conversion are achieved.

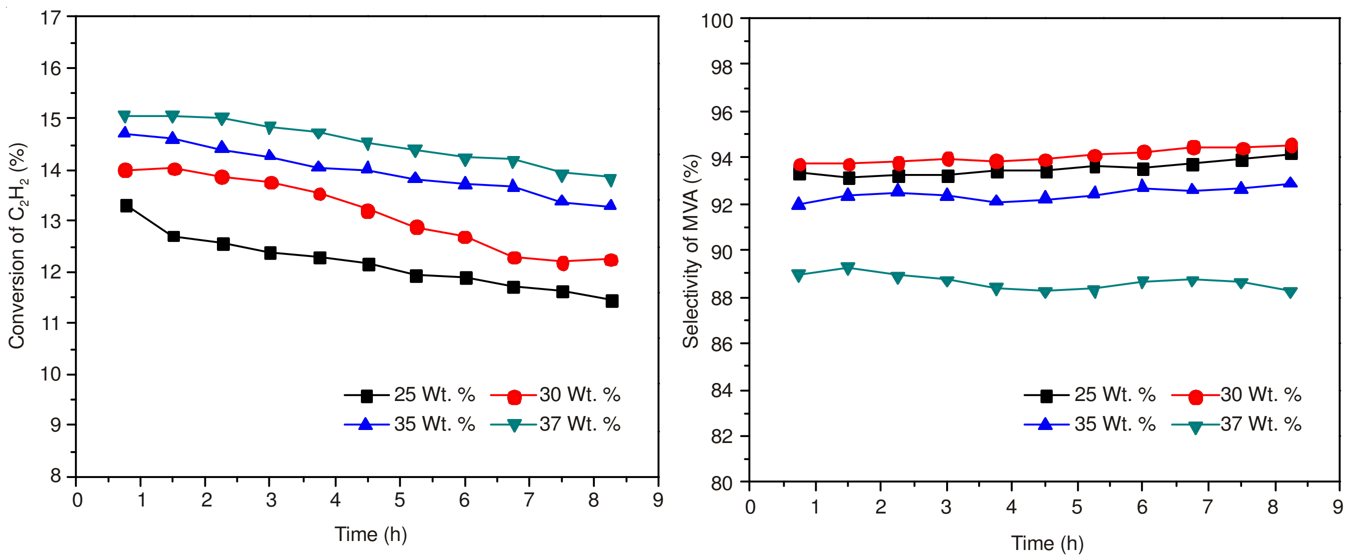


Fig. 4. Effect of CuCl mass percentage to $C_2H_2$ dimerization

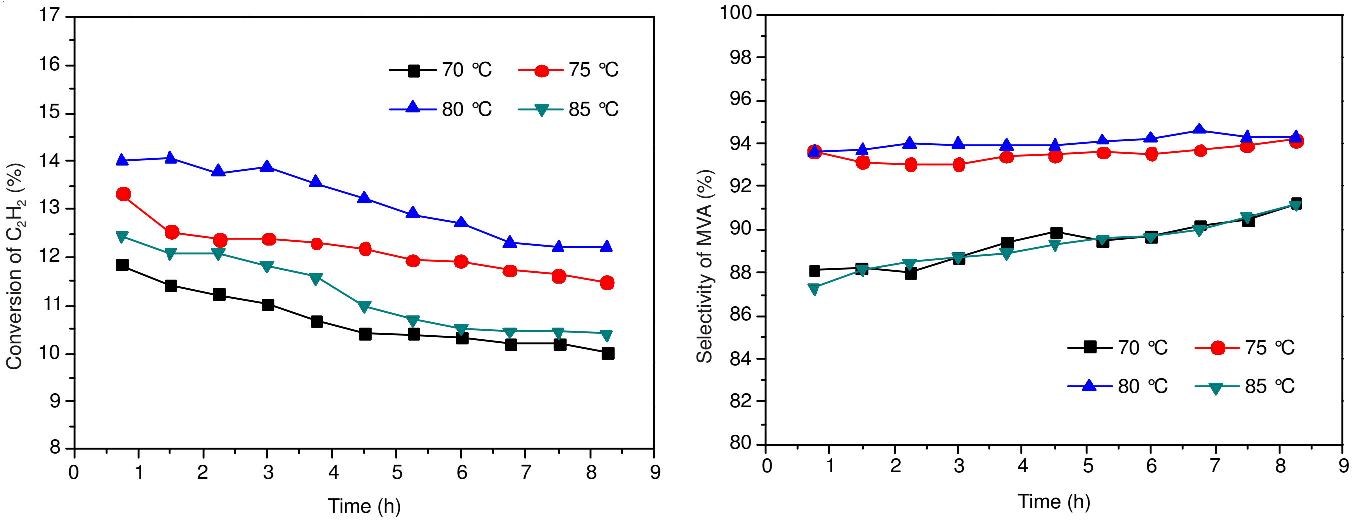


Fig. 5. Effect of reaction temperature to $C_2H_2$ dimerization

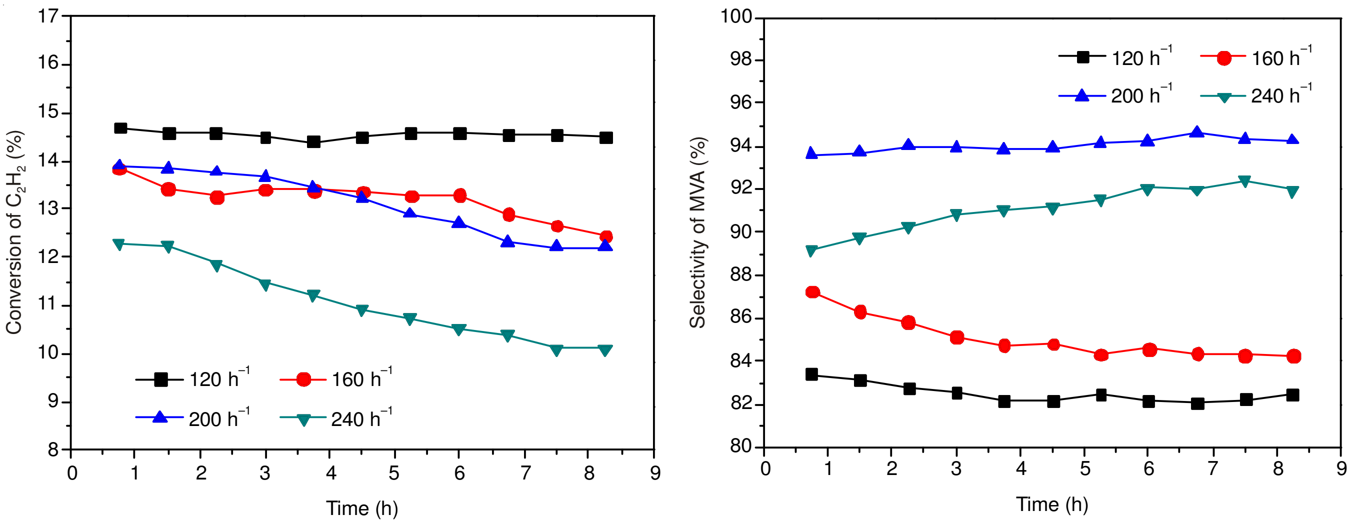


Fig. 6. Effect of $C_2H_2$ space velocity to $C_2H_2$ dimerization

## Conclusion

In conclusion, dimerization of $C_2H_2$ was successfully demonstrated using $SrCl_2$ as co-catalyst of Nieuwland catalyst. Under optimal experimental conditions (10 mol % $SrCl_2$, 30 wt. % CuCl, 80 °C and 200 h$^{-1}$), the $C_2H_2$ conversion was 13 % and monovinylacetylene selectivity reached to 94 %, which was beneficial for the subsequent separation of monovinylacetylene and the by-products in industrial production.


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