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

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SrCl₂ was used as a co-catalyst of CuCl in Nieuwland catalyst and CuCl as the main catalyst, NH₄Cl as the solubilizer, water as the solvent and a certain amount of hydrochloric acid, thereby forming Sr-Cu bimetallic cooperative catalysis reaction systems for C₂H₂ 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 C₂H₂ is an important industrial process for the production of monovinylacetylene (MVA), a starting material used in C₂H₂-based processes for chloroprene rubber production¹. Although largely being superseded in many developed countries by butadiene-based processes, C₂H₂ dimerization is still an important process for chloroprene production in locations where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 butanedione². A Nieuwland catalyst composed of CuCl and KCl or NH₄Cl in acidic aqueous solution has long been used for C₂H₂ dimerization on an industrial scales³. Crystallographic studies of the solid products recovered from Nieuwland aqueous solutions of CuCl and NH₄Cl have revealed that the active components in Nieuwland catalyst are chlorocuprates (Cu_mCl_n^{-(n-m)})⁴.

Dimerization of C₂H₂ with Nieuwland catalyst is usually conducted in a bubbling bed reactor. Acetylene gas is continuously introduced into a liquid catalyst solution and the unreacted C₂H₂, 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 C₂H₂, and C₂H₂ or monovinylacetylene can also react with H₂O 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 C₂H₂ trimerization, which can be considered as the further reaction of monovinylacetylene with C₂H₂⁵.

In recent years, studies related to C₂H₂ dimerization have attracted significant attention. Osakada and co-workers³ investigated the structure of Nieuwland catalyst in solid state and in solution and their results revealed that the Cu compounds are CuCl and K₂CuCl₃ in solid state and KCuCl₂ is the dominant component in solution. Han and co-workers reported the composition of the precipitate which is often formed in the C₂H₂ dimerization reaction. Their results indicated that the precipitate is composed of CuCl·2C₂H₂·1/5NH₃ obtained from the aqueous Nieuwland catalyst⁶ and 2CuCl·3C₂H₂·1/3CH₃CH₂NH₂·1/7C₃H₇NO 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 urea⁹, LaCl₃¹⁰, or CeCl₃¹¹ can improve monovinylacetylene selectivity, when they were used as co-catalyst to the Nieuwland catalyst. Mechanistic studies on dimerization of C₂H₂ with Nieuwland catalyst were conducted by Fukuzumi and co-workers¹²⁻¹⁴. The results indicated that deprotonation of the C₂H₂ 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 C₂H₂ π-complex, which leads to the formation of the trimerization product.

Although significant improvements have been achieved in C₂H₂ dimerization reaction, the drawbacks such as low C₂H₂ conversion and low monovinylacetylene selectivity also exist⁷. Herein, we report our efforts in finding Sr-Cu bimetallic cooperative catalysis reaction systems for C₂H₂ dimerization. In the catalyst system, CuCl was used as the main catalyst, SrCl₂

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

Formula	Number
$HC\equiv CH + HC\equiv CH \rightarrow CH_2=CHC\equiv CH$	(1)
$HC\equiv CH + HCl \rightarrow CH_2=CHCl$	(2)
$HC\equiv CH + H_2O \rightarrow CH_3CHO$	(3)
$CH_2=CHC\equiv CH + HCl \rightarrow CH_2=CHCCl=CH_2$	(4)
$HC\equiv CH + CH_2=CHC\equiv CH \rightarrow CH_2=CHC\equiv CCH=CH_2$	(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, φ_1 , φ_2 , φ_3 , φ_4 , φ_5 and φ_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 monovinylacetylene 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 selectivity¹⁵.

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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