

Available online at www.sciencedirect.com



Journal of Natural Gas Chemistry 21(2012)495-500



Stability improvement of the Nieuwland catalyst in the dimerization of acetylene to monovinylacetylene

Jianguo Liu, Yizan Zuo, Minghan Han*, Zhanwen Wang, Dezheng Wang

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China [Manuscript received November 19, 2011; revised February 13, 2012]

Abstract

In the process of dimerization of acetylene to produce monovinylacetylene (MVA), the loss of active component CuCl in the Nieuwland catalyst due to the formation of a dark red precipitate was investigated. The formula of the precipitate was CuCl·2C₂H₂·1/5NH₃, and it was presumed to be formed by the combination of NH₃, C₂H₂ and [Cu]-acetylene π -complex, which was an intermediate in the dimerization reaction. The addition of hydrochloric acid into the catalyst can reduce the formation of precipitate, whereas excessive H⁺ is unfavorable to the dimerization reaction of acetylene. To balance between high acetylene conversion and low loss rate of CuCl, the optimum mass percentage of HCl in the added hydrochloric acid was determined. The result showed the optimum mass percentage of HCl decreased from 5.0% to 3.2% when the space velocity of acetylene was from 140 h⁻¹ to 360 h⁻¹. The result in this work also indicated the pH of the Nieuwland catalyst should be kept in the range of 5.80–5.97 during the reaction process, which was good for both catalyst life and acetylene conversion.

Key words

monovinylacetylene; dimerization reaction; Nieuwland catalyst; acetylene; stability

1. Introduction

Monovinylacetylene (MVA) is produced worldwide as the starting material for chloroprene rubber, which is better than other synthetic rubbers due to its excellent mechanical property, as well as its high resistance to abrasion, aging and corrosion [1]. In addition, MVA can be used to produce other important chemical products, such as 4-chlorophthalic anhydride, benzene, styrene and butanedione [2,3]. MVA is made industrially by dimerization of acetylene with the Nieuwland catalyst (HC \equiv CH+HC \equiv CH \rightarrow CH₂ = CHC \equiv CH), which is composed of CuCl (active component) and NH₄Cl (solubilizer) in an aqueous media [4,5]. The introduction of acetylene into the aqueous catalyst gives not only the formation of MVA but also side products, such as divinylacetylene by trimerization reaction of acetylene (3HC \equiv CH \rightarrow CH₂ = CHC \equiv CCH = CH₂), acetaldehyde by hydration reaction (HC \equiv CH+H₂O \rightarrow CH₃CHO) chloroethylene hydrochlorination and by reaction $(HC \equiv CH + HCl \rightarrow CH_2 = CHCl)$. The trimerization reaction is a main side reaction, which can also be considered as the further reaction of MVA with acetylene [6,7].

In spite of the long history and high performance of the Nieuwland catalyst, however, it does not have good stability when used for the industrial process of acetylene dimerization, which is caused by the formation of a dark red precipitate containing active component CuCl. The loss of CuCl leads to a shorter lifetime of the catalyst and causes many problems. Although it is presumed that the precipitate may contain C_2H_2 and amines in addition to CuCl [8], the composition of precipitate has not confirmed yet.

It is also reported that the formation of the precipitate is associated with the loss of hydrogen chloride from the catalyst solution, which is removed by the acetylene flow, and the addition of HCl into the catalyst solution can reduce the formation of the precipitate [8]. On the other hand, recent studies have revealed that the concentration of H^+ in the catalyst should be maintained at a certain level, and its further increase leads to a noticeable drop in conversion of acetylene [9,10].

In the industrial process of acetylene dimerization, the hydrochloric acid is added into the catalyst during the reaction to keep acidity stable, and in order to keep the volume of Nieuwland catalyst unchanged, the volume of added hydrochloric acid is equal to that of loss of water, which is also taken out of the reactor by the acetylene flow.

^{*} Corresponding author. Tel: +86-10-62781469; Fax: +86-10-62772051; E-mail: hannh@tsinghua.edu.cn This work was supported by the National Basic Research Program of China (No. 2009CB219901).

Copyright©2012, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All rights reserved. doi:10.1016/S1003-9953(11)60396-4

However, the researches about the effect of added hydrochloric acid on the loss rate of CuCl and dimerization reaction of acetylene are still scarce. In this work, the composition of the precipitate and its possible formation mechanism were deduced. Moreover, we studied the effect of addition of hydrochloric acid on the loss rate of CuCl, conversion of acetylene as well as selectivity to MVA, and the optimum mass percentage of HCl in added hydrochloric acid was determined, which resulted in the reduction of the loss of CuCl without obvious adverse effect on the conversion of acetylene and selectivity to MVA.

2. Experimental

2.1. Preparation of the Nieuwland catalyst solution

50 g CuCl and 28 g NH₄Cl were added into 48 mL distilled water at 60 $^{\circ}$ C under nitrogen. The mixture was stirred for about 40 min until it turned orange and the Nieuwland catalyst was obtained.

2.2. Dimerization of acetylene

A schematic diagram of the experimental system is shown in Figure 1. The reactor is a bubble bed reactor (made of glass) with 29 mm inside diameter and 150 mm length, and it is equipped with acetylene inlet, product outlet, a side pipe for adding hydrochloric acid, thermometer and water bath. After the catalyst solution (90 mL) was put in the reactor, N₂ was introduced into it for 15 min to prevent oxidation of catalyst. The acetylene was purified by passing it through a K₂Cr₂O₇ solution to get rid of H₂S and PH₃, a Na₂S₂O₄ solution to get rid of O₂ and a NaOH solution to get rid of acidic gas, and then it flowed into the catalyst which was maintained at 70 °C.

During the reaction, the gas sample at the outlet was analyzed by gas chromatography (Shimadzu GC-14B equipped with Al₂O₃-PLOT chromatography column and flame ionization detector).

The space velocity of acetylene is expressed as the ratio



Figure 1. Schematic diagram of experimental system. $1-C_2H_2$, $2-N_2$, 3, 4-valve, $5-K_2Cr_2O_7$ solution, $6-Na_2S_2O_4$ solution, 7-NaOH solution, 8, 9-rotometer, 10-inlet gas, 11-reactor, 12-water bath, 13-exit gas

of acetylene volume flow (at atmosphere pressure and room temperature) to volume of catalyst. Conversion of acetylene is defined as moles of acetylene converted with respect to acetylene in feed, and selectivity to MVA is defined as the percentage of acetylene dimerized to MVA over totally converted acetylene.

2.3. Separation of the precipitate

After the reaction, nitrogen was passed into the Nieuwland catalyst until the products and acetylene were removed. After that, a dark red precipitate was separated from the catalyst solution by vacuum filtration, then washed with deionized water for three times and dried in a vacuum tank at 60 °C.

2.4. Characterization of the precipitate

Infrared spectroscopy (FT-IR) of the precipitate was recorded on a Nicolet Nexus FT-IR spectrometer (KBr pellet) equipped with a DTGS detector in the range of $400-4000 \,\mathrm{cm}^{-1}$ at room temperature. Thermal analysis (TG, Setaram instrumentation) of the precipitate was performed in the temperature range of 30-900 °C with a heating rate of 10 °C/min under N2 atmosphere. The thermal analysis is equipped with a quadruple mass spectrometer (NETZSCH QMS 403C), and the m/z signals of 26 and 17 were monitored using a channeltron detector. The XPS measurement of precipitate was carried out using AXIS-Ultra instrument (Kratos Analytical) with monochromatized Al K_{α} radiation (1486.6 ev). The binding energy scale (BE) was calibrated based on the C 1s signal (BE = 284.8 ev). The thermally decomposed product of the precipitate was characterized on a Bruker D8 advance X-ray diffractometer with a nickel-filtered Cu K_{α} radiation X-ray source at 40 kV and 20 mA.

3. Results and discussion

3.1. Composition of the precipitate

The IR spectrum of the precipitate is shown in Figure 2. The bands located at 3300 and 633 cm⁻¹ were assigned to ν_{C-H} stretching vibration and δ_{C-H} bending vibration respectively, and the band at 2360 cm⁻¹ assigned to $\nu_{C\equiv C}$ stretching vibrations [11]. The possible alkynes in the catalyst solution were C₂H₂, MVA and divinylacetylene. There was no peak in the range of 3070–3090 cm⁻¹, which suggested that there were no molecules containing = CH₂ fragment in the precipitate [11]. Therefore, the alkyne in the precipitate was C₂H₂. The band at 3440 cm⁻¹ was the symmetric stretching vibration of N-H unit, and the bands located at 1600 cm⁻¹ and 880 cm⁻¹ were due to its bending vibrations [11]. NH₃ produced by the deionization of NH₄⁺ is the only kind of amine in the catalyst solution, and thus we can conclude that the precipitate contains C₂H₂ and NH₃. Download English Version:

https://daneshyari.com/en/article/71361

Download Persian Version:

https://daneshyari.com/article/71361

Daneshyari.com