

Nieuwland catalysts: investigation of structure in the solid state and in solution and performance in the dimerization of acetylene

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Abstract

Catalysis by Cu salts (M_nCuCl_{n+1} ; $M = K^+, NH_4^+$) in concentrated aqueous solutions (approximately 5–8 M) is investigated using a flow reaction system at 75°C. Selective dimerization of acetylene gives vinylacetylene as a major product and much smaller amounts of 1,2-divinylacetylene, acetaldehyde, 1-ethynyl-1,3-butadiene, and uncharacterized black tarry products. Cooling the catalyst solution to room temperature causes the growth of a mixture of tetrahedral and needle-like colorless crystals. Observation of the crystals by microscopy and their crystallography, and analyses of the Cu compounds reveal that they are CuCl and K_2CuCl_3 , respectively. Plots of the graphs of the solubility of the Cu salts in water as a function of temperature and composition of the salt show the dominant presence of $KCuCl_2$ in the solution. A mechanism of the reaction is proposed based on the performance of the catalyst and its structure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A Nieuwland catalyst, which is composed of CuCl and KCl or NH_4Cl , has long been the representative catalyst for acetylene dimerization on an industrial scale [1–6]. Catalysis by a Nieuwland system has several unique characteristics. It enables selective dimerization of acetylene to give vinylacetylene, and the further reaction of acetylene with the product is effectively prohibited, resulting in the formation of the dimer of acetylene rather than that of benzene or a linear acetylene trimer. Vinylacetylene is easily turned into chloroprene which is an important starting mate-

rial for the synthetic rubber. The catalytic reaction is carried out in aqueous solutions containing high concentrations of the Cu^+ and K^+ (or NH_4^+). The reaction needs to be carried out under the proper pH range to inhibit formation of explosive copper acetylide and without exposure of the products to oxygen to prevent ignition of divinylacetylene formed as a by-product. This aqueous reaction seems to be environmentally more favorable than a number of synthetic organic reactions including transition metal complexes promoted dimerization of monosubstituted acetylenes in organic solvents.

The mechanism of the reaction is probably distinct from that of the previously studied homogeneous catalytic reactions which have mostly been carried out in dilute solutions of organic solvents. In spite of the long history and exclusively high performance of the

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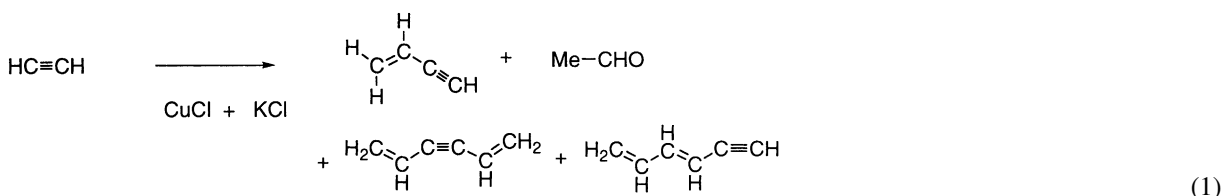
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Nieuwland catalyst, only a few detailed studies on the catalyst structure and performance have appeared in the literature. Crystallographic studies of solid products recovered from aqueous solutions of NH_4Cl and CuCl revealed several structures of chlorocuprates, $\text{Cu}_m\text{Cl}_n^{-(n-m)}$ [7,8]. Further elucidation of relationship between the catalyst performance and solution structure of the catalyst seems to be of importance to comprehend the mechanism of the unique catalytic reaction. In this paper, we report the structure of the Nieuwland catalyst in the solid state and in solution, and its catalytic activity which varies depending on the conditions.

2. Results and discussion

2.1. Performance of the Nieuwland catalyst

Passing acetylene into an aqueous solution of a Nieuwland catalyst composed of a mixture of CuCl and KCl using a flow reaction system produces vinylacetylene in high selectivity (approximately 90%) together with smaller amounts of 1,2-divinylacetylene, acetaldehyde, 1-ethynyl-1,3-butadiene, and uncharacterized black tarry products probably containing acetylene oligomers or polymers (Eq. (1)).



A typical example is shown in the following. An aqueous solution (240 ml) of a mixture of CuCl (6.7 M) and KCl (6.4 M) at 75°C converts acetylene (12.3% conversion) into a mixture of vinylacetylene (92.8% selectivity) and smaller amounts of acetaldehyde, 1,2-divinylacetylene, 1-ethynyl-1,3-butadiene and tarry acetylene oligomers. Vinyl chloride less than 0.1% was also formed. These results as well as those of the reactions using LiCl , NaCl , CsCl and NH_4Cl , instead of KCl are summarized in Table 1. The catalyst prepared from CuCl and NH_4Cl exhibits a level of catalytic activity similar to or slightly lower than the CuCl - KCl catalyst, whereas LiCl , NaCl ,

and CsCl promote the reaction to a much lesser extent than KCl or NH_4Cl . Since the catalysts prepared from CuCl and these three alkaline metal chlorides are partially soluble in water at the temperature used (36–44% of the original salts undissolved), the low level of catalytic activity is primarily due to the low concentration of the catalyst.

Table 1 also lists the results of the reactions catalyzed by the CuCl - KCl catalyst with different Cu concentrations and K/Cu ratios of the catalyst. The rate of conversion of acetylene, as well as the molar ratio of vinylacetylene to converted acetylene, is influenced by Cu concentration to a negligible extent (runs 6 and 8, and 7 and 9), whereas the Cu -to- K ratio has a considerable effect on the results (runs 7 and 8). The reactions with $\text{Cu}/\text{K} = 0.95$ convert acetylene into products more efficiently than those with $\text{Cu}/\text{K} = 1.10$, while the selectivity for vinylacetylene among the products is similar. These reactions were carried out with the acetylene flow rate which are large enough to exclude influence of diffusion rate of acetylene on the observed reaction rate and selectivity as described below. Fig. 1 shows the relationship of the uptake of acetylene with the flow rate of the substrate. The reaction rate is influenced by the flow rate of acetylene; low acetylene flow rates up to 1.21 min^{-1} cause a linear increase in the amount of vinylacetylene formed,

indicating that the reaction rate is governed by diffusion of acetylene in the solution. At an acetylene flow rate above 1.21 min^{-1} , the reaction rates become almost constant and no relationship is observed between the flow rate and the yield of the product. The reaction rates in Table 1 were determined at a flow rate of acetylene higher than 1.41 min^{-1} in order to minimize the effect of diffusion on the observed reaction rate.

2.2. Structure of the Nieuwland catalyst

Cooling the catalyst solution to room temperature causes the separation of Cu -containing crystals.

Table 1
Results of dimerization of acetylene catalyzed by the Nieuwland type catalysts (CuCl and MCl)^a

| Run | Catalyst (M) | | Composition of gas in output (%) | | | | | Reactivity (%) ^b | Selectivity (%) ^c |
|-----|--------------|--------------------------|----------------------------------|-----------------|-----------------------|-------------------------|-----------------------|-----------------------------|------------------------------|
| | CuCl | MCl ^d | Vinylacetylene | Acetaldehyde | 1,2-Divinyl-acetylene | 1-Ethynyl-1,3-butadiene | Acetylene (recovered) | | |
| 1 | 6.7 | 6.4 (KCl) | 6.09 | 0.28 | 0.19 | 0.03 | 93.38 | 12.3 | 92.8 |
| 2 | 6.7 | 6.4 (NH ₄ Cl) | 4.90 | 0.32 | 0.20 | 0.06 | 94.51 | 10.3 | 89.9 |
| 3 | 6.7 | 6.4 (LiCl) | 1.48 | ND ^e | ND ^e | ND ^e | ND ^e | 1.6 | 92.7 |
| 4 | 6.7 | 6.4 (NaCl) | 4.49 | ND ^e | ND ^e | ND ^e | ND ^e | 4.8 | 93.6 |
| 5 | 6.7 | 6.4 (CsCl) | 0 | 0 | 0 | 0 | 100.00 | 0.0 | 0.0 |
| 6 | 5.5 | 6.1 (KCl) | 5.67 | 0.25 | 0.25 | 0.05 | 93.78 | 11.8 | 90.8 |
| 7 | 6.7 | 6.4 (KCl) | 8.75 | 0.38 | 0.38 | 0.13 | 90.36 | 17.7 | 90.2 |
| 8 | 6.7 | 7.4 (KCl) | 5.61 | 0.24 | 0.24 | 0.16 | 93.75 | 11.9 | 88.6 |
| 9 | 8.0 | 7.6 (KCl) | 8.83 | 0.39 | 0.39 | 0.14 | 90.78 | 17.7 | 90.6 |

^a The reaction was carried out at 75°C in 240 ml aqueous solution (300 ml vessel) for runs 1–5 and at 75°C in 6.551 aqueous solution (71 vessel) for runs 6–9.

^b Reactivity (%) = $\frac{100 \times (2 \times [\text{vinylacetylene}] + [\text{acetaldehyde}] + 3 \times [1,2\text{-divinylacetylene}] + 3 \times [1\text{-ethynyl-1,3-butadiene}])}{(2 \times [\text{vinylacetylene}] + [\text{acetaldehyde}] + 3 \times [1,2\text{-divinylacetylene}] + 3 \times [1\text{-ethynyl-1,3-butadiene}] + [\text{acetylene}])}$, where [A] denotes the concentration of A in the gaseous output.

^c Selectivity (%) = $\frac{100 \times 2 \times [\text{vinylacetylene}]}{(2 \times [\text{vinylacetylene}] + [\text{acetaldehyde}] + 3 \times [1,2\text{-divinylacetylene}] + 3 \times [1\text{-ethynyl-1,3-butadiene}]}$.

^d MCl is shown in parentheses.

^e Not determined.

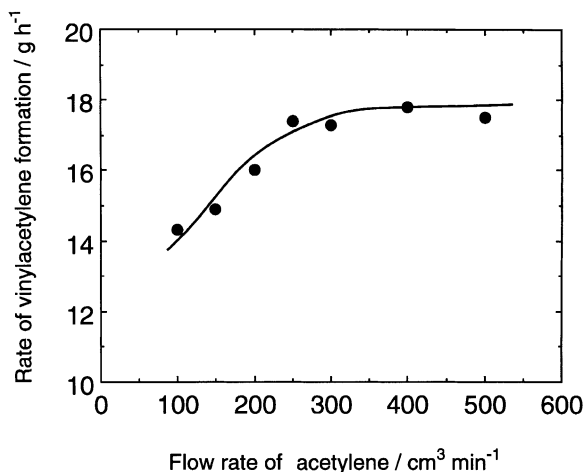
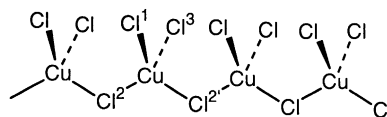


Fig. 1. Relationship between observed rate of the conversion of dimerization of acetylene catalyzed by CuCl-KCl and the flow rate of acetylene.

Microscope observation of the crystals revealed that they have two shapes, tetrahedral crystals (**A**) and needle-like crystals (**B**). The former crystals are obtained from the solution of a mixture of CuCl (6.7 M) and KCl (6.4 M), whereas the solution with higher CuCl (8.3 M) and KCl (7.9 M) content produced a mixture of both crystals. Fig. 2 shows photographs of crystals (**A**) and a mixture of (**A**) and (**B**). The exterior of crystals (**A**) resembles CuCl in photographs presented by Vestin [9]. Further characterization by X-ray diffraction (XRD) and metal analyses confirmed the structure. Crystals (**A**) are identified as CuCl by comparison of their wide angle XRD patterns ($2\theta = 28.4^\circ$, 47.4° and 56.2° , Cu $K\alpha$, JCPDS 06-0344) with standard data. The position and relative intensity of diffraction of crystal (**A**) are quite similar to those of standard data. Analytical results showing the absence of K (0.1%) and the content of Cu (59.2, 63.5% calculated as CuCl) also suggest the formula given above.

The needle-like crystals were obtained as a major product from the crystallization of the catalyst solution with higher K and/or Cu concentrations. Upon cooling, most of the solutions gave colorless needle-like crystals (**B**) at first and a crystalline colorless mass (**A**) later, indicating faster crystal growth of (**B**) than (**A**). X-ray crystallography was used to determine the structure of single crystals of (**B**). The compound



Scheme 1.

is composed of a linearly arranged CuCl_3^{2-} units and K^+ ions. Scheme 1 depicts the arrangement of CuCl_3^{2-} units. Each Cu center has two non-bridging Cl ligands and is bridged to two adjacent Cu atoms with Cl ions; the molecule contains a linear arrangement of alternating Cu and Cl atoms. The lengths of the two bridging Cu-Cl bonds differ significantly from each other. The crystallographic data and bond parameters are similar to the previously reported K_2CuCl_3 [10], although the results obtained with a diffractometer seem to provide more accurate bond parameters; Cu-Cl1 2.320(3), Cu-Cl2 2.365(10), Cu-Cl2' 2.48(1), Cu-Cl3 2.336(3), Cl1-Cu-Cl2 105.4(3), Cl1-Cu-Cl2' 108.4(3), Cl1-Cu-Cl3 110.7(1), Cl2-Cu-Cl2' 117.8(1), Cl2-Cu-Cl3 106.0(3), Cl2'-Cu-Cl3 108.4(3). Crystalline solids recovered from the solutions are composed of tetrahedral crystals of CuCl (**A**) and needle-like crystals of K_2CuCl_3 (**B**) exclusively and contain only negligible amounts of other Cu compounds such as KCuCl_2 , probably because of their much higher solubility in water than CuCl and K_2CuCl_3 .

The structure of the catalyst in solution is more closely related to the chemical properties of $\text{K}_n\text{CuCl}_{n+1}$ than the solid state structure. Chlorocuprates $[\text{CuCl}_{m+1}]^{m-}$ initially reported many years ago [10–14] were recently isolated as salts with organic cations and studied in solution with organic solvents [15]. The behavior of $\text{K}_n\text{CuCl}_{n+1}$ in aqueous solutions with high concentration has not been investigated in detail. The saturated concentration of $\text{K}_n\text{CuCl}_{n+1}$ can be regarded as a convenient probe to investigate the composition and structure of the complex salt because the value of n of $\text{K}_n\text{CuCl}_{n+1}$ influences the solubility of the Cu compound significantly. To obtain clear insight into the composition of the Cu compounds in solution, systematic measurement of solubility was examined by monitoring the saturation concentration.

The saturation concentration of $\text{K}_n\text{CuCl}_{n+1}$ can be estimated by direct observation of the temperature at

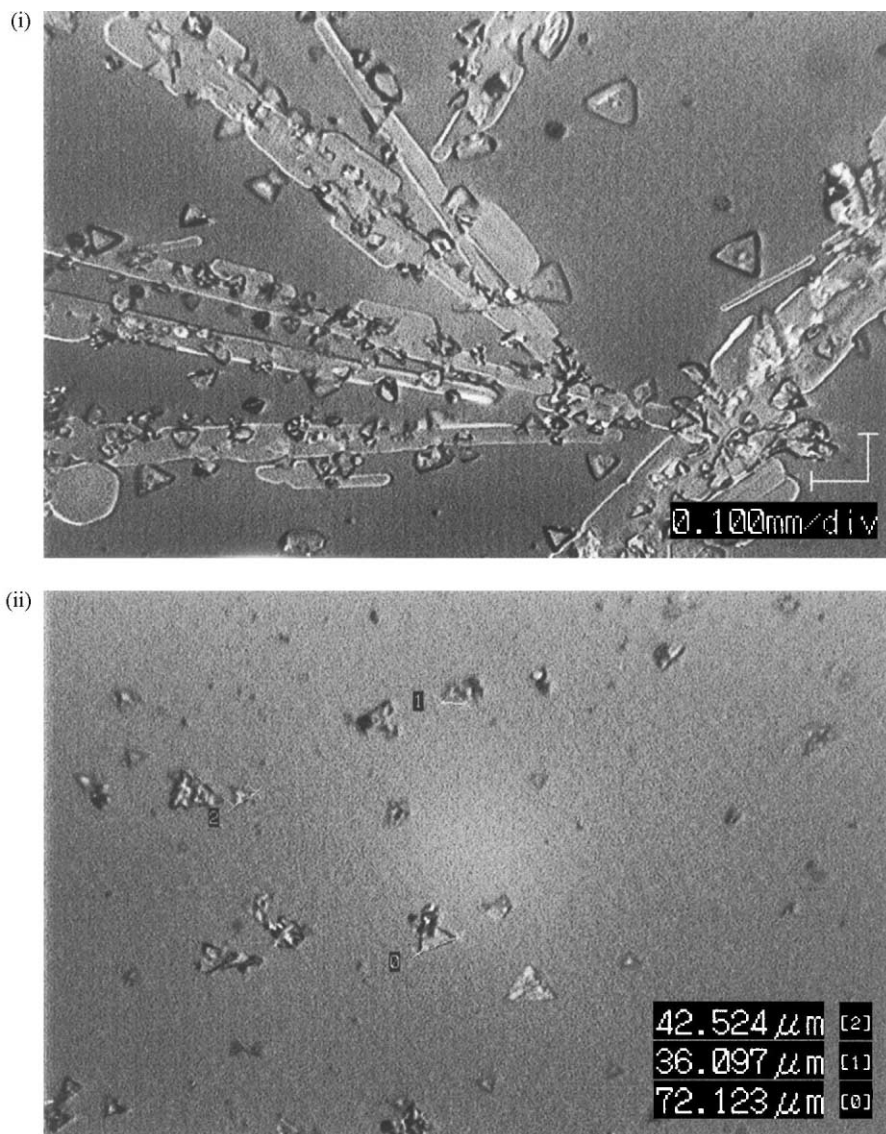


Fig. 2. Photographs of crystals: (i) a mixture of (A) and (B); (ii) (A) obtained with a microscope. Maximum size (mm) of three crystals ([2], [1], and [0]) in (ii) are shown at a corner of the photograph.

which separation of the Cu salt as a solid begins to occur upon cooling the unsaturated solution, but it is obtained more accurately by recording the temperature change of a gradually cooled solution. Fig. 3 shows the change in temperature of water and of the catalyst solution upon cooling, and the latter shows a clear wrinkle corresponding to the exothermic separa-

tion of the Cu salt from the aqueous solution. Fig. 4(i) shows a plot of the relationship between saturation temperature of a Cu salt solution and Cu concentration. Four to six aqueous solutions of K_nCuCl_{n+1} with a constant n value give rise to a V-shaped curve in the plots in the range $1.0 < n < 1.5$. The results are contrasted with the relationship of tempera-

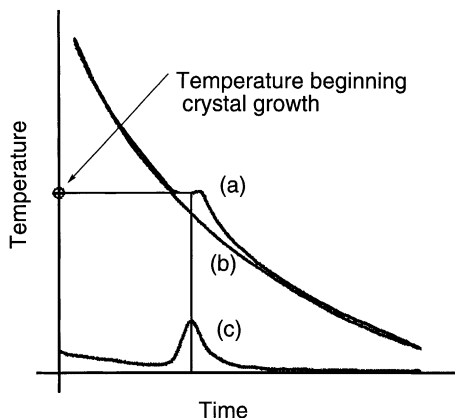
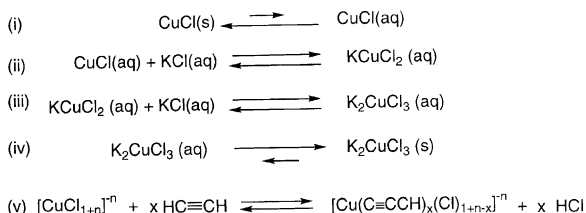


Fig. 3. DSC trace of a catalyst solution. Temperature change of; (a) catalyst solution; (b) bath in which the catalyst solution was immersed; and (c) difference of curves (a) and (b).

ture and solubility of a single compound, which exhibits a monotonous rise (or fall) in the plots of saturated concentration vs. temperature. The curves in Fig. 4(i) can be rationalized by assuming the presence of the following equilibria among the Cu compounds (Scheme 2).

The aqueous solution contains mainly three Cu compounds; CuCl, KCuCl_2 and K_2CuCl_3 . The compound CuCl is practically insoluble in water, and its concentration in aqueous solution is extremely low. The double cuprate, K_2CuCl_3 , also seems to show a limited solubility in water although it is much more soluble than CuCl. Preferential separation of crystalline solids of CuCl and K_2CuCl_3 from the aqueous catalyst solution indicates a much lower solubility of the compounds than KCuCl_2 . Thus, KCuCl_2 is mostly dissolved in water even at high concentrations of the Cu and K compounds ($>3\text{ M}$). It is not separated as a solid from the solution directly, but is in equilibrium



Scheme 2.

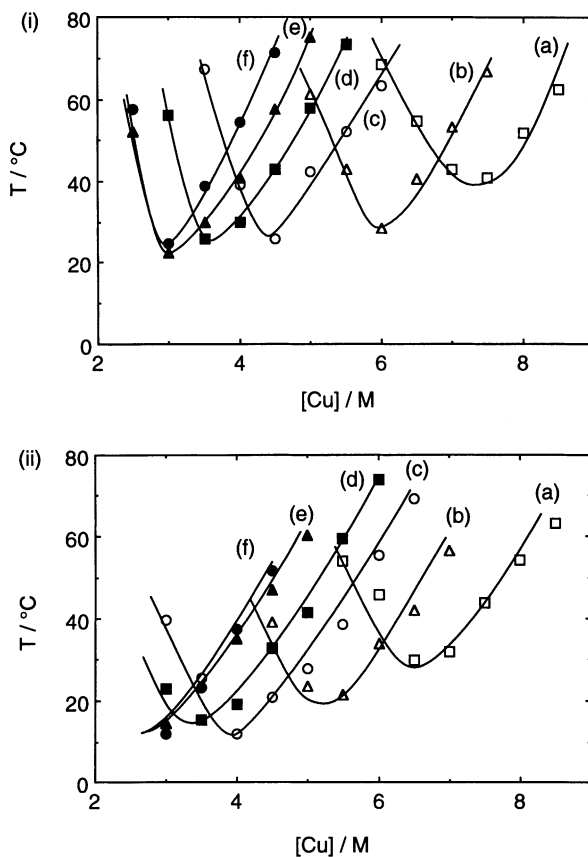


Fig. 4. Plotting of solid separation from the aqueous solutions containing CuCl and KCl in various ratios and concentrations. The upper area of each curve corresponds to the Cu and K concentrations higher than the limit of the solubility of $\text{K}_n\text{CuCl}_{n+1}$ ($1 < n < 1.5$) in water: (i) without acetylene; (ii) with acetylene. $[\text{Cu}] = 6.7\text{ M}$; $[\text{K}]/[\text{Cu}] = 1.0$ (a), 1.1 (b), 1.2 (c), 1.3 (d), 1.4 (e), 1.5 (f).

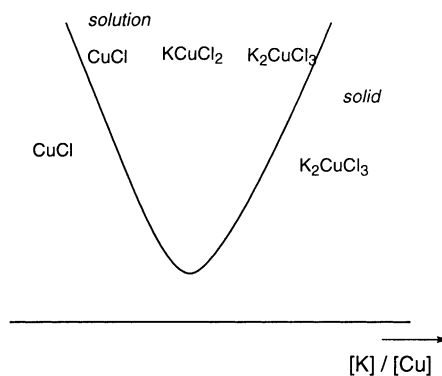
with much less soluble KCl and K_2CuCl_3 which are separated preferentially from the catalyst solution. At present, it is not feasible to conclude the size of the cuprate dissolved at such high concentrations since conventional methods of determining the molecular weight of a solute could not be applied for these reactions. We presume the presence of several species including mononuclear and oligonuclear cuprates. Scheme 3 depicts a general sketch of the solubility curve of the catalyst in aqueous solution. The main solute in the solution is KCuCl_2 , which is more soluble than CuCl and K_2CuCl_3 . A solution at a higher Cu concentration than the minimum point in the curve

contains a significant amount of K_2CuCl_3 is because the crystals obtained by cooling the solution contain mainly needle-like K_2CuCl_3 (**B**). On the other hand, a solid recovered from a solution with a lower Cu concentration than the minimum point in the curve contains a much smaller amount of (**B**) and contains tetrahedral crystals of $CuCl$ (**A**) and/or a crystalline mass with a composition similar to that of $CuCl$. These results suggest that the content of K_2CuCl_3 in the solutions with a constant K/Cu ratio increases with increase in the Cu concentration as suggested in Scheme 3. This is consistent with the observation that on increase in Cu concentration equilibria (ii) and (iii) in Scheme 2 shift to the right when the initial K/Cu ratio is fixed.

At KCl/CuCl ratio of 1.0 and 1.1, the curves in Fig. 4 exhibit minimum points at $[Cu] = 7.4$ M and 5.9 M, respectively. Since the dimerization of acetylene catalyzed by the Nieuwland system is carried out at $75^\circ C$ at 5–8 M Cu concentration and a K/Cu ratio of 0.95–1.10, the catalyst is dissolved completely under the reaction conditions. Increasing the K/Cu ratio up to 1.5 causes a significant shift of the curve to the right for the following reason. The addition of KCl leads to an increase in the amount of $KCuCl_2$ and a consequent decrease in the amount of $CuCl$ in the solution, resulting in the dissolution of solid $CuCl$ in the system. On the other hand, increasing $[K^+]$ in the solution leads to the separation of K_2CuCl_3 from the solution. Thus, curves in Fig. 4(i) and their shift caused by the change in K/Cu ratio are directly related to the equilibria of Cu compounds in Scheme 2.

2.3. Reaction of acetylene with the Nieuwland catalyst

Passing acetylene through an aqueous solution of K_nCuCl_{n+1} at $75^\circ C$ causes its pH to change approximately from 4.0 to 0.5. Acidification of the solution upon the addition of acetylene suggests the evolution of HCl caused by the exchange of the Cl ligand bonded to Cu with acetylide according to the following equation. Previous reports on the reaction of acetylene with Cu salts discussed the change in the composition of Cu compounds in solution [4,7,8] and ascribed the change in the chemical properties of the solution to the simple π -coordination of acetylene to the Cu center rather



Scheme 3.

than copper acetylide formation. The general preparation of copper acetylide requires basic conditions to complete the reaction [16]. However, it is reasonable to postulate that copper acetylide formation proceeds smoothly in concentrated solutions.

The solubility of the Cu compounds in the presence of acetylene was examined and is summarized in Fig. 4(ii). The V-shaped curves are similar to those in Fig. 4(i), although the solubility of the Cu compounds in the presence of acetylene is higher than those in the absence of acetylene. The curves are shifted to the left by increasing the K/Cu ratio from 1.0 to 1.5, similar to those in Fig. 4(i). All these results suggest the following situation for the Cu-containing species in these solutions. The Cu complexes with chloro and acetylide with the mixed cuprate formula, $K_nCuCl_{n+1-x}(C\equiv CH)_x$, are also involved in equilibria among neutral Cu(I) salts ($n = 0$) and single and double cuprates ($n = 1$ and 2, respectively), similarly to K_nCuCl_{n+1} . These three components show a tendency for solubility in water similar to the homoleptic chloro-compounds of Cu(I) (neutral ($n = 0$) < double cuprate ($n = 2$) < monocuprate ($n = 1$)). On the other hand, the curves in Fig. 4(ii) are at lower Cu concentrations than those in Fig. 4(i), suggesting that copper acetylide $Cu(C\equiv CH)$ or partially acetylide substituted chloro-copper, $Cu_yCl_z(C\equiv CH)_{y-z}$, exhibits a higher solubility in water than $CuCl$. Acetylide-containing cuprates $K_nCuCl_{n+1-x}(C\equiv CH)_x$ are also more soluble in water than K_nCuCl_{n+1} because the temperature of saturation of the acetylide-containing Cu

compounds is lower than that of the chlorocopper derivatives.

3. Conclusion

Although the Nieuwland catalyst is classic and has kept its form for several decades, a detailed study has not been applied except for crystallographic studies of the solid from catalyst solutions and several technical modifications. This study has revealed details of the Nieuwland catalyst structure and its reaction from various aspects. The dissolved species in the solution of a mixture of KCl and CuCl was determined as KCuCl_2 while the other possible species in the solution, KCl and K_2CuCl_3 , exhibit too low solubility to give the aqueous solution at the high concentration. Comparison of the solubility of the salts in the presence of acetylene with that of the above mixture under the conditions of the catalytic dimerization of acetylene, giving vinylacetylene selectively, indicated that the plausible active species of the catalyst is the cuprate with chloro and/or acetylde ligands. Selective dimerization of acetylene is a unique characteristic of the catalysis. Moreover, catalytic reactions of organic substrates in aqueous solutions will increase their importance since they are free from the issue of organic solvent waste or recovery, particularly for industrial applications.

4. Experimental

4.1. Catalytic dimerization of acetylene

A typical procedure for the dimerization of acetylene is as follows. Under a nitrogen stream, a mixture of KCl and CuCl was dissolved in water at 70°C . The solution (218 ml) was transferred to a reaction vessel equipped with an acetylene inlet, product outlet, thermometer, and water jacket. After the addition of triethylene glycol dibutyl ether (22 ml) for trapping by-products, the solution was maintained at 75°C by circulating hot water in the water jacket. Acetylene (1.51min^{-1}) was passed through the solution for 15 min at the indicated temperature. After the reaction, the gas sampled at the outlet was analyzed by gas chromatography.

4.2. Analysis of the Cu salts recovered from the catalyst solution

The solid obtained by cooling the catalyst solution ($[\text{CuCl}] = 6.7\text{ M}$, $[\text{KCl}] = 6.4\text{ M}$) was analyzed by XRD and elemental analyses. The XRD (Cu $\text{K}\alpha$ radiation) of the powder sample on the adhesive tape exhibited three major peaks at $2\theta = 28.4^\circ$, 47.4° and 56.2° , which agree with the standard data for CuCl (JCPDS 06-0344). Metals contained in the solid were determined after HNO_3 acidolysis to be Cu (59.2%) and K (<0.1%). The crystals grown from the cooled catalyst solution were tetrahedral as observed with a micrograph. All the data indicate that the solid recovered from the solution is CuCl.

4.3. Isolation of crystals and crystal structure determination

Crystals of CuCl (**A**) and K_2CuCl_3 (**B**) were obtained from the acetylene-saturated aqueous solutions containing the catalyst as follows. Nitrogen was passed into the solutions with $[\text{Cu}] = 6.7\text{ M}$, $[\text{K}] = 6.4\text{ M}$ and $[\text{Cu}] = 8.3\text{ M}$, $[\text{K}] = 7.9\text{ M}$ at 75°C until the organic products and acetylene were removed. Gradual cooling of the solutions gave crystals (**A**) and (**B**), respectively.

Crystals suitable for crystallography were obtained by cutting a large needle-like crystal (approximately 5 mm length or longer) to a suitable size for measurement (<1 mm). Crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by a least-squares refinement of the 2θ values of 20 reflections with $20^\circ \leq 2\theta \leq 22^\circ$. Intensities were measured on a Rigaku AFC-5R automated four-cycle diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$) and the $\omega - 2\theta$ method. An empirical absorption correction (ψ scan method) was applied to the collected data. Calculations were carried out using the program package teXsan on a VAX-II computer. Atomic scattering factors were taken from literature [17]. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. X-ray data: orthorhombic, $\text{Pna}2_1$ (No. 33), $a = 11.994(8)\text{ \AA}$, $b = 12.590(7)\text{ \AA}$, $c = 4.146(3)\text{ \AA}$, $V = 626.1(6)\text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 2.632\text{ g cm}^{-3}$, $F(000) = 472$,

$\mu(\text{Mo K}) = 5.951 \text{ mm}^{-1}$ for monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). $R(R_w) = 0.052$ (0.086) for 1316 reflections with $I > 3\sigma(I)$ among 1646 unique reflections ($R_{\text{int}} = 0.042$).

4.4. Determination of the solubility of Cu salts

A hot aqueous solution of $\text{K}_n\text{CuCl}_{n+1}$ was gradually cooled with gentle stirring. Plots of temperature show a single wrinkle due to a temperature rise caused by the onset of crystallization of the Cu salt. The temperature is similar to the temperature at which one can observe the onset of crystal growth, but it is more accurately determined than that. The temperature and concentration of the initially charged CuCl and the initial ratio of CuCl and KCl are plotted in Fig. 4.

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