Critical Review of Catalysis for Ethylene Oxychlorination

Hongfei Ma,* Yalan Wang,* Yanying Qi,* Kumar R. Rout,* and De Chen*

ABSTRACT: Ethylene oxychlorination is the key technology in vinyl chloride (VCM, the monomer of PVC, polyvinyl chloride) production to close the chlorine loop by consuming the HCl released from the former cracking step. Due to the high demand for PVC, this leads to ethylene oxychlorination being one of the most important processes in the industry. This Review covers an in-depth analysis of the dynamic nature of active sites for the main and side reactions involved in ethylene oxychlorination, featuring the findings and viewpoints from the dynamic kinetics study and analysis under industrial operating conditions. A unified picture of the mechanism of the surface reactions, and the effect of supports and promoters, has been presented based on the decoupled redox-cycle experiments, which leads to a significantly better understanding of the mechanism and provides valuable guidelines for effective catalyst design. Operando techniques and kinetic tools of the rate-diagram, as well as their application to the study of the redox-cycle in ethylene oxychlorination and kinetic models on both the main product and byproduct, are also reviewed. Perspectives on challenges and new process development and future research focus for better study of the VCM production chemistry are also proposed.

KEYWORDS: CuCl2/γ-Al2O3 active site, ethylene oxychlorination, kinetics, reaction mechanisms

1. INTRODUCTION

Polyvinyl chloride (PVC) is one of the most commonly used plastic materials that has a wide range of applications, such as in households and construction, electronics, pharmaceutical, and automotive industries. It is produced through the polymerization of its monomer vinyl chloride (VCM). The high demand and global increase in PVC led to VCM being one of the most precious chemicals. In 2018, the global VCM production capacity was approximately 49 million metric tons, which is expected to increase to around 52.9 million metric tons in 2023. There are two main routes by which VCM is produced industrially. One is direct hydrochlorination of acetylene, another is cracking of ethylene dichloride (EDC) provided by direct chlorination and/or oxychlorination of ethylene. The combination of direct chlorination, ethylene oxychlorination, and EDC cracking is named as the "balanced VCM process" (Figure 1). In addition to the above two routes, ethane oxychlorination is another promising route for VCM production due to the economic advantage of feedstock. However, despite the efforts of several decades, ethane-based technology is still under exploration and has not been commercialized yet. Other technologies are developed either based on feedstocks or catalysts of the three routes. To date, among these different technologies, the ethylene route is predominant and attracts much attention, based on that more than 90% of the VCM production plants worldwide are using the balanced VCM process.

The oxychlorination of lower hydrocarbons (C1−C4) was an active research topic for both academic research and industrial applications, and the topic was reviewed by two groups in the 1980s including thermodynamics, catalysts, kinetics, mechanisms, as well as the technology of the process. Recently Lin et al. have reviewed different processes for halogen-mediated conversion of hydrocarbons to commodities, among which the PVC (or VCM) production is one of the important topics. However, despite the excellent reviews, a critical review for ethylene oxychlorination which has played such a vital role in VCM production is still missing, which is essential for gaining a better understanding of the reaction and developing more efficient catalysts.

Herein, we will critically review the progress of the catalyst developments toward better activity, selectivity, and stability for ethylene oxychlorination with a focus on the reaction
mechanism, site requirement, and catalyst design. The goal will be approached by a detailed analysis of the effects of metal chloride identities, supports, and promoters on catalytic performances of most common CuCl₂-based catalysts including reactions leading to both main and byproducts formation. Particular attention will be paid to the effect of catalyst properties on the individual reaction steps in a catalytic cycle including reduction of CuCl₂ by ethylene, oxidation of CuCl by oxygen, and hydrochlorination of Cu₂OCl₂ by HCl and their effect on the dynamic evolution of active sites in the redox cycle, which is the key toward effective catalysts.

2. ETHYLENE OXYCHLORINATION CATALYSTS

As early as 1966, Todo, Kurita, and Hagiwara already discovered metal chlorides active for ethylene oxychlorination. The catalytic activity of these catalysts followed the order of CrCl₃ > CuCl₂ > FeCl₃ > MnCl₂ > NiCl₂. However, CuCl₂ was found to show higher selectivity for EDC formation than CrCl₃. Hall et al. have measured the adsorption heat of ethylene at low temperatures (<150 °C) on a series of unsupported transition metal chlorides with varied d-electrons by a gas-adsorption chromatography method in 1984. The ethylene adsorption heat follows an order of CuCl₂ > NiCl₂ > CrCl₃ > FeCl₂ > CoCl₂ > VCl₃ > MgCl₂ > CrCl₃ > MnCl₂ > CuCl. It was found that ethylene physically adsorbed on CrCl₂, MnCl₂, and CuCl had no activity. The transition metal chlorides can be classified into two groups, namely divalent and trivalent chlorides. The chemisorption of ethylene seemed to be occurring on divalent CuCl₂ and NiCl₂. CuCl₂ exhibited high activity of reduction and high selectivity for EDC, while there was no reaction between ethylene and NiCl₂. Intermediate adsorption of ethylene was observed on VCl₃, CrCl₃, FeCl₂, and CoCl₂. VCl₃ displayed activity to VCM but was prone to deactivation due to high volatility at high temperatures. VCM and EDC were formed on CrCl₃ at 523 K, but an undesired hydrocarbon polymer (nonchlorine-containing) was also produced. Besides the above transition metal chlorides, some noble metal chlorides were also tried as catalysts for ethylene oxychlorination with high selectivity to VCM, such as PdCl₂, PtCl₆, RhCl₃, and RuCl₃. The catalyst activity for formation of VCM followed the order PdCl₂ > RhCl₃ > PtCl₆ > RuCl₃. The highest selectivity to VCM was obtained over Pd-containing catalysts. However, the limited activity was a drawback of these catalysts. To summarize, no metal chlorides can compete with CuCl₂ in the selective formation of EDC.

In addition to the above studies, more efforts have been made to explore efficient catalysts for ethylene oxychlorination. A large number of catalysts have been developed over the past half-century, and their catalytic performances are summarized in Table 1. Among various catalysts, copper chloride (CuCl₂) was identified as a superior catalyst for ethylene oxychlorination owing to its high activity and selectivity. Why is this so? It might be roughly explained by an interesting hypothesis presented by Allen, namely the smaller the standard free energy changes related to individual steps of the Deacon reaction, the better the Deacon catalyst, such as CuCl₂ in eqs 1 and 2:

\[
\begin{align*}
2\text{CuCl}_2 + 1/2\text{O}_2(g) & \rightarrow \text{CuO-CuCl}_4(s) + \text{Cl}_2(g) \\
\Delta G_{298-900K} & = +57 \text{ to } +6 \text{ kJ/mol} \quad (1) \\
\text{CuO-CuCl}_4(s) + 2\text{HCl} & \rightarrow 2\text{CuCl}_2(s) + \text{H}_2\text{O} \\
\Delta G_{298-900K} & = -84.4 \text{ to } -5.4 \text{ kJ/mol} \quad (2) \\
2\text{CuCl}_2(s) & \rightarrow 2\text{CuCl}(s) + \text{Cl}_2(g) \\
\Delta G_{298-900K} & = +142 \text{ to } 60 \text{ kJ/mol} \quad (3)
\end{align*}
\]

The calculated standard free energies for each Deacon step were in the following order by replacing Cu with other divalent metals:

\[
\begin{align*}
\text{Mg} & < \text{Cu} < \text{Sn(II)} < \text{Ni} < \text{Zn} < \text{Rh} < \text{Fe(II)} < \text{V(II)} \\
< \text{Mn} < \text{Co} < \text{Pd} < \text{Cd} < \text{Hg} < \text{Pb} < \text{Ca} < \text{Sr} < \text{Ba}
\end{align*}
\]

It indicates that among all investigated metals, Mg is the only one more favorable than Cu. However, Mg cannot undergo redox reactions (eq 3) because of existing only in the +2-oxidation state. Like Mg, most lanthanides are not redox-active although they exhibit also low Gibbs free energy for reaction eqs 1 and 2. This might explain why Mg and rare earth are not superior catalysts but can be used as promoters for ethylene oxychlorination in combination with cupric chloride. Since the ethylene chlorination by reduction step is not considered in the above analysis, a direct prediction of Figure 1. Production of VCM by three different routes: acetylene hydrochlorination, ethylene direct chlorination/oxychlorination, and ethane oxychlorination.
| Year | Catalysts                      | T (K) | C=H/O2/HCl (mole) | C2H4 conversion (%) | EDC selectivity (%) | VCM selectivity (%) | EtCl selectivity (%) | Main Conclusions                                                                 |
|------|-------------------------------|-------|-------------------|---------------------|--------------------|--------------------|----------------------|----------------------------------------------------------------------------------|
| 1969 | iron oxide-containing catalyst | 773   | 1:2.5:2.5         | 50.7                | 9.7                | 61.8               | 0.2                  | Deuterium labeling experiments support a mechanism involving EDC as the VCM precursor. |
| 1971 | CuCl2/γ-Al2O3                  | 553   | 1:3:2             | 98.8                | 97.0               | 0.2                | 1                   | For CuCl2/γ-Al2O3, CuFeCl, and PtFeNaCl exhibited better performance than others.     |
| 1972 | PdCuNaCl                      | 589   | 1:1:3             | 41.5                | 17                 | 44.9               | 8.6                  | PdCuNaClx, PdFeNaClx, and PtFeNaClx exhibited better performance than others.         |
|      | PdFeCl                        | 561   | 1:1:3             | 88.1                | 25.2               | 60.2               | 3.1                  |                                                                                   |
|      | RuFeNaCl                      | 589   | 1:1:3             | 84.9                | 6.0                | 57.0               | 0.9                  |                                                                                   |
|      | IrFeNaCl                      | 616   | 1:1:3             | 81.7                | 60.4               | 11.5               | 0.9                  |                                                                                   |
|      | RhFeNaCl                      | 616   | 1:1:3             | 61.7                | 35.6               | 37.3               | 3.9                  |                                                                                   |
|      | PtFeNaCl                      | 589   | 1:1:3             | 77.2                | 74.7               | 20.6               | 1.8                  |                                                                                   |
|      | support: Al2O3                | 561   | 1:1:3             | 100.0               | 80.8               | 14.1               | 1.0                  |                                                                                   |
| 1978 | RhFeZnLiCl/α-Al2O3            | 623   | 1:2:2             | 29–46               | 17–53              | 42–77              | 0.1                  | Rh, Fe, and Zn are essential components, while Li is an optional component to extend catalyst life. |
| 1991 | fly ash                      | 773   | 1:6:4:3.5         | 61                  | 0.9                | 11.4               | 1                   | Low EDC and VCM selectivity                                                        |
| 2005 | LaOCl                        | 672   | 3:6:1:2           | 23.7                | 11.3               | 75.3               | 3.5                  | LaOCl exhibited better performance than other rare-earth catalysts and catalysts containing two rare-earth materials, as well as catalysts containing rare-earth materials with other additives. |
|      | NdOCl                        | 676   | 4:2:1:2.3         | 13.2                | 2.9                | 74.4               | 6.9                  |                                                                                   |
|      | PrOCl                        | 674   | 3:7:1:2           | 22.8                | 6.1                | 74.2               | 4.4                  |                                                                                   |
|      | SmOCl                        | 673   | 3:6:1:2           | 14.7                | 2.9                | 61.0               | 10.6                 |                                                                                   |
|      | HoCl3                        | 673   | 3:6:1:2           | 12.7                | 14.5               | 33.3               | 16.8                 |                                                                                   |
|      | ErCl3                        | 673   | 3:6:1:2           | 15.4                | 17.5               | 44.0               | 12.8                 |                                                                                   |
|      | YbCl3                        | 673   | 4:2:1:2.3         | 3.3                 | 8.8                | 6.1                | 37.0                 |                                                                                   |
|      | YCl3                         | 672   | 3:6:1:2           | 13.8                | 18.8               | 35.0               | 16.5                 |                                                                                   |
|      | LaCl3–NdCl3                  | 674   | 3:7:1:2           | 16.8                | 9.7                | 75.8               | 4.1                  |                                                                                   |
|      | LaCl3–SmCl3                  | 673   | 3:6:1:2           | 11.3                | 7.5                | 51.0               | 11.8                 |                                                                                   |
|      | LaCl3–YCl3                   | 673   | 3:6:1:2           | 12.5                | 12.4               | 51.4               | 8.9                  |                                                                                   |
|      | LaCl3–HCoCl3                 | 673   | 3:6:1:2           | 12.4                | 14.5               | 28.9               | 17.0                 |                                                                                   |
|      | LaCl3–HOCl3                  | 673   | 3:6:1:2           | 9.2                 | 20.6               | 11.1               | 23.8                 |                                                                                   |
|      | LaCl3–CeO2                   | 673   | 3:7:1:2           | 18.2                | 11.5               | 64.5               | 5.0                  |                                                                                   |
| 2016 | EuOCl                        | 673   | 1:1:1:6           | 10                  | 25                  | 75                 | 0                   | Except for CeO2 and EuOCl, other lanthanide (La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) catalysts mainly led to undesired CO2 production. EuOCl exhibited the best EDC/VCM selectivity; CeO2 showed the highest activity; coupling them led to a better VCM yield. |
|      | CeO2                          | 673   | 1:1:1:6           | 26                  | 76                  | 15                 | 0                   |                                                                                   |
|      | EuOCl–CeO2                   | 673   | 22                | 5                   | 95                 | 0                  | 0                   |                                                                                   |
| 2016 | CuKLaCl3/Al2O3               | 473   | 1:1:1:6           | 12                  | 100                 | 0                  | 0                   | CuKLaCl3/Al2O3 and CeO2-based catalysts displayed high EDC/VCM selectivity; IrO2 and RuO2 mainly led to undesired CO2 production. |
|      | IrO2                          | 673   | 11                 | 0                   | 0                   | 0                   | 0                   | For CuO, CuO/O2, and CuO2, the catalyst bulk phase is CuO2 with CuOCl contained in the surface. |
|      | RuO2                          | 673   | 9                  | 7                   | 3                   | 0                   | 0                   |                                                                                   |
|      | CeO2                          | 673   | 13                 | 92                  | 6                   | 0                   | 0                   |                                                                                   |
|      | CeO2–ZrO2                     | 673   | 60                 | 45                  | 43                  | 0                   | 0                   |                                                                                   |
| 2017 | RuO2                          | 573   | 2:1:2              | 7                   | 55                  | 15                 | 0                   | Performance needs to be improved.                                                  |
| 2018 | CeCl3                         | 723   | 1:1:1:6           | 58                  | 10                  | 40                 | 0                   | For CeCl3, CeOCl, and CeO2, the catalyst bulk phase is CeO2 with CeOCl contained in the surface. |
|      | CeOCl                         | 723   | 50                 | 8                   | 25                 | 0                   | 0                   |                                                                                   |
Oxychlorination catalysts cannot be achieved only based on Allen’s model. Therefore, more research was performed on this process.

In 1972, Dugan et al. conducted ethylene oxychlorination by using the PdFeNaCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalyst and a series of its derivative catalysts, with PdCuNaCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} as a benchmark (Table 1).\textsuperscript{25} Among all studied catalysts, PdFeNaCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} and PtFeNaCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} exhibited comparable performance to PdCuNaCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}, better than the others did. The superior performance of the two catalysts was attributed to the promotion effect of Na. It can be seen that without Na, the catalytic performance of the PdFeCl\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalyst was greatly reduced and cannot compete with that of the CuCl\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{26} Besides, the iron oxide-containing catalysts,\textsuperscript{27} the RhFeZnLiCl\textsubscript{x}/\alpha-Al\textsubscript{2}O\textsubscript{3} catalyst,\textsuperscript{28} fly ash,\textsuperscript{29} IrO\textsubscript{2},\textsuperscript{30} and RuO\textsubscript{2}\textsuperscript{30,31} have been also demonstrated active for ethylene oxychlorination. However, both lower activity and EDC/VCM selectivity were observed over these catalysts than the CuCl\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{26} Recently, the use of rare-earth catalysts for ethylene oxychlorination to VCM has stimulated great interest.\textsuperscript{30,32–34} In 2005, Jones et al. investigated ethylene oxychlorination over various rare-earth (La, Nd, Pr, Sm, Ho, Er, Yb, and Y) catalysts.\textsuperscript{32} Among them, LaOCl exhibited better performance than other rare-earth catalysts and catalysts containing two rare-earth materials, as well as catalysts containing rare-earth materials with other additives. The study of Scharfe et al. in 2016 illustrated that toward researched lanthanide (Eu, Ce, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) catalysts, EuOCl displayed the best EDC/VCM selectivity, and CeO\textsubscript{2} showed the highest activity; coupling them (EuOCl-CeO\textsubscript{2}) led to a better VCM yield.\textsuperscript{33} Inspired by the acceptable activity of CeO\textsubscript{2}, another study of Scharfe et al. attempted to improve the CeO\textsubscript{2} performance by coupling CeO\textsubscript{2} with ZrO\textsubscript{2}. The newly prepared CeO\textsubscript{2}–ZrO\textsubscript{2} catalyst conducted stable ethylene conversions (60%) and high selectivity to EDC/VCM (45% for EDC, 43% for VCM).\textsuperscript{30} The lanthanide catalysts have poor activity at low temperatures and were only active at high temperatures typically larger than 673 K. These catalysts have relatively high selectivity of VCM and can be considered as the promising ways for process intensification to integrate the oxychlorination and dehydrochlorination into one single step. Continuous efforts should be focused on this active area to make the VCM yield higher and cost-effective in the future.

Currently, CuCl\textsubscript{2}-based catalysts are still the most used industrial catalysts and show better catalytic performance for EDC production. Since the first industrial ethylene oxychlorination plant was built by Dow in the USA in 1955, the CuCl\textsubscript{2}-based catalysts have been used as the industrial catalysts. There has been a challenge of the high volatility of cuprous chloride, caused by a loss of the active component and aggregation on both fixed-bed and fluidized-bed catalysts. It has drawn great academic and industrial interests to gain a better understanding of the surface reaction mechanism, dynamics in redox cycle, active sites, effects of support, and promoters, to improve the catalytic performance in terms of activity, selectivity, and especially the stability through improving the formulation of the oxychlorination catalysts. Therefore, in the following part, we will focus on a review of CuCl\textsubscript{2}-based catalysts for ethylene oxychlorination to EDC production.
3. Cu-BASED CATALYSTS FOR ETHYLENE OXYCHLORINATION

3.1. Cu Species in CuCl$_2$/γ-Al$_2$O$_3$. CuCl$_2$/γ-Al$_2$O$_3$-based catalysts are widely used industrial catalysts, and considerable research has been employed to exploit the nature of active sites.\textsuperscript{15–40} Generally, the catalysts were prepared by the impregnation method; after impregnation, the samples were dried at 120 °C under the dry airflow for 12 h. In the catalysts, six Cu species, namely paratacamite, copper alumina surface species, cupric chloride (CuCl$_2$), CuCl$_2$ with the vacancy, Cu oxide chloride (Cu$_2$OCl$_2$), and cuprous chloride (CuCl), have been observed.

Paratacamite (Cu$_2$(OH)$_3$Cl). The CuCl$_2$-based catalysts are typically prepared by impregnation. The catalyst preparation and pretreatment were studied by Density Functional Theory (DFT) calculations.\textsuperscript{39} It is found that the adsorption of Cu$^{2+}$ and Cl$^-$ is structure sensitive and also significantly sensitive to hydration and dehydration. Both Cu$^{2+}$ and Cl$^-$ adsorb exclusively on the (110) and (100) surfaces of γ-alumina but not on the (111) surface. On the (100) surface, both chloride ions bind to the copper. On the (110) surface, only one chloride binds to the copper, and the other binds to the alumina surface. The predicted results were validated by experiments using temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR). The results reveal that catalyst preparation and properties are structure sensitive to the alumina. The γ-Al$_2$O$_3$ is an inert material to provide a large surface area to deposit CuCl$_2$. The morphology and particle size of the γ-Al$_2$O$_3$ should be addressed. Lamberti and co-workers characterized the fresh material to provide a large surface area to deposit CuCl$_2$. The properties of the amorphous CuCl$_2$ are briefly summarized here: (i) it shows spherical symmetry evidenced by a very broad EPR signal; (ii) it is soluble; (iii) it starts to appear when the alumina surface is saturated to form surface copper aluminate; (iv) it is characterized by a very intense d–d band at about 13,000 cm$^{-1}$ and an additional charge transfer band in the 28,000 to 31,000 cm$^{-1}$ range in UV–vis spectroscopy, and d–d band intensity is proportional to the concentration of CuCl$_2$; (v) it is not stable upon both thermal and vacuum treatments; (vi) the chlorine atoms are coordinated to Cu ions in the nearest local shell imposed by the structure of anhydrous CuCl$_2$ with a coordination number of 4 at 2.26 Å measured by EXAFS,\textsuperscript{37} which is consistent with the results of DFT calculations;\textsuperscript{43–49} (vii) CuCl$_2$ is reducible by ethylene.

Cuprous Chloride (CuCl). The reduction of CuCl$_2$ by ethylene forms CuCl. The properties of CuCl are briefly summarized here: (i) it is highly volatile and causes the problems of the lifetime of the CuCl$_2$ catalysts. The vapor pressure between 230 and 350 °C is described by eq 5.\textsuperscript{40}

\[
\log_{10} P (\text{mm Hg}) = -7574 T^{-1} + 10.29
\]

(ii) when CuCl$_2$ is reduced to CuCl, the electronic structure changes from 3d$^3$ to 3d$^4$. No absorption can be observed for CuCl in the near-infrared (NIR) region,\textsuperscript{38,47,48} and a decrease of the electron spin-flip transitions is observed in the EPR spectra;\textsuperscript{38} (iii) the coordination number of Cl to Cu is 2,\textsuperscript{43} (iv) it is inactive for ethylene reduction, and it cannot be reduced further at the ethylene oxychlorination reaction conditions.\textsuperscript{47,48}

Copper Oxide Chloride (Cu$_2$OCl$_2$). Cu$_2$OCl$_2$ has been long proposed as an important intermediate in the catalytic cycle of ethylene oxychlorination.\textsuperscript{49,50} It has been experimentally determined by EXAFS with an O coordination number of 1 and a Cl coordination number of 2, and Cu exists with an oxidation state of +2.\textsuperscript{42} The band energy of Cu$_2$OCl$_2$ measured by UV–vis spectroscopy is similar to CuCl$_2$.

Cupric Chloride (CuCl$_2$) with Cl Vacancy. The operando X-ray absorption near-edge structure (XANES) study illustrated a mixture of CuCl$_2$ and CuCl existing in the catalysts during the reaction.\textsuperscript{36,40,51} It was also illustrated by UV–vis-NIR that CuCl$_2$ decreases and the CuCl$_2$/CuCl ratio changes with time, as a result of the removal of Cl and forming Cl vacancies.\textsuperscript{37} The CuCl$_2$ with a vacancy is expressed as a mixture of CuCl$_2$ and CuCl. The UV–vis-NIR spectra showed a change in the charge transfer when Cl is gradually removed. The CuCl$_2$ with a Cl vacancy has a Cl coordination number of 3 with Cu.$^{43}$ The vacancy concentration is often measured as the CuCl$_2$/CuCl ratio.

3.2. Effects of Catalyst Supports. Several supports have been applied for ethylene oxychlorination, such as alumina, silica, zeolites, activated carbon, and others.\textsuperscript{16,22,41,52} The interaction between the CuCl$_2$ and the support surface has been recognized as an important factor to influence the catalyst activity, selectivity, and stability. The interaction between the CuCl$_2$ and support was studied by different techniques, like EPR, XRD, TPR, and solvent extraction. The main results are summarized in Table 2.

EPR has been long applied as a powerful technique to study the interaction between CuCl$_2$ and various supports.\textsuperscript{18,41,42,53,54} On CuCl$_2$/Al$_2$O$_3$ support, two different EPR signals were identified that related to different environments of the Cu(II) ion. The asymmetric or axial symmetric signal is assigned to isolated Cu(II) ions interacting with the...
support, which is dominating on low-copper-content alumina-supported catalysts. The symmetric signal is assigned to Cu(II) ions which do not interact with the support. The symmetric one could be selectively removed by washing treatment with solvent,\textsuperscript{41,42} demonstrating that this signal was indeed related to Cu(II) ions which did not interact with the support. The EPR study illustrated a significant interaction between the copper ions and the alumina support but not in the case of SiO\textsubscript{2}. On Al\textsubscript{2}O\textsubscript{3}, Cu\textsuperscript{2+} ions occupied the vacancy and formed surface species stabilized by the support. The results showed that alumina is not inert, which influenced the electronic properties of Cu ions. Rouco has studied the effect of the interaction of CuCl\textsubscript{2} and the supports on three steps, namely reduction of CuCl\textsubscript{2}, oxidation of CuCl, and hydrochlorination of Cu\textsubscript{2}OCl\textsubscript{2} in the catalyst cycle by the TPR combined EPR.\textsuperscript{50} The treatment of C\textsubscript{2}H\textsubscript{4} results in the complete reduction of CuCl\textsubscript{2} to CuCl on SiO\textsubscript{2}, whereas an incomplete reduction was seen on Al\textsubscript{2}O\textsubscript{3}. The sequential oxidation of CuCl clearly shows that oxidation to CuCl\textsubscript{2} is accomplished on Al\textsubscript{2}O\textsubscript{3} but not on SiO\textsubscript{2}.

In 1983, Zipelli et al. investigated the nature and stability of copper species on SiO\textsubscript{2}-, γ-Al\textsubscript{2}O\textsubscript{3}-, and α-Al\textsubscript{2}O\textsubscript{3}-supported CuCl\textsubscript{2} by using XRD and reflectance spectroscopy.\textsuperscript{75} The observed stability order of the formed complexes on these supports is the following: γ-Al\textsubscript{2}O\textsubscript{3} > SiO\textsubscript{2} ≥ α-Al\textsubscript{2}O\textsubscript{3}, which indicates a strong interaction between CuCl\textsubscript{2} and γ-Al\textsubscript{2}O\textsubscript{3} compared to other supports. The ethylene oxychlorination activity of Ag-promoted CuCl\textsubscript{2} decreased in an order of γ-Al\textsubscript{2}O\textsubscript{3} > Kiesel gel > mordenite > α-Al\textsubscript{2}O\textsubscript{3} > porous glass.\textsuperscript{56} Rouco also illustrated a stronger salt-support interaction for CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} compared to that of CuCl\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3} and CuCl\textsubscript{2}/SiO\textsubscript{2} by solvent extraction, where almost 100% of CuCl\textsubscript{2} on α-Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} can be extracted, while only about 16% of CuCl\textsubscript{2} can be extracted on CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3}.

Rouco demonstrated a signifi- cant interaction between CuCl\textsubscript{2} and the supports surface in ethylene oxychlorination. The SiO\textsubscript{2}-supported catalysts are not active at relatively low-temperature oxychlorination reactions both in the fluidized bed and fixed-bed reactors, since the cycle between CuCl\textsubscript{2} and CuCl cannot be accomplished. Besides, the interaction between CuCl\textsubscript{2} and the support plays a virtually important role in the mobility of the Cu species. The strong adsorption on γ-Al\textsubscript{2}O\textsubscript{3} reduced significantly the mobility and enhanced stability.\textsuperscript{51,57,60}

An important consequence of the interaction between CuCl\textsubscript{2} and the support is the particle size of CuCl\textsubscript{2}, which has not been well addressed so far. For the unsupported CuCl\textsubscript{2} powder, it is typically inactive for the ethylene oxychlorination. TPR in C\textsubscript{2}H\textsubscript{4} indicated the reduction of CuCl\textsubscript{2} to CuCl started at higher temperatures (about 663 K), which coincides with the decomposition temperature of CuCl\textsubscript{2}.\textsuperscript{50} The larger particles increased the barrier for the reduction of CuCl\textsubscript{2}. Many experimental results support the findings in which CuCl\textsubscript{2} can be stabilized on Al\textsubscript{2}O\textsubscript{3}\textsuperscript{15,52} and CuCl on SiO\textsubscript{2}.\textsuperscript{59} The study rationalizes the importance of the effect of supports, more precisely the interaction between the Cu species and the support surface in ethylene oxychlorination. The SiO\textsubscript{2}-supported catalysts are not active at relatively low-temperature oxychlorination reactions both in the fluidized bed and fixed-bed reactors, since the cycle between CuCl\textsubscript{2} and CuCl cannot be accomplished. Besides, the interaction between CuCl\textsubscript{2} and the support plays a virtually important role in the mobility of the Cu species. The strong adsorption on γ-Al\textsubscript{2}O\textsubscript{3} reduced significantly the mobility and enhanced stability.\textsuperscript{51,57,60}

The different supports were also used as the CuCl\textsubscript{2} catalysts and evaluated in the ethylene oxychlorination. In 1966, Todo et al. studied ethylene oxychlorination using 15 wt % of CuCl\textsubscript{2} with several different supports and reported the preferred order as alumina > silica gel > Celite.\textsuperscript{21} The well-dispersed CuCl\textsubscript{2} shows better reducibility. Murzin and co-workers recently demonstrated an order of ethylene oxychlorination rate on CuCl\textsubscript{2} on supports of γ-Al\textsubscript{2}O\textsubscript{3} > TiO\textsubscript{2} > H-Beta-25 > SiO\textsubscript{2}.\textsuperscript{61} In general, the observations are rather consistent, and the activity of CuCl\textsubscript{2} depends on its interaction with the support and follows an order of γ-Al\textsubscript{2}O\textsubscript{3} > TiO\textsubscript{2} > H-Beta-25 > SiO\textsubscript{2} > α-Al\textsubscript{2}O\textsubscript{3}.

The superior performance of γ-Al\textsubscript{2}O\textsubscript{3} might be due to its strong salt-support interaction, pore structure, high surface area, high mechanical strength, high thermal resistance, and acidity.\textsuperscript{62} These properties ensure high catalytic activity, enhance catalyst stability, and minimize the volatility of the CuCl relative to other supports, which make γ-Al\textsubscript{2}O\textsubscript{3} comparatively the best support for CuCl\textsubscript{2}-based oxychlorination catalysts. Reducing the mobility of the Cu species is vitally important to avoid pellets sticking in a fluidized bed reactor. Sticking pellets can change the flow pattern of the reactor and thus disturb the stable operation. The strong adsorption of Cu species with support and adding promoters to hold a higher concentration of CuCl\textsubscript{2} can effectively minimize the pellet sticking.

Experiments found that the strong interaction between the support and the active phase plays an essential role in the ethylene oxychlorination activity.\textsuperscript{23} Thus, it is necessary to involve the model of support in the theoretical exploitation of the active site. Louwerse et al.\textsuperscript{39} adopted the general accepted

---

Table 2. Summary of the Different Methods Used for the Research for Supports

| Supports | Interaction | Methods | Remarks |
|----------|-------------|---------|---------|
| γ-Al\textsubscript{2}O\textsubscript{3} | strong | EPR, XRD, solvent extraction | EPR identified the significant interaction between CuCl\textsubscript{2} and support. No CuCl\textsubscript{2} signals on XRD, with good dispersion of CuCl\textsubscript{2} (the most active than the others). CuCl\textsubscript{2} can be partially removed by acetone. \textsuperscript{42, 53–55} |
| TiO\textsubscript{2} | relatively strong | solvent extraction | CuCl\textsubscript{2} can partly be removed by acetone; the order is γ-Al\textsubscript{2}O\textsubscript{3} > TiO\textsubscript{2} ≥ SiO\textsubscript{2}. \textsuperscript{58} |
| α-Al\textsubscript{2}O\textsubscript{3} | relatively weak | XRD | Cu specie is not stable. γ-Al\textsubscript{2}O\textsubscript{3} > SiO\textsubscript{2} ≥ α-Al\textsubscript{2}O\textsubscript{3}. CuCl\textsubscript{2} can be easily removed by acetone. \textsuperscript{55} |
| SiO\textsubscript{2} | weak | EPR, XRD, solvent extraction | Weak interaction from EPR study. CuCl\textsubscript{2} forms a particle, and it can be easily removed by acetone. \textsuperscript{53–55} |

---

https://dx.doi.org/10.1021/acscatal.0c01698
ACS Catal. 2020, 10, 9299–9319
becomes weaker with the increase of the CuCl2 cluster size. Its stronger Lewis acidity of Al on (110). The interaction structure of uncalcined copper chloride on γ-Al2O3 suggested that the adsorption Cu2+ and Cl− between the support and CuCl2 strongly depends on the facet of support. Compared to γ-Al2O3 (100), a stronger CuCl2-support interaction was observed on γ-Al2O3 (110), owing to its stronger Lewis acidity of Al on (110). The interaction becomes weaker with the increase of the CuCl2 cluster size (i.e., the loading of Cu).44 The effect of γ-Al2O3 structures on ethylene oxychlorination needs to be addressed in the future. It should be noted that another important effect of the support is its influence on the catalyst selectivity. It will be reviewed in detail in section 4.3.3. Reaction Mechanisms. A better understanding of the reaction mechanism is of vital importance for the development of new catalysts and the improvement of current catalysts. Thus, substantial efforts have been devoted to the investigation of the reaction mechanism of ethylene oxychlorination. A Deacon mechanism was proposed at a very early stage of the process development, where HCl was oxidatively converted into Cl2 (eq 6). Further, substitution chlorination occurs in the gas phase (eq 7), and the product may continue to undergo substitution reactions, which results in the formation of more highly chlorinated hydrocarbons. The Deacon process was developed by H. Deacon and F. Hurter in 1868 for the recovery of chlorine and further developed by Hasenclever in 1883. Then in the 1920s, Ernst and Wahl adopted the Deacon system to chlorinate hydrocarbons (methane, ethane, ethylene, and benzene) at 573–923 K. Despite the possibility of chlorinating ethylene in the Deacon reaction, a rate equation based on the Deacon-type reaction mechanism failed to fit the kinetics of ethylene oxychlorination at 180 °C.46
The Kubelka–Munk function (KMF) at 793 nm is sensitive to the d–d transition band of CuCl₂.

CuCl with the electronic configuration of 3d¹⁰ does not exhibit an d–d band transition. Therefore, a decrease of CuCl₂ on the catalyst, accompanied by an increase of CuCl, results in a decreasing KMF as the reduction proceeds. As shown in Figure 3, the KMF decreased with the reduction of CuCl₂ to CuCl by ethylene. The KMF increased reversibly with the oxidation of CuCl to Cu₂OCl₂ by oxygen. The relative change in the normalized Kubelka–Munk function (NKMF) with time-on-stream (TOS) followed the changes in the relative Normalized ethylene conversion (NEC) in the reduction step, and also followed the relative changes in the reducible CuCl₂ in CuCl₂ (Figure 3) suggesting lattice Cl in CuCl₂ is responsible for ethylene oxychlorination.

The change in KMF units with time during the transient oxidation is opposite to the transient reduction. The changes in CuCl₂ are reversible in the reduction and oxidation steps. Combining the fast hydrochlorination step, the three steps form a cycle of the ethylene oxychlorination (Figure 2e).

It should be noted that the oxychlorination mechanism depends on the catalyst. For the alumina-supported CuCl₂ catalyst, a three-step mechanism is dominating and has relatively low adsorption strength of EDC, which leads to the highest EDC selectivity among all the oxychlorination catalysts reported so far. For other catalysts like rare-earth metal oxides or chlorides, they served as the bifunctional catalysts in the direct VCM production from ethylene oxychlorination, and the oxychlorination follows a Langmuir–Hinshelwood surface reaction mechanism. For example, with the Ce-based catalyst, the CeOCl₂ catalyst surface is found to contain CeOCl₂, while the bulk phase is CeO₂, regardless of the starting material CeCl₃, CeOCl₂, or CeO₂. Pérez-Ramírez and co-workers have performed the kinetic study and proposed a reaction mechanism on the CeO₂ surface by combining DFT with steady-state experiments and temporal analysis of products (TAP). The two steps of ethylene oxychlorination and EDC dehydrochlorination can be integrated into a one-pot process on a bifunctional catalyst, which catalyzes the surface ethylene oxychlorination.
As a result, the steady-state CuCl₂ concentration and the rate is relatively low, and the reduction rate is relatively high. RDS, which is in good agreement with other observations. For the three-step mechanism, the reduction, oxidation, and hydrochlorination are sequential reaction steps. Lamberti and co-workers suggested the CuCl oxidation was the rate-determining step (RDS) on neat Cu, and K-promoter changes the RDS to ethylene reduction steps based on the results of operando X-ray absorption spectroscopy.

We have recently developed a virtual approach using a rate-diagram to elucidate the active sites, illustrate the rate-determining step, and predict the reaction rate and Cu oxidation state at the steady state. The rate of the transient reduction and oxidation steps, as well as the steady-state kinetics of the ethylene oxychlorination reaction including the precise evolution of the catalytically active component, was measured by combined operando UV–vis-NIR and mass spectroscopy. In the rate-diagram, the reaction rates of the reduction and oxidation steps on the catalysts are plotted as a function of the concentration of CuCl₂ in Figure 4. At the steady state, the reduction and oxidation reaction rates are identical, represented as the cross point of the two curves. In this respect, the rate and the Cu oxidation state corresponding to the interaction point represent the steady-state rate and Cu oxidation state at the given reaction conditions. For example, the rate-diagram of the CuCl₂/γ-Al₂O₃ catalyst without promoters as shown in Figure 4a illustrated that the oxidation rate is relatively low, and the reduction rate is relatively high. As a result, the steady-state CuCl₂ concentration and the reaction rate are relatively low, which is consistent with the experimental measured CuCl₂ values. The low CuCl₂ and high CuCl cause Cu loss and deactivation due to the high volatility of CuCl. The reoxidation of reduced catalysts is the RDS, which is in good agreement with other observations. The industrial catalysts are always promoted by alkaline metals, alkaline-earth metals, or rare-earth metals for practical use. As shown in Figure 4b, the promoters such as K and Ce improved the oxidation of the reduced Cu catalysts and thus reduced the concentration of CuCl₂.

The rate-diagram is a powerful tool to predict the dynamic active sites by taking into account the kinetic balance of the three steps in the catalytic cycle to predict the steady-state CuCl₂ concentration and the reaction rate. It leads to an important conclusion that the steady-state rate depends on not only the redox reaction rate but also the number of active sites, namely the concentration of CuCl₂ and CuCl under working conditions, instead of the initial oxidation state. Moreover, the rate-diagram can guide the catalyst design to tune the reduction and oxidation rates to remarkably improve the activity and stability. The rate-diagram suggests that the desired CuCl₂-based catalysts should have a much higher oxidation rate than the neat Cu catalysts but without lowering too much the reduction rate, in order to achieve a higher rate and CuCl₂ concentration, thus active and stable catalysts, as illustrated by the red dashed line in Figure 4a. The promoter is a good choice to achieve the goal such as K- and Ce-promoted catalysts shown in parts b and c, respectively, of Figure 4. The approach of the rate-diagram will be applied to analyze the detailed effect of promoters on the catalyst performance in the role of promoters in section 3.4. Therefore, it is concluded that the RDS varies at different reaction conditions, supports, and additives, although it generally follows the three-step redox mechanism.

3.4. Active Sites in CuCl₂/γ-Al₂O₃-Based Catalysts. Large efforts have been devoted to understanding the Cu species on alumina by various techniques such as EPR, EXAFS, and UV–vis-NIR. Active sites are entities on a catalyst surface to which molecules bind, for a reaction to occur. They directly participate in a catalytic reaction cycle and are energetically favored to support the reaction. The nature and reactivity of active sites of the oxychlorination catalysts have been intensively investigated. However, the identified active sites in the literature are rather controversial. Here, we review all the proposed active sites and the experimental evidence, try to make a critical analysis, and unify the active site at the end.

TPD results found the ethylene can be chemisorbed on CuCl₂ at low temperatures. Pulse and direct reduction of CuCl₂ by ethylene revealed the highly dispersed CuCl₂ is active for the reaction. It was also revealed that a high CuCl₂ concentration in the working catalyst could improve the
activity, selectivity, and stability by the transient and steady-state operando kinetic studies.\textsuperscript{48} Therefore, it was generally accepted that the active phase is a highly dispersed CuCl\textsubscript{2}.\textsuperscript{37,38,50,57,58} Besides, it has been reported that the CuCl\textsubscript{2} can disperse spontaneously onto the surface of the support and form a monolayer type structure because the monolayer is a thermodynamically stable form by Xie et al.\textsuperscript{74} With the help of DFT, a molecular view of the active site structures without a promoter and with the K-promoter is illustrated in Figure 5.\textsuperscript{44} The monolayer of CuCl\textsubscript{2} is epitaxially bonded with the alumina surface, where Cu is bonded with O, and Cl is bonded with Al in the alumina. This also pointed out the importance of the support surface on the properties of the epitaxially bonded CuCl\textsubscript{2} layer. Moreover, Figure 5 illustrated the evolution of the active sites from the CuCl\textsubscript{2} to CuCl\textsubscript{2}-vacancy and the end of CuCl. The K promoter forms a complex layer with CuCl\textsubscript{2}. Due to a larger size of K, it results in a distortion of the CuCl\textsubscript{2} layer, which influences its activity.

On the contrary, Xie et al.\textsuperscript{75} observed that two active sites with different reactivities existed on the support. The first was described as CuCl\textsubscript{2} with four coordination in a square planar configuration, whereas the second is a five- or six-coordinated Cu species formed from the adsorption of HCl. They further explained that the first site is more active than the second site due to stereo- and electronic effects that inhibit the adsorption of ethylene.

Although the CuCl\textsubscript{2} has been generally identified as the main active site, the three reaction steps might require different sites. Arcaya et al. studied for the first time the reactions for three individual steps in 1982 and reported that the reoxidation of reduced Cu catalysts is a slow process and the K promoter could enhance the oxidation. They found that the ethylene oxochlorination reaction rate was proportional to the amount of CuCl\textsubscript{2} in the KCuCl\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3} and CuCl\textsubscript{2} was the main active site. We also observed that the CuCl\textsubscript{2} reduction and CuCl oxidation are proportional to the amount of CuCl\textsubscript{2} and CuCl as shown in Figure 4.\textsuperscript{47,48} Lamberti and co-workers investigated the evolution of catalyst activity and of the average oxidation state of copper in the catalyst followed under real-time working conditions by using operando XANES spectroscopy.\textsuperscript{36,51,72} The technique allows a measurement of the CuCl\textsubscript{2} and CuCl in real-time. Both CuCl\textsubscript{2} and CuCl existed under the working reaction conditions. Moreover, the concentration of CuCl\textsubscript{2} and CuCl was highly dynamic in the temperature-programmed reactions. We recently also demonstrated the CuCl\textsubscript{2} concentration changes with time by the combined UV−vis-NIR and MS. The technique allows us to measure the timely and spatial distribution of CuCl\textsubscript{2} in the reaction.\textsuperscript{43} The changes in ethylene conversion are closely related to the CuCl\textsubscript{2} concentration change (Figure 6). For the neat CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} catalyst, the CuCl\textsubscript{2} was mostly reduced, and the remaining 40% CuCl\textsubscript{2} was the copper-alumina species and a small amount of CuCl. It caused catalyst deactivation due to Cu loss.

The Cu oxidation state increased with increasing the oxygen pressure (Figure 6). Both CuCl\textsubscript{2} and CuCl or more precisely the Cl vacancy always coexists but varies on the reaction conditions and catalysts.\textsuperscript{47,48} Therefore, the active site is the CuCl\textsubscript{2} with the Cl vacancy. Importantly, the active site is highly dynamic under working conditions. It points out the importance of controlling the CuCl\textsubscript{2}/CuCl concentration under working conditions to achieve a stable catalyst, through tuning the reaction conditions and catalyst composition.

Based on the critical analysis of the experimental and theoretical observation in the literature, we can conclude the active sites under working conditions, where there is no single active site, and the CuCl\textsubscript{2} with vacancies, CuCl\textsubscript{2} and Cu\textsubscript{2}OCl\textsubscript{2} are the active sites since three reaction steps require different active sites. The dominating active sites depend on the RDS. The CuCl\textsubscript{2} is dominating when the oxidation step is the RDS, where CuCl\textsubscript{2} with vacancies is the dominating active site when the oxychlorination compared to other catalysts, it suffices a fast deactivation due to agglomeration and vaporization of CuCl. As evidenced by the previous research, there are two types of Cu-species on the catalyst: the inactive Cu-aluminate and the active-supported CuCl\textsubscript{2}. The dopants can increase the fraction of the active phase by first filling in the vacancies of alumina. Quantitative analysis of EXAFS and XANES shows that all dopants can contribute more or less efficiently in increasing the fraction of the active copper species, and the efficiency is proportional to the ability of the corresponding cations to

![Figure 6](https://dx.doi.org/10.1021/acscatal.0c01698)
compete with CuCl, occupying the vacancies.\textsuperscript{35} Therefore, the industrial catalysts are typically promoted to maintain and enhance the activity and stability of CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3}. Based on the promoter chemical identity, the promoters can be classified into alkali metals (K, Na, Li, and Cs)\textsuperscript{40,47,49,57,60,68} alkali-earth metals (Mg, Ca, Sr, etc.)\textsuperscript{40,60,76,77} and rare-earth metals such as La, Ce, Pr, etc.\textsuperscript{73,35,40,48,57,60,77} Based on the number of promoters employed in one catalyst, the promoters can be classified as mono-, bi-, and multipromoters.

3.5.1. Monopromoters. Alkali Metal Chlorides. The K promoter presents commercial oxychlorination catalysts.\textsuperscript{82–91} and has been studied extensively.\textsuperscript{35,36,40,53,57,72,92–95} The first reported K promoter for the CuCl\textsubscript{2} catalyst for ethylene oxychlorination was back in 1966.\textsuperscript{96}

Arcoya et al. for the first time in 1982 demonstrated that the oxidation reaction rate doubled upon the addition of K to the catalyst using the α-Al\textsubscript{2}O\textsubscript{3} support.\textsuperscript{95} It was identified that the oxidation is the RDS on CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} while K shifts the RDS to the reduction step since K significantly enhances the oxidation of the catalyst and renders the reduction reaction.\textsuperscript{36} It should be noted that the conclusion was drawn solely based on the individual steps, ignoring the competitive reactions of the three steps under working conditions. The operando study is necessary to elucidate the nature of the promoter under working conditions. Muddada et al.\textsuperscript{40} performed an in situ XANES study of the temperature-programmed ethylene oxychlorination. Both the O\textsubscript{2} conversion represented as activity and the Cu\textsuperscript{I} fraction of the K\textsubscript{3.6}Cu\textsubscript{5.0} catalysts, where the number in the catalyst code represents the weight fraction of components, were measured and compared to the Cu\textsubscript{5.0} catalysts, as shown in Figure 7. The starting temperature of the reaction is higher on Cu\textsubscript{5.0} (480 K) than K\textsubscript{3.6}Cu\textsubscript{5.0} (520 K), suggesting a lower activity on the K-promoted catalyst. The pulse experiments indicated also the rate of CuCl\textsubscript{2} reduction by ethylene is lower on K\textsubscript{3.6}Cu\textsubscript{5.0} than Cu\textsubscript{5.0}. Contrary, the activity of CuCl oxidation is higher on the K-promoted catalyst than the neat Cu. The XANES results revealed that CuCl is dominating on Cu\textsubscript{5.0} owing to the oxidation of CuCl is the RDS, while CuCl\textsubscript{2} is dominating on K\textsubscript{3.6}Cu\textsubscript{5.0} due to the reduction of CuCl\textsubscript{2} being the RDS. The results illustrate that the addition of K favors the Cu\textsuperscript{I} state, leading to an increase in the oxidation rate or a decrease in the reduction rate.

Applying the rate-diagram analysis to the typical K-promoted CuCl\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst (K\textsubscript{1.54}Cu\textsubscript{5}S) shown in Figure 7, the CuCl oxidation rate is significantly higher, while the CuCl\textsubscript{2} reduction is lower than the neat Cu catalyst.\textsuperscript{77} As a result, at the steady state, the CuCl concentration was much higher than the neat Cu catalyst, while the reaction rate was not significantly affected. It rationalized why K is the most applied promoter in the industry.

In general, the presence of K in the catalysts increased the apparent activation energy of the oxychlorination reactions.\textsuperscript{34,97} DFT calculations confirmed the formation of a mixed K\textsubscript{x}CuCl\textsubscript{2+} salt (Figure 5) on the alumina surface and demonstrated that KCl reduced the interaction between the support and the active phase. It supports the experimental observation that the K promoter increased the CuCl\textsubscript{2} concentration to 0.81 mol/mol\textsubscript{Cu\textsubscript{II}} from 0.56 mol/mol\textsubscript{Cu\textsubscript{II}} of the neat copper chloride catalysts.\textsuperscript{35} The DFT study suggested a complex structure of Cu\textsubscript{x}KCl\textsubscript{y} on γ-Al\textsubscript{2}O\textsubscript{3}, similar to the reported salt. Charge density difference analysis elucidates that the electron transfer between K and neighboring Cu and Cl atoms results in substantial electron accumulation around the Cu and chlorine atoms and the decline of the Bader charge of Cl and Cu. Thus, it raised the formation energy of Cl vacancy and facilitated the oxygen adsorption, dissociation, and CuCl oxidation upon the addition of KCl. The formation energy of Cl vacancy increases with the decreasing of Cl/Cu ratios on both unprompted and K-promoted catalyst surfaces, which attributes to the decline in the Cl charge at lower Cl/Cu ratios. The effects of K on the oxychlorination catalysts from observations of different researchers could be concluded as the following:

1) K forms mixed salts (Cu\textsubscript{x}K\textsubscript{y}Cl\textsubscript{z}) with the base catalyst, which modifies the redox properties of the catalyst and the reducibility of the active CuCl\textsubscript{2} and facilitates the regeneration of Cu\textsubscript{(II)} from Cu\textsubscript{(I)}. The RDS is changed from CuCl oxidation to CuCl\textsubscript{2} reduction due to the addition of K.\textsuperscript{35,36,40,72}

2) K causes an increase in the apparent activation energy. The effect of K on activity depends on the temperature, that is, a negative effect when the temperature is lower than 525 K and a positive effect at a temperature higher than 525 K.\textsuperscript{57}

3) K is selectively adsorbed on tetrahedral Lewis A1\textsuperscript{3+} sites of the γ-Al\textsubscript{2}O\textsubscript{3} surface, which modifies the physical and electronic properties of γ-Al\textsubscript{2}O\textsubscript{3}. This effect is pronounced with an increasing molar concentration of K.\textsuperscript{93}

4) The addition of K reduces the surface area of the active phase.\textsuperscript{72}

5) K reduces the volatility of CuCl and therefore makes the catalyst more stable.

In addition to K, research on other promoters has also attracted great interest. It has been found that Cs affects the catalyst and support similarly to K\textsubscript{6}, albeit to varying degrees.\textsuperscript{30,72,76} In contrast to K and Cs, Li increases the dispersion of the active phase and does not form a mixed salt with CuCl\textsubscript{2}.\textsuperscript{72,93}

Muddada et al.\textsuperscript{40} performed in situ XANES coupled with temperature-programmed reactions on the CuCl\textsubscript{2}-based catalyst doped with K, Cs, and Li promoters. At the steady state, all dopants had a positive effect on the available fraction of the active CuCl\textsubscript{2} phase. However, the activity test revealed that not all dopants positively influence the ethylene chlorination reaction. The detailed activity was not measured.
but was approximately estimated as the activity tendency based on the CuCl₂ reduction temperature, and a lower starting temperature accounts for higher activity.

There are two other factors added to the complexity of the promoter effects, namely dependence of the promoter loading and the support. The effect of the K promoter on the activity of the oxychlorination reaction depends on the loading of the relative loading of K. A "volcano curve" between the K loading and the activity was observed where small amounts of K increased the activity, whereas excess K diminished it.⁴⁹⁻⁵⁰,ⁱ⁰⁰ The effect of the promoter on the activity of oxychlorination depends also on the support. For CuCl₂/Al₂O₃, NaCl and KCl have a significant positive effect on ethylene conversion on α-Al₂O₃, that is there is a substantial increase in conversion for the α-Al₂O₃ and SiO₂, while the promoting effect for γ-Al₂O₃ is less pronounced.⁴⁹

Therefore, the classification of the promoters into two types in terms of the RDS might be not universal but depends on the promoter loading as well as the supports. It needs a more systematic study to gain a better understanding of the promoter effect.

**Rare-Earth Metal Chlorides.** La is one of the most used promoters in industrial catalysts. La is traditionally considered as a structural additive in many patents where La makes CuCl₂ highly dispersed and prevents catalyst particles from sintering and agglomerating or sticking, especially in fluidized-bed operations.⁴¹⁻⁵⁰ Ce has been found to have a similar effect on the CuCl₂-based catalysts.¹⁰¹ La is often added to K-promoted industrial oxychlorination catalysts though in a small amount. It has also been found that La preferably occupies the octahedral vacancies of CuCl₂, and enhances the Bronsted acidity of the support.⁴⁹⁻⁵⁰,⁷⁶,¹⁰³ Rouco³ found that the La promoter accelerated the reaction rate without changing the apparent activation energy with a feed molar ratio (C₂H₄:HCl:O₂) of 1:1.8:1.1 at temperatures ranging from 185 to 240 °C, which is different from K, suggesting a purely structural promotion.

However, a large body of experimental results pointed out that La does not serve only as the structural additive but also significantly alters the surface reactions through the chemical promotion. We recently found that La⁶⁸ and Ce⁴⁸ promoters significantly enhanced both the reduction of CuCl₂ and oxidation of CuCl. In the rate-diagram, as shown in Figure 4, the Ce promoter increased the steady-state reaction rate, but there was not a significant increase in the concentration of CuCl₂.⁶⁸ It is consistent with the observation from operando experiments that La and Ce increased the CuCl₂ reduction rate, and the reduction was the RDS of the oxychlorination reaction where the CuCl₂ was dominating.⁴⁰ La showed a similar promotion effect as Ce but with a less degree since La-promoted catalysts enhanced HCl adsorption and then suppressed the reaction to a certain degree. A negative reaction order with respect to HCl was found on La-promoted Cu catalysts.⁶⁸ This could explain the observed strong temperature dependence of La promotion effects on the activity. The rate of ethylene oxychlorination of La-promoted catalysts is similar to neat Cu at 503 K and much higher than neat Cu catalysts at 573 K. The adsorption became weaker at a higher temperature.⁷⁷ This can also explain the observation of Villadsen and Livbjerg that La increased the rate of sublimation of CuCl₂, possibly increasing the CuCl concentration, which is an undesirable effect in terms of catalyst stability.¹⁰⁵ Dotson suggested that this undesirable effect occurs because La forms strong chloride complexes with Cl and, thus, competes with CuCl for Cl to form neutral Cu species, which sublimes faster than CuCl.⁶⁰ From the rate-diagram analysis, La and Ce enhanced both the reduction and oxidation rate thus leading to a relatively high concentration of CuCl₂ at the steady state, and it can enhance the sublimation of CuCl₂.

Zhizao et al.⁸⁰ attributed the positive impact of Ce on the existence of surface cerium oxide, which supplied oxygen for the oxidation step. XRD results show that cerium chloride was transformed into cerium oxide at the beginning of the reaction. Li et al.¹⁰⁶ detected that three different species of CeO₂ existed (i.e., dispersed CeO₂, small aggregated crystalline CeO₂, and large CeO₂ particles) with the increase of Ce loading, where the small aggregated crystalline ceria species was highly active. The promotion effect of Ce was attributed to the formation of O²⁻ or O₁⁻, which enhanced the oxidation of CuCl and provided extra weak acidic sites for the rupture of the C=H bond in ethane. CeOCl and CeAlO₃ species may cause the deactivation. A highly active and stable Ce-promoted CuCl₂ catalyst was developed, which achieved about 87% and 66% higher activity than unpromoted catalysts and K-promoted catalysts.⁴⁸ It is found that the various promoters play distinct roles in the reaction. The effects of rare-earth metal oxides or chlorides on the oxychlorination catalysts from observations of different researchers could be concluded as the following:

1) La and Ce increased the dispersion of CuCl₂ on the surface and increased the reducibility of the active CuCl₂.
2) La⁶⁸ and Ce⁴⁸ modified the redox properties of the catalyst, increased both the reducibility of the active CuCl₂, and facilitated the reduction of Cu(II) to Cu(I). The oxidation step is the RDS.⁴⁰
3) This type of promoter is immobile and often used to stabilize the Cu catalyst and prevent aggregation.

**Alkaline-Earth Metal Chlorides.** Mg is the most reported promoter in alkaline-earth chlorides, but it has been more often applied in catalysts for ethane oxychlorination. In ethylene oxychlorination, Mg behaves similarly to La and Ce promoters, which increases the reaction rate,⁷⁷ by enhancing both reduction and oxidation rates. The oxidation step is also the RDS, and CuCl₂ is dominating in the steady-state operation. The addition of Mg and Ca promoters gave a good rate with high selectivity larger than 99%.⁵⁶

In summary, the neat Cu has a high rate of CuCl₂ reduction and a lower rate of CuCl₂ oxidation leading to CuCl₂ dominating at the steady-state operation. The promoter greatly altered Cu properties and activities. Based on the measured CuCl₂ concentration at the temperature region of the typical ethylene oxychlorination reaction condition, the dopants can be classified into two types, where type I consisted of La, Mg, and Li, while type II consisted of K and Cs. For the type I catalysts, the RDS is the oxidation step, where the CuCl₂ is dominating on the catalyst, while type II catalysts change the RDS to the reduction step, where CuCl₂ is dominating.⁴⁰ The reducibility of these catalysts is measured by pulse reaction of ethylene followed by La₁₀.₉⁴Cu₅.₅₀ > Mg₁₉.₉₄Cu₅.₅₀ > Li₆.₅₄Cu₅.₅₀ > Ca₁₀.₄₅Cu₅.₅₀. However, the steady-state activity did not follow the same order of the reduction; it followed an order of Ce₁₁₀Cu₅.₅₀ > Cu₅.₅₀ >
on both CuCl2 reduction and CuCl oxidation. However, the Cu4.5Mg1.5K0.4Pd0.01 > Cu4.5Mg1.5K0.4 (B). Ag was also found in dichloroethane (1,1-EDC, C2H4Cl2), chloroacetaldehyde (chloral) 0.3–0.5, trichloroethylene (chloroform) 0.1–0.2, tetrachloromethane 0.1–0.2 dichloroethylenes 0.1–0.2.

The oxychlorination reaction network is rather complex as numerous routes, such as substitution, addition, elimination, and oxidation, leading to a series of chlorinated and oxidized products, can take place.114 Based on the critical analysis of the literature, the reaction pathways of different organochlorine products are proposed in Figure 8.

The byproducts except for ethyl chloride (EC) are formed from the second reaction of EDC, as shown in Figure 8. The Cu active sites, as well as the active sites on alumina, catalyze the secondary reactions. Catalysis for byproduct formation in ethylene oxychlorination was investigated mostly in laboratories in Russia, which has been well summarized by Flid including many Russian references.114 Here we critically review the progress in the study of byproduct formation in the ethylene chlorination on Cu catalysts in terms of the reaction mechanism and site requirement, by combining Flid’s work and other literature.

EC and VCM by Hydrochlorination and Dehydrochlorination. EC is formed by the ethylene hydrochlorination reaction, following a first-order with respect to ethylene and hydrogen chloride, and is inhibited by water vapor. Higher water pressure can suppress the formation of EC.114 The reaction occurs at the same site of the oxychlorination. The EC can undergo dehydrochlorination to ethylene catalyzed by acidic sites.114

The formation of chlorogenic byproducts in the ethylene oxychlorination process has been summarized by Flid.114 The dehydrochlorination reaction is a crucial reaction step for the byproduct formation, which is typically catalyzed by acidic sites.99,73,118,119,122 Muddada et al.76,77 have performed a systematic study of the conversion of EDC on various supports and catalysts and correlated to the different active components, such as alumina, chlorinated alumina, CuCl2, CuCl, Cu2OCl2, and promoted CuCl2. The authors studied Brensted and Lewis sites of catalysts using the IR spectra of CO dosed on the catalyst. The Al3...CO and Al–OH...CO adducts caused blue shifts of ν(CO), which usually is in the 2230–2180 cm⁻¹ and in 2155–2175 cm⁻¹ ranges, respectively. In this way, the role

| byproducts                              | fixed-bed technology | fluidized-bed technology |
|-----------------------------------------|----------------------|--------------------------|
| CO₂ + CO                                | 0.5–0.7              | 1–2                      |
| 1,1,2-trichloroethane                   | 0.1–0.3              | 0.3–0.8                  |
| trichloroacetaldehyde (chloral)         | 0.3–0.5              | 0.1–0.3                  |
| trichloromethane (chloroform)           | 0.1–0.2              | 0.1–0.2                  |
| tetrachloromethane                      | 0.1–0.2              | 0.1–0.2                  |
| dichloroethylenes                       | ≤0.1                 | ≤0.1                     |

Table 3. Yield of Byproducts, mol %, in Industrial Ethylene Oxychlorination Processes114

(Mg2.9Cu5.0 > La10.9 > K3.1Cu5.0 > Li0.5Cu5.0 > Cs10.4Cu5.0. The results pointed to that the effects of promoters on the oxychlorination reaction are highly dynamic and complicated based on the kinetic balance of three steps in the catalytic cycle. Here we redefine the categories, and the promoter can be divided into two types. The alkaline metal promoters increased the CuCl oxidation rate and reduced the CuCl₂ reduction rate leading to CuCl₂ dominating and slightly increased the reaction rate at steady-state operation, typically shown in Figure 4b. Class II is the rare-earth and alkaline-earth metal promoters that enhanced both the reduction and oxidation rate leading to CuCl₂ dominating but a significantly increased reaction rate at the steady-state operation, typically shown in Figure 4c. Therefore, the monopromoter could not meet the requirement of more active and stable catalysts simultaneously. The copromoter is a good solution to achieve the goal.

3.5.2. Bi- and Multipromoters. Commercially available catalysts usually contain more than one promoter,82 and several studies have explored copromoting oxychlorination catalysts.41,54,57,77,106,111 The most often reported copromoter is the K–La system.55,41,101–103 It is reported that the CuCl₂ catalyst copromoted by La and K improved the activity and stability at 397 °C.115 It has been demonstrated that the adding of La to K-promoted catalysts enhanced the stability by inhibiting the segregation of K.57 However, it was found that the catalyst deactivated due to carbon formation and loss of Cu active species at 500 °C over γ-Al2O₃-supported K/La/CuCl₂ after 40 h on stream.105 We found a synergy effect of K and La on both CuCl₂ reduction and CuCl oxidation. However, the synergy effect did not lead to a significant increase in the overall reaction rate, due to the strong adsorption of HCl.68 Arcoya et al.109 revealed that the presence of rare-earth metal chlorides such as Ce, Nd, and Pr in K-CuCl₂ catalysts increased the conversion.

Multiple promoters are only reported in the patents. A small number of noble metals or noble metal chloride (Eu, Pd, Au)-promoted Cu₄.₅Mg₁.₅K₀.₄ catalysts can increase the activity and selectivity of ethylene oxychlorination and reduce the oxidation of the products to CO₂.112 The reaction follows an order of Cu₄.₅Mg₁.₅K₀.₄Au₀.⁰⁵ > Cu₄.₅Mg₁.₅K₀.₄Ru₀.₁ > Cu₄.₅Mg₁.₅K₀.₄Pa₀.⁰₁ ≈ Cu₄.₅Mg₁.₅K₀.₄ (B). Ag was also found to be a good promoter. 450

4. Reaction Pathways and Active Sites for Byproduct Formation

The CuCl₂ catalysts are very selective to EDC, and typical selectivity is higher than 98%. The selectivity depends on the catalysts, reaction conditions (like temperature and feed composition), and reactor type.113 The exposing acid sites (Brensted and Lewis type) on the γ-Al₂O₃ support are one main reason for the side reactions. While the exposing acid sites can be modified by adding proper promoters, the side reaction can be prohibited further. The typical yields of the byproducts in both industrial fixed and fluidized bed processes of ethylene oxychlorination are presented in Table 3.114

Although the selectivity of 1,2-EDC is high, it still has environmental and economic benefits to further improve the selectivity. A number of undesirable byproducts are produced in the industrial plants, for example, vinyl chloride (VCM, C₂H₃Cl), 1,1,2-trichloroethane (TEC, C₂H₃Cl₂), ethyl chloride (EC, C₂H₃Cl), trichloroethylene (TCE, C₂HCl₃), 1,1-dichloroethane (1,1-EDC, C₂H₂Cl₂), chloroacetaldehyde (CH₂OCl), carbon tetrachloride (CCl₄), 1,2-dichloroethylene (DCE, C₂H₃Cl₂), methyl chloride (CH₃Cl), 1,1,2,2-tetrachloroethane (C₂H₂Cl₄), CO/CO₂, etc. The byproducts can be classified into two main groups, namely organochlorine compounds and deep oxidation products CO and CO₂. The process can be characterized by “chlorine selectivity” and “ethylene selectivity” considering Cl conversion in HCl to EDC and other organic compounds involved chloride and carbon conversion in ethylene to organochlorine compounds and CO. In the best-operating regimes, chlorine selectivity to EDC exceeds 99%; ethylene selectivity to organochlorine compounds is 96–98%, depending on the oxidizer that is used (concentrated or atmospheric oxygen).115

Oxychlorination Processes114
of various additives on the density of Lewis and Bronsted acidic sites of the γ-Al₂O₃ support was investigated. CsCl and KCl eliminated all the surface Lewis acidity, and LiCl, MgCl₂, and LaCl₃ also suppressed it significantly. All the dopants except CsCl increased the strength of the Bronsted sites. They concluded that Lewis and Bronsted acid sites on the Al₂O₃ surface were responsible for the conversion of EDC to chlorinated byproducts, such as VCM, 1,1-EDC, and 1,2-dichloroethene (DCE). HCl can chlorinate the Al₂O₃ surface, and the surface Cl on alumina will be involved in the byproduct formation. The selectivity toward chlorinated byproducts correlates directly with the density of Lewis acid sites at a temperature of 300 °C or higher, in the order Cu5.0 > La10.9Cu5.0 > Li0.9Cu5.0 > Mg1.9Cu5.0 > K3.1Cu5.0 > Cs10.4Cu5.0. At 230 °C, the content of byproduct is very low, typically lower than 0.01–0.02.

It is generally accepted that the acidic sites catalyze the EDC dehydrochlorination to VCM. Consistent with the work of Muddada et al., it has been proposed that pure alumina or chlorinated alumina are most active for dehydrochlorination. Adding promoters significantly reduces the dehydrochlorination of EDC and EC. The following order of the dehydrochlorination has been suggested:

\[ \text{Pure Al}_2\text{O}_3 > \text{CuCl}_2/\text{Al}_2\text{O}_3 > \text{MgCl}_2/\text{Al}_2\text{O}_3 > \text{KCl/Al}_2\text{O}_3 \]

Based on the above analysis, alkaline metal chloride-promoted CuCl₂ catalysts are superior from the viewpoint of increasing the selectivity. Mile et al. investigated the reaction mechanism and kinetics of dehydrochlorination of 1,2-EDC on different catalysts by kinetic isotope techniques. They observed a positive kinetic isotope ratio \( k_{HD}/k_{D} \) for the production of 1,2-EDC on the undoped catalysts, which suggested C–H bond breaking is the rate-determining step. The promoter additives shifted the RDS from C–H bond breaking on unpromoted catalysts to C–Cl bond breaking. Besides, they found that the 1,2-EDC dehydrochlorination reaction is a first-order reaction with an activation energy of 103 kJ mol⁻¹ at 558 K, and the addition of promoters increased the activation energies in the order of LiCl > CsCl > NaCl > KCl ~ RbCl.

1,1,2-Trichloroethane (TEC) by Oxychlorination of VCM. From a quantitative viewpoint, 1,1,2-trichloroethane (TEC) is the most crucial chloro-organic admixture, and it accounts for about 35–40% total chloro-organic byproducts. Muddada et al. proposed that TEC was formed from EDC via VCM on Cu catalysts. CuCl₂ is more active than CuCl for the further reaction of VCM, and the reaction mechanism is similar to the ethylene oxychlorination where lattice Cl in CuCl₂ is involved in the reaction. It was suggested that the reaction is preferred to be operated at the reduction-favorable conditions to reduce the CuCl₂ concentration to inhibit the TEC formation. However, the CuCl concentration should be controlled at the conditions with compromise of the selectivity and stability. Moreover, it should be noted that the VCM is the key intermediate for the TEC formation, and acidic sites are required. Suppressing VCM formation is a preferred way to suppress the formation of TEC. The copromoter (K1.5La5.45Cu5) increased the activity of the Cu phase with moderate CuCl₂ concentration and decreased the acid sites on the alumina surface. Besides the promotion, the Cu loading is also an important parameter to reduce the TEC formation. By increasing Cu loading at a level up to a nominally complete “monolayer” coverage and poisoning the alumina surface nucleophilic sites, the activity increases due to the increased density of active sites, while EDC selectivity increases due to decreasing acidic sites. In addition to modifying the catalyst, the reaction temperature is another parameter to tune the selectivity. The TEC yield increased exponentially with increasing the temperature.

Chloral, Chloroform, and Carbon Tetrachloride. These compounds are another group of important chloro organic admixtures. Their total content in crude 1,2-dichloroethane is usually 0.3–0.4%. It was shown that chloral is a product of the partial oxidation of EDC to an intermediate of chloroacetaldehyde following an oxychlorination reaction on Cu catalysts as shown in Figure 9.

\[ \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{CH}_2\text{C} = \text{CH}_2 \rightarrow \text{CCl}_3\text{CHO} \]

Figure 9. Reaction pathways for CO and CO₂ formation.

\[ \text{C}_2\text{HOC} = \text{C} \rightarrow \text{CHCl}_3 + \text{CO} \] (11)

Carbon tetrachloride is formed via a chloral oxychlorination:

\[ \text{C}_2\text{HOC} = \text{C} + \text{HCl} + 1/2\text{O}_2 \rightarrow \text{CCl}_4 + \text{CO} + \text{H}_2\text{O} \] (12)

The reaction mechanism of the oxychlorination can be similar to the ethylene oxychlorination on CuCl₂ catalysts. The
ratio between the chloral decomposition and oxychlorination rates can be estimated at approximately 2:1 at low temperatures (210–215 °C).\textsuperscript{114,124}

CO\textsubscript{2} (CO and CO\textsubscript{2}) is another group of byproducts which influences the product cost in industrial oxychlorination. There have several kinetic studies of the CO\textsubscript{2} formation in oxychlorination mostly in the 1970s.\textsuperscript{115} Three precursors for chlorination is the dominating reaction, while at temperatures over 300 °C, the deep oxidation increased significantly. The mechanism of EDC oxidation can be rather different from the ethylene oxidation, which is presented in Figure 10.

\textbf{CO2 mole fraction in ethylene oxychlorination on promoted CuCl2/CuCl.} It was found that the optimum CO\textsubscript{2} content in the gas phase. It was found that the optimum CO\textsubscript{2} content in the gas phase.\textsuperscript{57} The CuCl\textsubscript{2} concentration under working conditions. Based on the above discussion, adding alkaline metal chlorides into Cu catalysts can suppress CO\textsubscript{2} formation by increasing the CuCl\textsubscript{2}/CuCl ratio. The hypothesis is confirmed by Arcoya et al. in ethylene oxychlorination on promoted CuCl\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3}, where the CO and CO\textsubscript{2} selectivity follows an order of Cu > Cu–K > Cu–Na > Cu–La. The CO\textsubscript{2} selectivity decreased from 5.2% on Cu to 0.6% on Cu–K, while adding the second promoters (Ce, Nd, Pr) into Cu–K catalysts, the CO\textsubscript{2} selectivity reduced further to 0.1%.\textsuperscript{49}

The effect of alkaline- and rare-earth metal chloride promoters on the CO and CO\textsubscript{2} selectivity is further examined by combining the tendency of CuCl\textsubscript{2} and the CO/CO\textsubscript{2} ratio under working conditions. Table 4 summarized the CO and CO\textsubscript{2} mole fraction in ethylene oxychlorination on promoted CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} at 498 K and C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}:HCl = 1:1.8–0.9.\textsuperscript{57}

\textbf{Table 4. Effect of Promoters on the EDC Selectivity and CO and CO2 Model Fraction in the Gas Phase as well as the CuCl2/CuCl Ratio in Ethylene Oxychlorination}  

| cat     | Cu1.2La | Cu   | CuK1.2La | CuK |
|---------|---------|------|----------|-----|
| EDC%\textsuperscript{a} | 97.0 | 96.9 | 97.5 | 97.8 |
| CO%\textsuperscript{b} | 1.3 | 2.3 | 0.7 | 0.5 |
| CO\textsubscript{2}%\textsuperscript{b} | 2.4 | 5.2 | 2.1 | 1.7 |
| (CO+CO\textsubscript{2}) % | 3.7 | 7.5 | 2.8 | 2.2 |
| CO/CO | 1.84 | 2.3 | 3 | 3.4 |
| CuCl\textsubscript{2}/CuCl\textsuperscript{f} | +++ | +++ | ++++ | ++++ |

\textsuperscript{a}Ethylene dichloride selectivity. \textsuperscript{b}Mole fraction in gas phase.\textsuperscript{57} The ratio was measured by UV–vis spectroscopy.\textsuperscript{68}

In general, adding promoters to CuCl\textsubscript{2} reduced CO\textsubscript{2} formation as shown in Table 4.\textsuperscript{57} The CuCl\textsubscript{2} concentration or CuCl\textsubscript{2}/CuCl at the steady state was measured by UV–vis spectroscopy.\textsuperscript{68} Although the catalyst and the reaction conditions are not the same, the tendency of the CuCl\textsubscript{2}/CuCl is expected to be similar. The catalysts with higher CuCl\textsubscript{2}/CuCl resulted in a higher CO/CO\textsubscript{2} ratio, especially for K and La–K copromoted catalysts. It is confirmed with the hypothesis of the CO/CO\textsubscript{2} ratio as an indicator of CuCl\textsubscript{2}/CuCl at the reaction conditions. Lower CuCl yielded a lower CO\textsubscript{2} selectivity and higher selectivity to EDC. Muddada et al.\textsuperscript{77} demonstrated that CO\textsubscript{2} can be also formed in EDC converting on alumina, and O on the alumina surface contributed to the formation of CO.\textsuperscript{93}
Table 5. Reaction Rate Expressions for Ethylene Oxychlorination

| catalyst            | T (K)  | equation                                                                 | reaction order | activation energy (kJ/mol) | ref |
|---------------------|--------|---------------------------------------------------------------------------|----------------|---------------------------|-----|
| 1 CuCl₂/γ-Al₂O₃    | 454–469| \( r = 2.49 \times 10^{-6} \times (C₂H₄)^{0.73} \times (O₂)^{0.34} \times (H₂O)^{0.18} \) | C₂H₄ O₂ HCl H₂O | 0.73 0.34 0 −0.18         | 102.6 | 66 |
| 2 KC1+CuCl₂/silica | 473–573| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 |                | 0.6 0.5 0.2 0             | 16   |
| 3 CuCl₂/charcoal   | 473–553| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 |                | 1 0 0.2 0                 | 0    |
| 4 CuCl₂/γ-Al₂O₃    | 473–553| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 |                | 1 1 0.3 0                 | 0    |
| 5 CuCl₂/γ-Al₂O₃    | 483–523| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 |                | 1.61 0 0 0               | 51.5 | 127|
| 6 CuCl₂/γ-Al₂O₃    | 484–524| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 |                | 1.61 0.25 0 0            | 94.7 | 128|

Table 6. Reaction Rate Expressions for Ethylene Oxychlorination

| catalyst            | T (K)  | equation                                                                 | activation energy (kJ/mol) | ref |
|---------------------|--------|---------------------------------------------------------------------------|---------------------------|-----|
| 1 CuCl₂/γ-Al₂O₃    | 457    | \( r = \frac{kP_{O₂}}{[1 + AP_{C₂H₄}P_{HCl}]} \)                           | 102.5 (454–469 K)         | 66  |
| 2 CuCl₂/γ-Al₂O₃    | 473–553| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 | 269 {+37.5 RT} C₂H₄ 2O₂C₂Cl \( \times \) 0.86_{\text{CuCl₂}} \) | 130 |
| 3 CuCl₂/γ-Al₂O₃    | 423–523| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 | 111.5                    | 131 |
| 4 CuCl₂/γ-Al₂O₃    | 473–533| \( r = kP_{C₂H₄}P_{O₂}P_{HCl}P_{H₂O} \)                                 | 111.5                    | 131 |

reaction. However, the contribution to CO₂ formation is much lower than on Cu catalyzed CO and CO₂ formation.

5. KINETICS FOR THE MAIN AND BYPRODUCT FORMATION

5.1. Kinetics on the EDC Formation. A deep understanding from the molecular level on the kinetics and the determination of structure–activity relationships has the fundamental meaning in the development of the heterogeneously catalyzed process. This knowledge is limited in ethylene oxychlorination, because of the demanding experimental conditions involving corrosive, toxic, and flammable reactant gases, which make it quite difficult to use the commonly used techniques and setups to tackle the mechanistic investigations, due to the significant industrial impact of ethylene oxychlorination. The studies that have been reported in the literature about the kinetics of ethylene oxychlorination are fewer than the studies that have been reported on the other catalytic reactions. The first kinetic study of ethylene oxychlorination was carried out on the CuCl₂/γ-Al₂O₃ catalyst at the temperature of 473–573 K. It was observed that the reaction rate of ethylene conversion is independent of the partial pressure of C₂H₄ but does depend on the partial pressure of O₂, what is more, the reaction is inhibited by EDC and HCl.

\[ r = \frac{kP_{O₂}}{[1 + AP_{C₂H₄}P_{HCl}]} \]  \hspace{1cm} (15)

The kinetic model suggests the reaction is fully controlled by the CuCl oxidation. Afterward, a great deal of effort has been devoted to the study of the kinetics of the main reaction. The simple power-law model was widely used to correlate the reaction rate and the process variables. It has also proved the very good fitting with analogous experimental results, and the conclusions are summarized in Table 5.

Some rate equations based on the Langmuir–Hinshelwood-Hougen-Watson type were also proposed and summarized in Table 6.

The reported kinetics varies very much. In general, the reaction order for ethylene and HCl is close to 1 and 0, respectively. It is in good agreement with the observation that hydrochlorination is fast and kinetically irrelevant. Thus, the reaction rate is independent of HCl pressure. However, the reaction order to oxygen varied very much between 0 and 1. For the commercial catalysts which are typically promoted by promoters, the reaction order to oxygen is about zero, which possibly pointed out the CuCl₂ reduction by ethylene is the rate-determining step, which is consistent with the experimental observation for K-promoted catalysts as discussed above. The kinetics is also related to the catalyst support. It suggests that the support can change the properties of CuCl₂ catalyst properties, and especially the oxidation of CuCl, which lies well above the discussion of the support effect. It seems that the charcoal facilitates the oxygen activation and CuCl oxidation, leading to a zero-order to oxygen. On some catalysts, the reaction order to oxygen is 1, suggesting adsorption and dissociation of oxygen could become the RDS. Moreover, most of the apparent activation energy on CuCl₂/γ-Al₂O₃ is in the range of 94.7–111.5 kJ/mol. The activation energy for the step of the CuCl₂ reduction step by ethylene was measured to be 37.8 kJ/mol. The value is similar to the one (51.5 kJ/mol) for the reaction with reduction as the RDS. Some rate equations based on the Langmuir–Hinshelwood-Hougen-Watson type were also proposed and summarized in Table 6.

5.2. Kinetics on Byproduct Formation. As known, the selectivity determines the technology and finally affects the economic efficiency of the process. CO₂ is one of the important byproducts formed by deep oxidation from ethylene and EDC in ethylene oxychlorination. It was first established...
that the rate of the deep oxidation reaction increased along with the \( \text{O}_2 \) and \( \text{C}_2\text{H}_4 \) partial pressures and slows upon an increase in the \( \text{HCl} \) partial pressure.\(^{115}\) The rate of the ethylene and EDC oxidation reaction can be written in a general form as\(^{114}\)

\[
r_{\text{CO}_2} = \frac{k \cdot \text{C}_i \cdot \text{O}_2}{1 + k \cdot \text{C}_i + K \cdot \text{C}_{\text{HCl}}}
\]

where \( \text{C}_i \) is the concentration of ethylene or EDC. It is noted that when a catalyst is highly active in the target ethylene oxychlorination reaction (the \( \text{HCl} \) conversion exceeds 99%), the above equation can be simplified as

\[
r_{\text{CO}_2} = \frac{k \cdot \text{C}_i \cdot \text{O}_2}{1 + k \cdot \text{C}_i}
\]

The Arrhenius parameters of \( \text{C}_2\text{H}_4 \) and EDC oxidation reactions within the temperature range of 215–235 °C are expressed as

\[
k_{\text{EDC}} = 5.6 \times 10^9 \exp[-105000/RT]
\]

\[
k_{\text{C}_2\text{H}_4} = 6.3 \times 10^6 \exp[-80500/RT]
\]

It can be easily calculated that at the standard reaction temperature of the ethylene oxychlorination process, the ratio between the rates of EDC and \( \text{C}_2\text{H}_4 \) oxidation is nearly 2:1. Higher temperatures (230–255 °C) favor an increase in the contribution from EDC oxidation to the formation of \( \text{CO}_2 \).

Another type of byproduct is the organochlorine products containing chlorine-substituted \( \text{C}_1 \)–\( \text{C}_2 \) paraffin and olefins, along with some \( \text{O}_2 \)-containing chlorinated hydrocarbons.\(^{114}\) Herein, we will choose a part to show the kinetic study on the byproduct formation.

Ethyl chloride (\( \text{C}_2\text{H}_5\text{Cl} \)) is formed by the ethylene hydrochlorination reaction. It occurs according to an equation of first-order with respect to \( \text{C}_2\text{H}_4 \) and \( \text{HCl} \) and is inhibited by water vapor, following the equation of

\[
r_{\text{C}_2\text{H}_5\text{Cl}} = \frac{k \cdot \text{P}_{\text{C}_2\text{H}_4} \cdot \text{P}_{\text{HCl}}}{1 + \text{K} \cdot \text{H}_2\text{O} \cdot \text{P}_{\text{H}_2\text{O}}}
\]

The equation suggests that the selectivity of ethyl chloride can be minimized by using water vapor as a fluidizing agent instead of \( \text{N}_2 \) in the air process or a recycled gas in the \( \text{O}_2 \) process.

Another important byproduct is VCM (\( \text{C}_2\text{H}_3\text{Cl} \)), formed by dehydrochlorination of EDC. It was reported that the rate of vinyl chloride formation at a relatively lower temperature (200–215 °C) can be described by the first-order equation

\[
r_{\text{VCM}} = k \cdot \text{P}_{\text{EDC}}
\]

When the temperature is raised to 240 °C, some deviation from the linear relationship is observed, probably due to the inhibition by \( \text{HCl} \), which is also one of the products. The rate of the reaction can be formulated in a general form of

\[
r_{\text{VCM}} = \frac{k \cdot \text{P}_{\text{EDC}}}{1 + k \cdot \text{P}_{\text{HCl}}}
\]

To sum up, we have summarized the kinetic study on ethylene oxychlorination on both the product of EDC and several main byproducts, as summarized in Figure 11. It is noteworthy that it is a very complex catalytic reaction involving a number of reactions, like oxychlorination, hydrochlorination, deep oxidation, dehydrochlorination, etc. Enrico and co-workers\(^{131}\) developed a new kinetic model for the ethylene oxychlorination reaction network including nine chemical reactions to describe the evolution of 12 species (including six major byproducts) based on 28 kinetic runs performed over a commercial \( \text{CuCl}_2/\gamma-\text{Al}_2\text{O}_3 \) catalyst in a dedicated tubular flow reactor. The main byproducts are ethyl chloride (\( \text{C}_2\text{H}_5\text{Cl} \)), 1,1,2-trichloroethane (\( \text{C}_2\text{H}_3\text{Cl}_3 \)), chloroform (\( \text{CHCl}_3 \)), carbon tetrachloride (\( \text{CCl}_4 \)), chloroform (\( \text{CHCl}_3 \)), CO, and \( \text{CO}_2 \).

Although numerous studies have been devoted to the kinetic study in ethylene oxychlorination over the \( \text{CuCl}_2/\gamma-\text{Al}_2\text{O}_3 \)-based catalyst, many possible and potential correlations remain open and need to be studied further.

## 6. CONCLUSIONS AND PERSPECTIVE

The balanced VCM process is still the leading-edge technology for PVC production in the world, where ethylene oxychlorination plays a key role in the process. Although the \( \text{CuCl}_2 \)-based catalysts with proper promoters have been commonly used as the industrial catalyst for several decades, formidable challenges remain to be solved regarding the design of more efficient catalysts suppressing Cu volatilization and agglomeration to make more stable catalysts as well as reducing the byproduct formation. Here, the in-depth analysis of the fundamental understanding of the reaction mechanism, ethylene oxychlorination chemistry, materials, and active sites including the interaction of \( \text{CuCl}_2 \) with support and promoters has been conducted.

The yield of products depends on the catalyst properties, feedstocks, reaction conditions, and reactor types such as a fixed-bed or fluidized bed reactor. In the catalytic cycle, three steps are involved: in the reduction step, \( \text{CuCl}_2 \) is reduced by ethylene with EDC formed; in the oxidation step, \( \text{CuCl} \) is oxidized by \( \text{O}_2 \) to \( \text{Cu}_2\text{OCl}_2 \) in the hydrochlorination step, the \( \text{Cu}_2\text{OCl}_2 \) is recovered to \( \text{CuCl}_2 \) by \( \text{HCl} \). The lattice \( \text{Cl} \) vacancy will be filled by oxygen once \( \text{Cl} \) was removed from \( \text{CuCl}_2 \) by attacking of ethylene. At the steady-state operation, the catalyst reduction and oxidation are kinetically balanced to hold the certain distribution of \( \text{CuCl}_2 \) and \( \text{Cl} \) vacancy, and the combined \( \text{CuCl}_2 \) and \( \text{Cl} \) vacancy is the active site. Different from the conventional heterogeneous catalysts, the active sites are highly dynamic, depending on the local chemical atmosphere such as concentrations and temperatures through the kinetic balance. The composition of the active sites is the key to control the activity, selectivity, and stability. The catalyst should be designed to keep as high as possible the \( \text{CuCl}_2 \) and less \( \text{Cl} \) vacancy to suppress the \( \text{Cu} \) loss due to the high volatility of \( \text{CuCl} \) and reduce the \( \text{CO}_2 \) formation catalyzed by \( \text{CuCl} \). The rate-diagram is a powerful tool to predict the reaction rate and \( \text{CuCl}_2 \) concentration at the steady state and
to guide tuning the reduction and oxidation rate to achieve better catalysts. The reduction and oxidation properties of the catalyst can be modified by the catalyst supports and the promoters. The epitaxial growth of the CuCl<sub>2</sub> layer on the supports results in a significant support dependence of the support. New catalyst supports should be explored to manipulate the CuCl<sub>2</sub> properties. γ-Al<sub>2</sub>O<sub>3</sub> is the most commonly used support for an industrial CuCl<sub>2</sub> catalyst, and the properties of γ-Al<sub>2</sub>O<sub>3</sub> can be optimized in terms of exposure of facets such as (111), (100), and (110).

Certain promoters (like K and Cs) can form a complex with CuCl<sub>2</sub> on the support surface, playing a significant role in improving the catalytic performance, which is why we dedicated the majority of this Review to their delineation. The promoter can be categorized into two classes: one leading to a relatively low reaction rate but high CuCl<sub>2</sub> reduction and the CuCl oxidation, leading to a high reaction rate but mediate CuCl<sub>2</sub> concentration. Adding promoters can increase the fraction of the active Cu species, due to the ability of the corresponding cation to compete with CuCl<sub>2</sub> filling in the vacancies of Al<sub>2</sub>O<sub>3</sub>. Continued efforts should be put on the promoter effect in this industrial reaction to further increase the fraction of the active Cu species by enhancing the oxidation of CuCl. Bi- or multipromoters can be designed to enhance the activity, selectivity, and stability. There is a large family expected that can be combined to tune the reduction, oxidation, and hydrochlorination activity, thus compromising the activity and stability at the steady state. More fundamental studies are highly required to understand the interaction of multipromoters with CuCl<sub>2</sub> and gain a better principle for catalyst design to achieve better performance.

Additionally, the process intensification occurs by integrating the current two-step (ethylene oxychlorination to form EDC and EDC dehydrochlorination to produce VCM) into one single step. However, only a few results were reported so far, since the operating conditions vary a great deal for the two reactions (oxychlorination-dehydrochlorination) as we discussed above. The CuCl<sub>2</sub>-based catalyst, commonly used in the industry for ethylene oxychlorination nowadays, cannot meet the requirement for dehydrochlorination at higher temperatures, at which the volatilization of CuCl becomes remarkable, which will further cause the deactivation. Therefore, more efforts can be focused on developing the bifunctional catalysts, which can catalyze the ethylene oxychlorination and EDC dehydrochlorination simultaneously with high energy efficiency. Another process we can put more attention towards is utilizing the ethane oxychlorination to directly produce VCM. Ethane obtained from natural gas is cheap and is almost an inexhaustible resource for the petrochemical industry. Developing an ethane-based technology would be a breakthrough for VCM manufacturing in the future. However, despite its great potential, an ethane-based technology is still under exploration. More efforts can be made to develop better catalysts making this process more efficient.

Catalyst development relies on a better fundamental understanding of the process. It would benefit significantly from the in situ characterization techniques to monitor structure and active site evolution under working conditions, as well as advanced computational tools to further explore reaction dynamics. Detailed kinetic modeling coupling with DFT calculation of the whole catalytic cycle could help provide a deeper understanding of the catalysis and provide a predictive model for kinetics and rational catalyst design. More effort should be devoted to the kinetic study and modeling of the whole catalytic cycle and provide a detailed microkinetic model to predict not only the reaction rates of the formation of the products but also the active site evolution in the redox cycle in chemical reactors. Effective techniques to characterize alumina surface properties will be highly beneficial for controlling the alumina properties and guiding industrial production. Thus, academia should work together with industry to devote more to greatly accelerate the development of ethylene oxychlorination both fundamentally and commercially.

### AUTHOR INFORMATION

**Corresponding Authors**

Kumar R. Rout — Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway; Sintef Industry, N-7491 Trondheim, Norway; Email: kumarranjan.rout@sintef.no

De Chen — Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway; orcid.org/0000-0002-5609-5825; Email: dc.chen@ntnu.no

**Authors**

Hongfei Ma — Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Yalan Wang — Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Yanying Qi — Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c01698

**Author Contributions**

H.M., Y.W., and Y.Q. contributed equally.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors greatly acknowledge the financial support from the center of industrial Catalysis Science and Innovation (iCSI), a center for Research-based Innovation funded by the Research Council of Norway (Grant No. 237922).

**REFERENCES**

1. Lin, R.; Amrute, A. P.; Perez-Ramirez, J. Halogen-Mediated Conversion of Hydrocarbons to Commodities. *Chem. Rev.* 2017, 117, 4182–4247.

2. Davies, C. J.; Miedziak, P. J.; Brett, G. L.; Hutchings, G. J. Vinyl Chloride Monomer Production Catalysed by Gold: A Review. *Chin. J. Catal* 2016, 37, 1600–1607.

3. Global Production Capacity of Vinyl Chloride Monomer 2018 & 2023. Published by M. Garside. https://www.statista.com/statistics/1083677/global-vinyl-chloride-monomer-production-capacity/ (accessed 2019-11-06).

4. Hutchings, G. J.; Kieley, C. J. Strategies for the Synthesis of Supported Gold Palladium Nanoparticles with Controlled Morphology and Composition. *Acc. Chem. Res.* 2013, 46, 1759–1772.

5. Xu, H.; Luo, G. H. Green Production of PVC From Laboratory to Industrialization: State-of-the-art Review of Heterogeneous Non-
(31) Higham, M. D.; Scharf, M.; Capdevila-Cortada, M.; Perez-Ramirez, J.; Lopez, N. Mechanism of Ethylene Oxochlorination over Ruthenium Oxide. J. Catal. 2017, 353, 171–180.
(32) Jones, M. E.; Olken, M. M.; Hickman, D. A. Process for the Conversion of Ethylene to Vinyl Chloride and Novel Catalyst Compositions Useful for Such Process. US Patent, US9690924B1, 2005.
(33) Scharf, M.; Lira-Parada, P. A.; Amrute, A. P.; Mitchell, S.; Perez-Ramirez, J. Lanthanide Compounds as Catalysts for the One-Step Synthesis of Vinyl Chloride from Ethylene. J. Catal. 2016, 344, 524–534.
(34) Scharf, M.; Capdevila-Cortada, M.; Kondratenko, V. A.; Kondratenko, E. V.; Colussi, S.; Trovarelli, A.; Lopez, N.; Perez-Ramirez, J. Mechanism of Ethylene Oxochlorination on Ceria. ACS Catal. 2018, 8, 2651–2663.
(35) Gianolio, D.; Muddada, N. B.; Olksbe, U.; Lambert, C. Doped-CuCl2/Al2O3 Catalysts for Ethylene Oxochlorination: Influence of Additives on the Nature of Active Phase and Reducibility. Nucl. Instrum. Methods Phys. Res., Sect. B 2012, 284, 53–57.
(36) Lambert, C.; Prestipino, C.; Bonino, F.; Capello, L.; Bordiga, S.; Spoto, G.; Zecchina, A.; Moreno, S. D.; Cremaschi, B.; Garilli, M.; Mantovani, A.; Carmello, D.; Vidotto, S.; Leofanti, G. The Chemistry of the Oxochlorination Catalyst: an in situ, Time-resolved XANES Study. Angew. Chem., Int. Ed. 2002, 41, 2341–2344.
(37) Leofanti, G.; Padovan, M.; Garilli, M.; Carmello, D.; Marra, G. L.; Zecchina, A.; Spoto, G.; Bordiga, S.; Lambert, C. Alumina-supported Copper Chloride 2. Effect of Aging and Thermal Treatments. J. Catal. 2000, 189, 105–116.
(38) Leofanti, G.; Padovan, M.; Garilli, M.; Carmello, D.; Zecchina, A.; Spoto, G.; Bordiga, S.; Palmino, G. T.; Lambert, C. Alumina-supported Copper Chloride 1. Characterization of Freshly Prepared Catalyst. J. Catal. 2000, 189, 91–104.
(39) Louwerse, M. J.; Rothenberg, G. Modeling Catalyst Preparation: The Structure of Impregnated–Dried Copper Chloride on γ-Alumina at Low Loadings. ACS Catal. 2013, 3, 1545–1554.
(40) Muddada, N. B.; Olksby, U.; Caccialupi, L.; Cavani, F.; Leofanti, G.; Gianolio, D.; Bordiga, S.; Lambert, C. Influence of Additives in Defining the Active Phase of The Ethylene Oxochlorination Catalyst. Phys. Chem. Chem. Phys. 2010, 12, 5605–5618.
(41) Garcia, C. L.; Resasco, D. E. Effects of the Support and The Addition of a Second Promoter on Potassium Chloride-Copper (II) Chloride Catalysts Used in the Oxochlorination of Methane. Appl. Catal. 1989, 46, 251–267.
(42) Leofanti, G.; Marsella, A.; Cremaschi, B.; Garilli, M.; Zecchina, A.; Spoto, G.; Bordiga, S.; Fiscaro, P.; Prestipino, C.; Villain, F.; Lambert, C. Alumina-supported Copper Chloride 4. Effect of Exposure to O2 and HCl. J. Catal. 2002, 205, 375–381.
(43) Neurock, M.; Zhang, X. Y.; Olken, M. J.; Jones, M.; Hickman, D.; Calverley, T.; Gulotty, R. A. First-Principle Analysis of Ethylene Chemisorption on Copper Chloride Clusters. J. Phys. Chem. B 2001, 105, 1562–1572.
(44) Qi, Y.; Fenex, E.; Ma, H.; Wang, Y.; Rout, K. R.; Fuglerud, T.; Piccinini, M.; Chen, D. Origin of Potassium Promotion Effects on CuCl2/γ-Al2O3 Catalyzed Ethylene Oxochlorination. Appl. Surf. Sci. 2020, 521, 146310.
(45) Qi, Y.; Fenex, E.; Ma, H.; Wang, Y.; Rout, K. R.; Fuglerud, T.; Piccinini, M.; Chen, D. Cluster-Size-Dependent Interaction between Ethylene and CuCl2, Clusters Supported via γ-Alumina. J. Phys. Chem. C 2020, 124, 10430–10440.
(46) Hammer, R. R.; Gregory, N. W. Vaporization Reactions in the Copper Chloride-Chlorine System. J. Phys. Chem. 1964, 68, 3229–3233.
(47) Rout, K. R.; Baidoo, M. F.; Fenex, E.; Zhu, J.; Fuglerud, T.; Chen, D. Understanding of Potassium Promoter Effects on Oxochlorination of Ethylene by Operating Spatial-time Resolved UV-vis-NIR Spectrometry. J. Catal. 2017, 352, 218–228.
(48) Rout, K. R.; Fenex, E.; Baidoo, M. F.; Abdollahi, R.; Fuglerud, T.; Chen, D. Highly Active and Stable CeO2-Promoted CuCl2/Al2O3 Catalysts.
Catalysts for the Oxychlorination of Ethylene.

Oxyhydrochlorination Catalysts on Alumina.

Segregation of Active Species During Heating/cooling Cycles.

Catalysts for the Oxychlorination of Ethylene.

Phase by Interaction with the Support in CuCl2 Oxychlorination Catalysts: Role of LaCl3 as an Inhibitor of the Characterization of CuCl2/PdCl2/activated Carbon Catalysts for the Synthesis of Diethyl Carbonate. Energy Fuels 2002, 16, 182–188.

SEGARIA, C. L.; Resasco, D. E. High-temperature Oxychlorination Catalysts: Role of LaCl3 as an Inhibitor of the Segregation of Active Species During Heating/cooling Cycles. J. Catal. 1990, 122, 151–165.

Zipelli, C.; Bart, J.; Petroini, G.; Galvagno, S.; Cimino, C. Study of CuCl2 Supported on SiO2 and Al2O3. Z. Anorg. Allg. Chem. 1985, 520, 199–208.

Wolf, F.; Kreiissl, S.; Sonntag, O. Oxidation of Ethylene. Chemische Technik 1973, 25, 156–158.

Rouco, J. A. Low-temperature Ethylene Oxyhydrochlorination: Effects of Supports and Promoters on The Mobilities of Active Species in CuCl2 Catalysts. J. Catal. 1995, 157, 380–387.

Forni, E.; Garcia, C.; Resasco, D. Stabilization of the Active Phase by Interaction with the Support in CuCl2 Oxychlorination Catalysts. J. Catal. 1986, 99, 12–18.

Pieters, W. J. M.; Conner, W. C.; Carlson, E. J. The Oxyhydrochlorination of Methane on Fumed Silica-based Cu1-xKx Catalysts. J. Catal. 1984, 11, 35–48.

Dotson, R. L. Selected Properties and Electronic Spectra for A Series of Copper (II) Alkali, Alkaline Earth, and Lanthanide Metal Chloride Oxyhydrochlorination Catalysts on Alumina. J. Catal. 1974, 33, 210–218.

Vajglowa, Z.; Kumar, N.; Eranon, K.; Tokarev, A.; Peurla, M.; Peltonen, J.; Murzin, D. Y.; Salminen, T. Influence of the Support of Copper Catalysts on Activity and 1,2-Dichloroethane Selectivity in Ethylene Oxychlorination. Appl. Catal., A 2018, 556, 41–51.

Stiles, A. B. Catalyst Supports and Supported Catalysts; Butterworth: Boston, 1987; Chapter 5.

Deacon, H. Manufacture of Chlorine. US Patent, US85370, 1868.

Deacon, H. Improvement in the Manufacture of Chlorine. US Patent, US118209, 1871.

Ernst, O.; Wahl, H. D. E. Patent, 486952, 1929.

Carrubba, R. V.; Spencer, J. L. Kinetics of Oxychlorination of Ethylene. Ind. Eng. Chem. Process Des. Dev. 1970, 9, 414–419.

Leofanti, G.; Marsella, A.; Cremaschi, B.; Garrili, M.; Zecchina, A.; Spoto, G.; Bordiga, S.; Fisicaro, P.; Berlier, G.; Prestipino, C.; Casali, G.; Lamberti, C. Alumina-supported Copper Chloride 3. Effect of Exposure to Ethylene. J. Catal. 2001, 202, 279–295.

Baidoo, M. F.; Fenes, E.; Rout, K. R.; Fuglerud, T.; Chen, D. On the Effects of K and La Co-promotion on CuCl2/γ-Al2O3 Catalysts for the Oxychlorination of Ethylene. Catal. Today 2018, 299, 164–171.

Weckhuysen, B. M. Determining the Active Site in A Catalytic Process: Operando Spectroscopy Is More Than A Buzzword. Phys. Chem. Chem. Phys. 2003, 5, 4351–4360.

Loos, M.; Goulon, J.; Bertiucci, M.; Bachelard, R. Structural Studies Using XAS of the Active Species Catalysing the Oxychlorination of Ethylene - II. Phys. B 1989, 158, 188–190.

Prestipino, C.; Bordiga, S.; Lamberti, C.; Vidotto, S.; Garrili, M.; Cremaschi, B.; Marsella, A.; Leofanti, G.; Fisicaro, P.; Spoto, G. Structural Determination of Copper Species on the Alumina-Supported Copper Chloride Catalyst: A Detailed EXAFS Study. J. Phys. Chem. B 2003, 107, 5022–5030.

Muddada, N. B.; Olsbye, U.; Leofanti, G.; Gianolio, D.; Bonino, F.; Bordiga, S.; Fuglerud, T.; Vidotto, S.; Marsella, A.; Lamberti, C. Quantification of Copper Phases, Their Reducibility and Dispersion in Doped-CuCl2/Al2O3 Catalysts for Ethylene Oxychlorination. Dalton Trans. 2010, 39, 8437–8449.

Finocchio, E.; Rossi, N.; Busca, G.; Padovan, M.; Leofanti, G.; Cremaschi, B.; Marsella, A.; Carmelo, D. Characterization and Catalytic Activity of CuCl2-γ-Al2O3 Ethylene Oxychlorination Catalysts. J. Catal. 1998, 179, 606–618.

Xie, Y.; Tang, Y. Q. Spontaneous Monolayer Dispersion of Oxides and Salts onto Surfaces of Supports: Applications to Heterogeneous Catalysis. Advances in Catalysis; Elsevier: 1990; Vol. 37, pp 1–43, DOI: 10.1016/S0065-3028(01)80052-6.

Xie, Y.; Zhang, H.Z.; Wang, R. Kinetic Behaviour and Mechanism of Oxychlorination Catalyst. Science China Mathematics 1980, 23, 979–991.

Muddada, N. B.; Olsbye, U.; Fuglerud, T.; Vidotto, S.; Marsella, A.; Bordiga, S.; Gianolio, D.; Leofanti, G.; Lamberti, C. The Role of Chlorine and Additives on the Density and Strength of Lewis and Bronsted Acidity Sites of gamma-Al2O3. Support Used in Oxychlorination Catalysis: A FTIR Study. J. Catal. 2011, 284, 236–246.

Muddada, N. B.; Fuglerud, T.; Lamberti, C.; Olsbye, U. Tuning the Activity and Selectivity of CuCl2/γ-Al2O3 Ethene Oxychlorination Catalyst by Selective Promotion. Top. Catal. 2014, 57, 741–756.

Baidoo, M. F. Ethylene Oxychlorination on CuCl2-based Oxychlorination Catalyst: Operando Kinetic Studies. Doctoral Thesis, Norwegian University of Science and Technology, Norway, 2019.

Podkolzin, S. G.; Stanigel, E. E.; Jones, M. E.; Peringer, E.; Lercher, J. A. Methyl Chloride Production from Methane over Lanthanum-based Catalysts. J. Am. Chem. Soc. 2007, 129, 2569–2576.

Zhao, C.; Minhas, H.; Dezehng, W.; Wei, W. Influence of Cerium on the Stability of Copper-based Oxychlorination Catalyst. Chin. J. Catal. 2008, 29, 951–953.

Li, C.; Zhou, G. D.; Wang, L. P.; Li, Z.; Xue, Y. X.; Cheng, T. X. Effect of Impregnation Procedure of La2O3 Precursor on Copper-based Catalysts for Ethene Oxychlorination. Catal. Commun. 2011, 13, 22–25.

Eden, J. S.; Cowfer, J. A. Catalyst and Process for the Fluid-bed Oxychlorination of Ethylene to EDC. US Patent, US4849393, 1989.

Hirschmann, R. P.; Beard, W. O., Jr.; Mainz, E. L.; Smith, E. B.; Little, B. M. Oxychlorination Catalyst Compositions and Process of Making Same. US Patent, US598878A 199, 1992.

Mainz, E. L.; Beard, W. Q., Jr.; Hirschmann, R. P.; Little, B. M.; Smith, E. B. Oxychlorination Process Using a Catalyst Which Comprises Copper Chloride Supported on Rare-Earth Modified Alumina. US Patent, US1153072A, 1992.

Mainz, E. L.; Beard, W. Q., Jr.; Hirschmann, R. P.; Little, B. M.; Smith, E. B. Oxychlorination Catalysts Comprising Copper Chloride Supported on Rare-Earth-Modified Alumina, Process for Making Such Catalysts, and Oxycchlorination Processes Using Them. US Patent, US5192733A, 1993.

Carmelo, D.; Fatutto, P.; Marsella, A. Oxychlorination of Ethylene in Two Stage Fixed-bed Reactor. US Patent, US5841009A, 1998.

Schussler, H. W., III Oxychlorination Catalyst. US Patent, US6748343, 2001.

Marsella, A.; Fatutto, P.; Carmelo, D. Catalyst and Oxychlorination Process Using It. US Patent, US6465701, 2002.

Marsella, A.; Vidotto, S.; Cremaschi, B. Hollow Pellet Suitable as Carrier of Catalysts for Selective Exothermic Reactions. US Patent, US7141708B2, 2006.

Strebelle, M.; Petitjean, A. Oxychlorination Catalyst and Process Using Such a Catalyst. US Patent, US7870640B2, 2010.

Orsenigo, C.; Casagrande, F.; Civati, M. Catalysts for Fixed Bed Oxychlorination of Ethylene to 1,2-Dichloroethane. US Patent, US821690B2, 2012.
(92) Zurowski, K. DTA analysis of the System Carrier-CuCl₂, KCl. J. Therm. Anal. 1990, 36, 947–955.
(93) de Miguel, S. R.; Scelza, O. A.; Castro, A. A.; Soria, J. Characterization of γ-alumina Doped with Li and K by Infrared Studies of CO Adsorption and 27 Al-NMR. Top. Catal. 1994, 1, 87–94.
(94) Żurowski, K. Some Aspects of the Phase Changes of the CuCl₂―KCl System. J. Therm. Anal. 1995, 44, 197–204.
(95) Liu, J.; Xueju, L.; Zhou, G.; Zhen, K.; Zhang, W.; Cheng, T. Effect of KCl on CuCl₂/γ-Al₂O₃ Catalyst for Oxychlorination of Ethane. React. Kinet. Catal. Lett. 2006, 88, 315–324.
(96) Kosaka, Y.; Hayata, M.; Toyo Soda Co, Y. J. Oxychlorination of Hydrocarbons. I. Synthesis of 1,2-Dichloroethane by Oxychlorination of Ethylene Using a NaHSO₄-NH₄HSO₄-CuCl₂ catalyst. Kagyo Kagaku Zasshi 1966, 69, 244–248.
(97) García, C. L.; Resasco, D. E. Promotion of KCl on CuCl₂/SiO₂ Catalysts Used for the Oxyhydrochlorination of Methane. Appl. Catal. 1987, 29, 55–66.
(98) Zurowski, K. The Mechanism of the Ethene Oxychlorination Process when CuCl₂-KCl-Support Catalyst is Used. Polym. J. Chem. 1995, 69, 1718–1728.
(99) Repelevich, M. Activity of Cupric Chloride-Potassium Chloride-Carrier Catalysts in Oxidation and Oxychlorination of Ethylene. Polym. J. Appl. Chem. 1992, 36, 177–182.
(100) Prasad, P. S. S.; Rao, P. K. Low-temperature Ethylene Chemisorption (LTEL) a Novel Technique for the Characterization of CuCl₂-KCl gamma-Al₂O₃ Oxychlorination Catalysts. J. Chem. Soc., Chem. Commun. 1987, 951–953.
(101) Carmello, D.; Garilli, M.; Fatutto, P.; Caccialupi, L. Catalyst, Process for Its Preparation, and Its Use in the Synthesis of 1,2-Dichloroethane. US Patent US6777373B1, 2004.
(102) Orsenigo, C.; Casagrande, F.; Civati, M. Catalysts for Fixed Bed Oxycarbonation of Ethylene to 1,2-Dichloroethane. US Patent US8816960B2, 2010.
(103) Xueju, L.; Jie, L.; Guangdong, Z.; Kaji, Z.; Weiming, L.; Tiexin, C. Ethane Oxychlorination’ over gamma-Al₂O₃ Supported CuCl₂-CoKCl-CoLaCl₃. Catal. Lett. 2005, 100, 153–159.
(104) Little, J. A.; Kenney, C. N. A Microstructural Study of a Supported Liquid Phase Oxychlorination Catalyst. J. Catal. 1985, 93, 23–29.
(105) Villadsen, J.; Livejerg, H. Supported Liquid-Phase Catalysts. Catal. Rev.: Sci. Eng. 1978, 17, 203–272.
(106) Li, C.; Zhou, G.; Wang, L.; Dong, S.; Li, J.; Cheng, T. Effect of Ceria on the MgO-γ-Al₂O₃ Supported CeO₂/CuCl₂/KCl Catalysts for Ethane Oxychlorination. Appl. Catal., A 2011, 400, 104–110.
(107) Cavalli, L.; Rubini, C. Catalysts for the Oxychlorination of Ethylene, Method for Preparing Them, and Oxychlorination Method Using the Same. US Patent, US5905054A, 1999.
(108) Eden, J. S. Copper Catalyst Compositions for Fluid-bed Oxyhydrochlorination of Ethylene. US Patent, US4446249A, 1984.
(109) Derleth, H.; Adem, D.; Strebelle, M. Catalytic Composition and Process for the Oxychlorination of Ethylene Using Such a Composition. US Patent, US6803342B1, 2004.
(110) Eichhorn, H. D.; Mross, W. D.; Schachner, H.; Schwarzmann, M. Molded Supported Catalyst. US Patent, US4753914A, 1988.
(111) Ma, H.; Fenes, E.; Qh, Y.; Wang, Y.; Rout, K. R.; Flugertud, T.; Chen, D. Understanding of K and Mg Co-promoter Effect in Ethylene Oxychlorination by Operando UV-vis-NIR Spectroscopy. Catal. Today 2020, DOI: 10.1016/j.cattod.2020.06.049.
(112) Kuhrs, C.; Meissner, R. Catalyst Composition for Oxychlorination. US Patent, US7126035B2, 2006.
(113) Heinemann, H.; Spector, M. L.; Wender, L.; Yearz, J. C.; Kellogg Co, M. W.; P. N. J. U. S. A. Oxychlorination of Ethylene by Homogeneous Catalysis. Erdcel Kohle 1967, 20, 400–404.
(114) Flid, M. R. Problems of Increase in the Selectivity of Ethylene Oxychlorination Processes: II. General Patterns in the Formation of Chloroorganic Byproducts in the Ethylene Oxychlorination Process. Catal. Ind. 2016, 8, 23–31.