Kinetic modeling of dynamic changing active sites in a Mars-van Krevelen type reaction: Ethylene oxychlorination on K-doped CuCl$_2$/Al$_2$O$_3$

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A kinetic model was developed by taking into account the dynamic nature of the active sites in Mars–van Krevelen type catalytic reactions to predict the evolution of the reactant and product composition in the gas phase and the CuCl$_2$ concentration in the solid catalyst. The kinetic model at the steady-state of ethylene oxychlorination was obtained by combining transient experiments of the two half-reactions in the redox cycle, namely CuCl$_2$ reduced to CuCl by ethylene and CuCl oxidation by oxygen on the K-promoted CuCl$_2$/γ-Al$_2$O$_3$ catalyst. The dynamic transitions between CuCl$_2$ and CuCl of the active sites during the reactions are also modeled, and the contributions of two active sites, namely Cu coordination numbers of 4 and 3 in CuCl$_2$ were distinguished and included in the kinetic model. The kinetic models describe well the transient response of the reduction and oxidation steps as well as the reaction at the steady-state at different reaction conditions. Moreover, by combining the reactor modeling through a steady-state approach, the spatial-time resolved CuCl$_2$ profile and the CuH$_2$ reaction rate can be well predicted in comparison with the experimental results. The approach of both transient and steady-state kinetic modeling and simulation is supposed to have general relevance for a better understanding of Mars–van Krevelen type reactions.

1. Introduction

The oxidation reaction is one of the most common and significant catalytic processes in the field of heterogeneous catalysis [1,2]. From the view of fundamental research, it is a good type of probe reaction to perform the reaction mechanism studies. On the other hand, in the view of industrial, many commercial catalytic processes are related to redox reactions, like NH$_3$-SCR, NO oxidation, ethylene oxychlorination, etc. [3–6], a better understanding of the mechanism in the process can further improve the catalytic performance, which is closely related to costs and profits. All these reactions involve redox cycles where both reactants and catalyst undergo electron-transfer reactions through reduction and oxidation. For the oxidation reaction, the main reaction mechanism is the Mars–van Krevelen (MvK) mechanism [1,3–7], which besides the Langmuir–Hinselwood (LH) and the Eley–Rideal (ER) mechanism are the most classical reaction mechanisms in heterogeneous catalysis [12,13]. In brief, the redox catalytic cycles can be simplified as Eqs. (1) and (2):

\[
\text{[CatO]} + \text{R} \rightarrow \text{RC} \rightarrow \text{O} + \text{[Cat]} \quad (1)
\]

\[
\text{[Cat]} + 0.5\text{O}_2 \rightarrow \text{[CatO]} \quad (2)
\]

where [CatO] represents the oxidized catalyst surface and [Cat] is the reduced state. In a typical oxidation reaction, different states exist on the surface, the oxidized and free centers, as well as the adsorbed centers where the reactants and (or) products can be adsorbed. The characteristic feature of the MvK mechanism is that at least one component of the catalyst participates in the reaction of product formation, eventually making the components on the catalyst surface part of the reaction products [8,12]. In this mechanism, part of the catalyst surface is an active part and partakes in the reaction, one reactant forms a chemical bond with the surface, forming a thin layer of the metal–reactant bond [12]. The chemical state of the metal on the catalyst can be regenerated.
### Nomenclature

#### List of Latin Symbols

| Symbol | Description |
|--------|-------------|
| A | Arrhenius frequency factor $g_{\text{Cu}} \text{ mol}^{-1} \text{ atm}^{-1} \text{ s}^{-1}$ |
| C | Concentration $\text{ mol L}^{-1}$ |
| $C_p$ | Mass-based heat capacity $\text{ J kg}^{-1} \text{ K}^{-1}$ |
| $C_{\text{Cl}}$ | Cl concentration mol/$g_{\text{Cu}}$ |
| $C_{\text{Cl}^+}$ | Concentration at which 4-coordinated Cu was completely converted mol/$g_{\text{Cu}}$ |
| $C_{\text{Cl}^{**}}$ | Concentration at which the 3-coordinated Cu starts to form mol/$g_{\text{Cu}}$ |
| $C_{\text{CuCl}}$ | CuCl concentration mol/$g_{\text{Cu}}$ |
| $C_{\text{CuCl}^+}$ | The point of $C_{\text{CuCl}^+}$ represents 2-coordinated Cu does not exist mol/$g_{\text{Cu}}$ |
| $C_{\text{CuCl}^{**}}$ | The starting point where the 2- and 3-coordinated Cu occur mol/$g_{\text{Cu}}$ |
| $C_{\text{CuCl}_2}$ | Reducible CuCl$_2$ concentration mol/molCu |
| $C_{\text{CuCl}_{\text{max}}}$ | Maximum concentration of CuCl mol/molCu |
| d | Diameter m |
| d$_s$ | The diameter of a sphere with the same surface to volume ratio as the particle |
| d$_p$ | The diameter of a sphere with the same volume as the particle m |
| D$_{AB}$ | Molecular diffusivity for A in a binary mixture of A and B m$^2$ s$^{-1}$ |
| D | Diffusion coefficient m$^2$ s$^{-1}$ |
| $E_A$ | Activation energy kJ mol$^{-1}$ |
| f | Friction factor – |
| $j_A$ | Diffusive mass flux of species A $\text{ kg m}^{-1} \text{ s}^{-1}$ |
| k | Reaction rate constant dep. |
| $K_{\text{eq}}$ | O$_2$ Adsorption equilibrium constant atm$^{-1}$ |
| m | Mass kg (or g) |
| n | Overall reaction order – |
| N | Molar quantity mol |
| p | Pressure Pa (or atm) |
| P | The emissivity of the catalyst particle – |
| $P_e$ | Peclet number – |
| $P_r$ | Prandtl number – |
| q | Heat flux W m$^{-2}$ |
| Q | Radiations heat flux W m$^{-2}$ |
| r | Radial coordinate m |
| $r_p$ | Radius of pellet m |
| R | The total volume-based reaction rate mol m$^{-3}$ s$^{-1}$ |
| Re | Reynold number – |
| $R_e$ | Gas constant $\text{J K}^{-1} \text{ mol}^{-1}$ |
| s | Scalar – |
| Sc | Schmidt number – |
| Sp | Fractional selectivity – |
| t | Time s |
| T | Temperature K |
| u | Superficial velocity m s$^{-1}$ |
| U | Overall heat transfer coefficient W m$^{-2}$ K$^{-1}$ |
| V | Volume m$^3$ |
| F | Volumetric flow rate ml/min |
| $\omega$ | Weighting factor – |
| X | Conversion % |
| z | Axial coordinate m |
| y | Molar ratio – |

#### Greek Symbols

| Symbol | Description |
|--------|-------------|
| $\alpha$ | Heat transfer coefficient W m$^{-2}$ K$^{-1}$ |
| $\beta$ | Coefficient depending on the particle geometry and packing density – |
| $\epsilon$ | Void fraction – |
| $\Delta \mu$ | Heat of reaction kJ mol$^{-1}$ |
| $\Delta G'$ | Gibbs free energy kJ mol$^{-1}$ |
| $\Delta P$ | Pressure drop bar |
| $\lambda$ | Thermal conductivity W m$^{-1}$ K$^{-1}$ |
| $\mu$ | Dynamic gas viscosity kg s$^{-1}$ m$^{-1}$ |
| $\mu_j$ | The chemical potential of species j – |
| $\upsilon$ | Stoichiometric coefficient – |
| $\omega$ | Mass fraction – |
| $\phi$ | Thiele modulus – |
| $\rho$ | Total density kg m$^{-3}$ |
| $\tau$ | Space-time/shear stress s Pa$^{-1}$ |
| $\theta$ | Angular coordinate |
| $\theta^*$ | The fraction of empty active sites – |
| $\theta$ | Coverage – |
| $\xi$ | Extent of reaction mol |

#### Subscripts

| Symbol | Description |
|--------|-------------|
| * | Adsorbed |
| + | Forward |
| – | Backward |
| A, B, C, D | Chemical compound |
| atm | Atmosphere |
| cal | Calculated |
| cat | Catalyst |
| eff | Effective |
| er | Effective radial |
| exp | Experimental |
| g | Gas |
| i | Inner |
| in | Initial/reactor inlet |
| o | Outlet |
| obs | Observation |
| out | Outside tube |
| par | Parameter |
| r | Radial coordinate |
| ref | Reference |
| s | The surface of the catalyst |
| sp | Specific |
| ss | Steady-state |
| v | Volume-based |
| w | Tube wall |
| 0 | Initial |

#### Abbreviations and acronyms

- BET: Brunauer–Emmett–Teller
- BJH: Barrett–Joyner–Halenda
- CN: Coordination number
- EDC: Ethylene dichloride
- ER: Eley–Rideal
- ICP-OES: Inductively coupled plasma optical-emission spectrometry
- KFM: Kubelka–Munk Function
- LH: Langmuir–Hinshelwood
- MS: Mass spectroscopy
- MvK: Mars–van Krevelen
- TPO: Temperature-programmed oxidation
- TPR: Temperature-programmed reduction
- UV–vis-NIR: Ultraviolet–visible and near-infrared spectroscopy
- VCM: Vinyl chloride monomer
- XRD: X-ray diffraction
by reacting with another reactant (s). The oxidation state of the catalysts and amount of vacancy (like O) can also affect the activity, selectivity, and stability. Many redox reactions involving C, Cl, N, and S follow a similar simplified mechanism on metal carbides, chlorides, nitrides, and sulfides [8]. These lattice components (O, S, Cl, H) participate in the formation of products lead to a reaction of the catalytic activity. The active sites and the oxidation states are entirely dynamic and depending on the relative re-reduction and re-oxidation rates. And based on the fractional coverages, the surface state can be well described. However, due to the importance of redox reactions, an efficient method for predicting and controlling the catalytic cycles is still highly needed.

Ethylene oxychlorination (Eq. (3)) is the most important process to produce ethylene dichloride (C₂H₄Cl₂, EDC), the key intermediate used to produce vinyl chloride monomer (VCM) [5,14–22]. It was commonly reported that the ethylene oxychlorination reaction is catalyzed by a promoted CuCl₂/γ-Al₂O₃-based catalyst, and following the MvK mechanism, involving the reduction, oxidation, and hydrochlorination steps (Eqs. (4)–(6)) [14,15,23–33].

\[
\begin{align*}
\text{Total reaction:} & \quad \text{C}_2\text{H}_4 + 0.5\text{O}_2 + 2\text{HCl} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{H}_2\text{O} \quad (3) \\
\text{Reduction:} & \quad 2\text{CuCl}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + 2\text{CuCl} \quad (4) \\
\text{Oxidation:} & \quad 2\text{CuCl} + 0.5\text{O}_2 \rightarrow \text{CuOCl}_2 \quad (5) \\
\text{Hydrochlorination:} & \quad \text{Cu}_2\text{OCl}_2 + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O} \quad (6)
\end{align*}
\]

From the reaction mechanism, the chemical state of Cu transfers among CuCl₂, CuOCl₂, and CuCl, and Cl is extracted by C₂H₄ with EDC formed as the product in the half-reaction and leaving Cl vacancy on the catalyst. The oxidation and hydrochlorination steps are dedicated to the regeneration of CuCl to CuCl₂. The oxidation state of Cu in the catalytic cycle at the steady-state reaction depends on the kinetic balance of the reduction, oxidation, and hydrochlorination steps. Based on the mechanism, CuCl is involved in the reaction cycle. However, it can be well known that the sublimation and aggregation of CuCl remain the commercial catalyst’s challenges. Controlling CuCl concentration sufficiently low at the steady-state conditions is an efficient way to improve the stability of CuCl₂/Al₂O₃-based oxychlorination catalysts. Recently we systematically studied the mechanism of the catalytic cycle of ethylene oxychlorination on CuCl₂/Al₂O₃-based catalysts employing the operando Ultraviolet-visible and near-infrared spectroscopy (UV–vis-NIR) and monitored the CuCl₂ and CuCl evolution during the reaction [25,32,34]. It demonstrated that the oxidation state of Cu or Cl vacancy is highly dynamic, and changes with operating conditions and CuCl which no absorption can be observed for CuCl in the near-infrared manner, while the probe kept fixed. More information about the setup and the experiments were on the home-made operando fixed bed reactors (with the cross-section size of 5 mm × 10 mm) combined with MS (Omnistar GSD 3010; Pfeiffer Vacuum, Germany) and UV–vis-NIR spectroscopy (Availight-DHS, Avantes) with a scanning circular area with a radius of 1 mm from the top of the catalyst bed at the gas inlet direction. The spatial distribution of CuCl₂ was measured by scanning along the catalyst bed where the reactor was moved in a controlled manner, while the probe kept fixed. More information about the setup can be obtained from our previous reports [32]. CuCl₂ concentration profile can be obtained from the d-d transition bands [25,32,34], in which no absorption can be observed for CuCl in the near-infrared range.
region. The CuCl₂ concentration can be quantified by the normalized Kubelka–Munk function with the obtained calibration curve.

Reactant gases were introduced into the reactor step-by-step with specified mass flow controllers. The catalyst was heated to the target reaction temperature in Ar with a ramping rate of 10 K/min, followed by activation with HCl to remove the paratacamite (Cu₂(OH)₃Cl) formed due to store in the atmosphere. The reduction and oxidation experiments were performed by introducing C₂H₄ and O₂ separately with the desired partial pressures with Ar served as the diluted gas and He as the tracer gas. The effluent gas was flowed to an online MS, with the UV–vis-NIR probing the top of the catalyst bed. Between the reduction and reaction steps, Ar was flowed for at least 15 min to purge out the rest of C₂H₄ or O₂, which was left by the former step. Followed by flowing HCl for 4 min for the hydrochlorination step as the closure of the first cycle. The first and second cycles were used to fully activate the catalyst, the data got from the third cycle was used to perform the kinetic analysis. The method for calculating the reaction rate and removable Cl was reported in our previous reports [25,32]. Herein, the Gaussian multi-peak method was employed for deconvolution in the software of Origin.

2.4. Steady-state experiments

During the steady-state experiments, all the reactant gases, C₂H₄, O₂, and HCl were co-fed into the reactor with the required reactant gas molar ratio at the reaction temperature of 503 K. Two reaction conditions, with different reactant gas molar ratios and space velocities, were employed, one is stoichiometric (2:1:4), one is excess O₂ (1:2:2). The effluent gas stream was analyzed by MS and the UV–vis-NIR probe recording at the top of the catalyst bed. After reaching the steady-state, the probe of the UV–vis-NIR was moved along the catalyst bed to scan the catalyst for analysis of the CuCl₂ distribution.

The plug flow condition, pressure drop of the laboratory reactor, possible external and internal mass, and heat transport limitations at the reaction conditions were evaluated by a Eurokin fixed bed tool [44]. The results suggest that the kinetic studies at the conditions were limited by external and internal limitations, and the pressure drop can be ignored. The details can be seen in the S1 of the Supporting information.

2.5. Reactor models

The laboratory fixed-bed quartz reactor is simulated by using a dynamic 1D pseudo-homogeneous model. There are two independent variables: z and t, the following assumptions have been incorporated in the development of the mathematical model (Table 1) [45],

(a) Temperature gradients between the catalyst bed and the fluid are small.
(b) Negligible changes of concentration and temperature gradients in the radial direction are assumed.
(c) The operation is isothermal.
(d) Diffusion along the axial direction is negligible compared to the convection.
(e) The average molecular mass of the reactants and products is constant along the axial direction.

(f) Pressure, density, and velocity of the gases in the system are assumed to be constant with time.

2.5.1. Initial and boundary conditions

The model equations can only be solved with appropriate initial and boundary conditions. The conditions for the dynamic model are listed below:

Initial conditions (t = 0):
Initially, it is assumed that the reactor is filled with a stagnant gas mixture with a given composition, pressure, and copper coordination (for all z)

\[
\rho = \rho_0; \quad u = u_0; \quad p = p_0; \quad T = T_0; \quad \omega_A = \omega_{A,0}; \quad C_{\text{CuCl}_2} = C_{\text{CuCl}_2, \text{max}}
\] (10)

Boundary conditions (t > 0):

\[
\rho = \rho_0; \quad u = u_0; \quad p = p_0; \quad T = T_0; \quad \omega_A = \omega_{A,0}
\] (11)

2.6. Temperature programmed reduction and oxidation

Ethylene temperature-programmed reduction (C₂H₄-TPR) was performed on the same fixed bed reactor and setup with MS recording the EDC signal. Before the TPR experiment, the catalyst was treated with two redox cycles as mentioned above to make sure the catalyst was fully oxidized to CuCl₂. Once a stable MS baseline was obtained at room temperature, the catalyst was reduced by 30% C₂H₄ in Ar with a flow rate of 120 ml/min, and at a ramping rate of 2 K/min to 503 K. The product EDC was recorded by an online MS, and the final temperature was kept until a stable MS signal was obtained.

Oxygen temperature-programmed oxidation (O₂-TPO) was performed after two redox cycles to make sure the CuCl₂ was fully reduced to CuCl. Afterward, the catalyst was exposed to 2% O₂ in Ar with a flow rate of 120 ml/min until a stable MS signal was obtained. Then the catalyst was heated to 503 K at a ramping rate of 10 K/min with the effluent gas stream recorded by an online MS. The O₂ consumption peak was obtained and used for analysis.

2.7. Derivation of reaction rate expressions from transient experiments

To well describe the experimental results, a kinetic model merging into a reactor model will be proposed and discussed. Herein, the kinetic model for ethylene oxychlorination is proposed based on transient experiments. In the oxychlorination process, EDC was produced in the reduction step as the product, as shown in Eq. (4), with CuCl₂ being reduced to CuCl. The catalyst was regenerated by the oxidation of CuCl to copper oxychloride (Cu₂OCl₂). We have reported that the third step of hydrochlorination was assumed to proceed too fast, hence it is kinetic irrelevant [25,32,33]. Thus, the reaction rate expressions are derived from the reduction and oxidation steps.

In the transient experiment, the ethylene reduction rate was measured as a function of time. The accumulative removed Cl from CuCl₂ was calculated from the consumed C₂H₄ based on the stoichiometric reaction of Eq. (4). It was found that the maximum Cl of 0.012 mol/g was less than the theoretical value (0.016 mol/g). The Cl that can be removed from CuCl₂ by the ethylene reduction is

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Table 1

| Equation type       | Equation                                                                 | No.     |
|---------------------|--------------------------------------------------------------------------|---------|
| Species mass fraction | \( \frac{d\omega_A}{dt} = -\frac{1}{\rho_\omega} (\text{reaction terms}) \) | (7)     |
| Momentum balance    | \( \frac{d\rho}{dt} = -f \frac{d\rho}{dz} \)                           | (8)     |
| Continuity          | \( \frac{d\rho u}{dz} = 0 \)                                           | (9)     |
defined as removable Cl. The difference between the theoretical and measured maximum removable Cl is caused by the strong covalent bonding with alumina. The estimated reaction rates are shown in Fig. 1 as a function of removable Cl concentration on CuCl/Al$_2$O$_3$.

The experimental reaction rate curve (black line) can be deconvoluted into two parts using the Gaussian multiple peaks fit, as shown in Fig. 1. It suggests two types of active sites are possibly contributing to the reaction. The requirement of the active sites during the ethylene reduction of CuCl$_2$ was studied by DFT calculation [35,46]. During the reduction process, CuCl$_2$ is reduced to CuCl with Cl removed from the catalyst by CH$_4$, and the coordination number (CN) of Cu (i.e. the number of Cl atoms bonded with Cu) changes from 4 to 2 [35]. The surface Cl is rather mobile and randomly redistributed on the surface. It forms another type of Cu species with a 3-coordinated Cl, namely CuCl with one Cl vacancy. Also, it should be noticed that the CuCl$_2$ catalyst is highly dispersed, close to a monolayer [26,47], and the concentration gradients between the bulk and surface can be ignored. DFT study also revealed that CH$_4$ directly attracted two adjunct Cl atoms at the Cu with 4-coordinated Cl, while the Cl atom can only be extracted one by one to produce EDC on the lower CN Cu [35,46]. It has been proved that the CuCl (Cu with 2-coordinated Cl) was inactive in this ethylene oxychlorination [29,36]. The region of high Cl concentration in Fig. 1 corresponds to the beginning of the reduction when Cu is in its original chemical state as CuCl$_2$. The first part (I) indicated by the blue line in Fig. 1 is the rate contributed from the Cu with 4-coordinated Cl, where the Cl–Cl pair is the active site. The second part (II) indicated by the red line in Fig. 1 is the rate contributed from Cu with 3-coordinated Cl, where the Cu–Cl pair is the active site [35]. The diverse changing of the Cu coordination number of Cu also indicated the dynamic character of the active site.

Therefore, the rate expressions for the reduction step are divided into two parts.

\[ r_1 = r_{1I} + r_{1II} \]  

On Cu with 4-coordinated Cl (CN = 4), ethylene extracts two Cl atoms and forms EDC (Eq. (15)) as indicated by DFT calculation [46].

\[ 2\text{CuCl}_2^* + \text{C}_2\text{H}_4 \rightarrow 2\text{CuCl} + \text{C}_2\text{H}_4\text{Cl}_2^* \]  

The reaction rate for the elementary step of Eq. (13) is described by Eq. (14):

\[ r_{1I} = k_{1I} P_{\text{C}_2\text{H}_4} (C_{\text{Cl}} - C_{\text{Cl}}^*)^2 \]  

where C$_{\text{Cl}}^*$ is the threshold that Cu with 3-coordinated Cl, C$_{\text{Cl}}^*$–C$_{\text{Cl}}$ corresponding to the vacancy concentration, and first-order is to Cl and the vacancy.

When Cl concentration is higher than C$_{\text{Cl}}^*$, the reaction rate representing the second active site (r$_{1II}$) is zero, while the Cl concentration is lower than C$_{\text{Cl}}^*$, the reaction rate representing the first active site (r$_{1I}$) is zero.

The reduction ends with all the reducible CuCl$_2$ was reduced to CuCl. As shown in Eq. (5), in the oxidation step, CuCl$_2$ was re-oxidized to Cu oxychloride (CuOCl$_2$) [15,25,28,32]. The oxygen conversion was measured as a function of time. The accumulative insertion of O into CuCl was calculated from the consumed O$_2$-based on the stoichiometric reaction of Eq. (5). The reaction rate (black line) with the concentration of CuCl is plotted in Fig. 2. Similar to the reduction rate curve in Fig. 1, the rate curve was deconvoluted into two curves (red and
The physical properties like surface area, pore volume, and pore size of the fresh catalysts are summarized in Table 2. The Cu and K loadings were verified by ICP-OES, as shown in Table 2. Adding promoter to the catalyst, the surface area, pore volume, and pore size slightly decreased compared with the neat CuCl/Al₂O₃ catalyst. Fig. 3 shows the XRD patterns for the fresh neat CuCl/Al₂O₃ and K-promoted catalysts. No obvious diffraction peaks for CuCl₂ and KCl can be observed, indicating that CuCl₂ on the Al₂O₃ support is well dispersed. It was reported that CuCl₂ is highly dispersed on the alumina surface with different techniques, like chemisorption, and EXAFS, etc. [25,29,47,48]. When the neat Cu catalyst was doped with K, no obvious difference was displayed on the XRD patterns [33]. But at 20 ~ 15 °C, for the neat Cu catalyst, there is a peak assigned to the paratacamite (Cu₂(OH)₃Cl), which was produced due to the catalyst being stored in the air [25,32]. However, no traces of paratacamite were found on the K-promoted catalyst, which is confirmed with the previous reports [25,30]. No differences in the XRD patterns were observed on the spent catalysts compared to the fresh ones.

3.2. Verification of the kinetic model

The kinetic parameters (k₁,b, k₂,b, k₂,II,b) were estimated at each temperature by the non-linear model regression (see the Supporting Information S5). All the F-value for the global significance of the regression were found to be considerably larger than the tabulated one, i.e., 3.27. The statistical significance of each parameter estimate is also assessed by a T-test. The individual confidence intervals of the estimated parameters were calculated at a 95% probability.

The kinetic models are then validated by the comparison between model-simulated and experimental values. The comparison between the simulated removable Cl in the reduction step and CuCl in the oxidation step based on the kinetic models with the experimental values at different temperatures is presented in Fig. 4. As the reduction proceeds, CuCl₂ is reduced to CuCl, Cl is removed from the catalyst by CuCl, and KCl is removed from the catalyst by C₂H₄ with the forming of EDC as the product. The simulation and experimental curves of CCl with time on stream fit quite well as shown in Fig. 4a of the reduction step. As is expected, the higher temperature, the higher the reaction rate. In the oxidation step, CuCl₂ was oxidized to copper oxychloride by O₂, with no gas-phase product formed. The CuCl concentration with time on stream was shown in Fig. 4b, the simulation, and experimental results are also well fitted. It is noted that the experimental Cl or CuCl concentration is calculated by using the mass balances from the reaction, and simulated Cl concentration is calculated using the differential reactor model.

\[
\frac{dC_{Cl}}{dt} = r_i \quad t = 0 : \quad C_{Cl} = C_{Cl,0}
\]
Fig. 4. The simulated Cl and CuCl concentration obtained from integration of the two-part rate expressions (line) and experimental (symbol) reaction for the KCu/Al₂O₃ catalyst (a) reduction; (b) oxidation. Reaction conditions: $P_{C_2H_4} = 0.065\ \text{atm}$ or $P_{O_2} = 0.3\ \text{atm}$, $P_{\text{tot}} = 1\ \text{atm}$.

Fig. 5. The simulated (line) Cl and CuCl concentration obtained from integration of the two-part rate expressions, and experimental (symbol) reaction for the KCu/Al₂O₃ catalyst (a) reduction; (b) oxidation. Reaction conditions: $P_{C_2H_4} = 0.1\ \text{atm}$ or $P_{O_2} = 0.1\ \text{atm}$, $T = 503\ \text{K}$, $P_{\text{tot}} = 1\ \text{atm}$.

Fig. 6. Arrhenius plot for reduction and oxidation steps for KCu/Al₂O₃ catalyst. Part I and part II of the two-part rate expression for the a) reduction, and b) oxidation steps. The error bars represent the 95% confidence interval of the estimated $k$. 
The laboratory reactor is simulated using Eqs. (7)–(9), and the related parameters are listed in Table S1. The consumption ethylene rate of \( R_1 \) in Eq. (7) is the rate of the ethylene oxychlorination.

The simulation is performed without any change in kinetic parameters in Table 3 obtained from the transient kinetic modeling. Furthermore, the dynamic evolution of CuCl\(_2\) concentration (Eq. (32)) is also solved together with reactor simulation. The transient kinetic model can be simplified to the steady-state kinetic model, at the steady-state:

\[
\frac{dC_{\text{CuCl}_2}}{dt} = 0 \quad (33)
\]

\[
r_1 = r_2 \quad (34)
\]

The evolution of ethylene conversion and the CuCl\(_2\) concentration of the simulated and experimental CuCl\(_2\) profiles during the steady-state is shown in Fig. 7. From Fig. 7a and the previous reports [25,32,33], we have demonstrated that the reaction was in the region of high CuCl\(_2\) (or Cl) concentration at the steady-state. As we discussed above, at a high concentration of Cl, the rate representing the first active site, \( r_{1,1} \) is dominating, hence, the total reaction rate can be approximately expressed by \( r_{1,1} \). At a low concentration of CuCl\(_2\), the rate representing the second active site, \( r_{2,II} \) is dominating, and the oxidation rate can be approximated by \( r_{2,II} \): Eq. (34) becomes:

\[
r_{1,1} = r_{2,II} \quad (35)
\]

To get the steady-state expression, it was assumed that the \( C_{\text{CuCl}_2}^{eq} \) may be approximated by the maximum concentration of CuCl at the steady-state. Also, it was assumed that the \( C_{\text{Cl}} \) was negligible at steady-state.

### Table 3

Estimated pre-exponential factors (A) and activation energies (E) for the respective reduction and oxidation half cycles for the KCu/Al\(_2\)O\(_3\) catalyst, with 95% confidence intervals and correlation coefficients of \( R^2 \), and the threshold concentrations in Figs. 1 and 2.

| Parameter | Unit | Reduction | Oxidation |
|-----------|------|------------|-----------|
| \( k_{eq} \) | \( \text{atm}^{-1} \) | - | 0.2 |
| \( A_1 \) | \( \text{gCu} \text{ mol}^{-1} \text{ atm}^{-1} \text{ s}^{-1} \) | \( 2.78 \times 10^5 \pm 4.90 \times 10^5 \) | \( 3.64 \times 10^5 \pm 2.00 \times 10^4 \) |
| \( A_II \) | \( \text{gCu} \text{ mol}^{-1} \text{ atm}^{-1} \text{ s}^{-1} \) | \( 1.58 \times 10^5 \pm 5.00 \times 10^5 \) | \( 2.00 \times 10^5 \pm 3.00 \times 10^6 \) |
| \( E_{a,1} \) | \( \text{kJ mol}^{-1} \) | 45.25 ± 0.48 | 40.35 ± 0.42 |
| \( E_{a,II} \) | \( \text{kJ mol}^{-1} \) | 51.90 ± 0.41 | 70.10 ± 0.65 |
| \( R^2 \) | | 0.992 | 0.996 |
| \( \text{K}^{II} \) | | 0.998 | 1.000 |
| \( \text{K}^{IV} \) | \( \text{mol/gCu} \) | 0.002 | - |
| \( \text{K}^{VI} \) | \( \text{mol/gCu} \) | 0.012 | - |
| \( \text{K}^{VII} \) | \( \text{mol/gCu} \) | - | 0.002 |
| \( \text{K}^{VIII} \) | \( \text{mol/gCu} \) | - | 0.008 |

The percentage changes in the redox process [25,34]–[36] are related to the parameter values in Table 3 obtained from the transient kinetic modeling. Further- more, dynamic evolution of CuCl\(_2\) concentration (Eq. (32)) is also solved together with reactor simulation. The transient kinetic model can be simplified to the steady-state kinetic model, at the steady-state:

The dynamic change of CuCl\(_2\) concentration can be derived from the rate expressions. Firstly, the Cl concentration is equivalent to the reducible CuCl\(_2\) concentration:

\[
\frac{dC_{\text{Cl}}}{dt} = 0 \quad (30)
\]

Secondly, the total Cu concentration is conserved,

\[
C_{\text{CuCl}_2} = C_{\text{CuCl}_2}^{eq} - C_{\text{CuCl}_2}^{eq} \quad (31)
\]

By inserting the rate expressions of reduction and oxidation, the rate of disappearance of CuCl\(_2\) is

\[
\frac{dC_{\text{CuCl}_2}}{dt} = r_1 - r_2 = C_{\text{CuCl}_2} - C_{\text{CuCl}_2}^{eq} \quad (29)
\]

### 3.3. Simulation and kinetic modeling of the steady-state experiments

Based on the above discussion, it has been proved that the developed kinetic model can correctly describe the transient behavior of the reduction and oxidation for the K-promoted CuCl\(_2\)/Al\(_2\)O\(_3\) catalyst. In our previous reports, we utilized the home-made operando setups combined UV–vis-NIR and MS to study the kinetics and catalyst composition changes in the redox process [25,32–34]. Using our developed methodology, the CuCl\(_2\) profiles and C\(_2\)H\(_4\) reaction rate (or conversion) can be monitored simultaneously during the steady-state experiment where C\(_2\)H\(_4\), O\(_2\), and HCl are co-fed together.

Since the active sites of the catalyst are highly dynamic, it is necessary to calculate the rate of change of CuCl\(_2\) concentration with time.
The CuCl can be expressed as:

\[
C_{\text{CuCl}} = C_{\text{CuCl, max}} - C_{\text{Cu}}
\]  

(36)

It is noted that in the steady-state, the \(O_2\) adsorption term \((1 + K_r P_{O_2})\) should also be included in the reduction process. The Cl concentration in CuCl2 and the rate expression at the steady-state are described as Eqs. (37) and (38), respectively, (the detailed derivation of the equations can be seen in S3 Supporting information):

\[
C_{\text{Cl}} = \frac{C_{\text{CuCl, max}}}{1 + \frac{k_1 P_{O_2}}{k_2 P_{O_2}}}
\]  

(37)

\[
\dot{C}_{\text{CuCl, steady-state}} = \frac{k_1 (C_{\text{CuCl, max}})^2 P_{C_2H_4} P_{O_2}}{(P_{O_2} + \frac{k_1}{k_2} P_{C_2H_4}) (1 + K_r P_{O_2})}
\]  

(38)

We have reported that the gradual decrease of \(C_{\text{CuCl}}\) concentration in the initial period was attributed to the dynamic process to achieve the steady-state [25]. The results indicated the kinetic model fitted well with the experimental results. It shows that half of the reducible Cu is in the oxidized chemical state. It is greatly increased compared to the unpromoted Cu catalyst, in which we have reported that roughly 0.4 mol Cu was kept oxidized of CuCl2 [32]. It indicates the positive effect of K as a promoter in the regenerating of CuCl2 in ethylene oxychlorination. Besides, the dynamic changes of the CuCl2 were studied at the different positions along the reactor by moving the UV-vis-NIR probe during the steady-state, gaining a better understanding of the kinetic model, as shown in Fig. 7c. It is evident that K promotion favors the CuCl2 oxidation state, which dominates along the catalyst bed, thus the catalysts are stable. Table 4 shows \(C_2H_4\) reaction rate and CuCl2 concentration at the steady-state for both simulated and experimental data, which matched very well with less than 5% deviation. The simulation was also performed for different feeding conditions (1:2:2, excess \(O_2\)), shown in Fig. S2 of SI, the experimental and simulated \(C_2H_4\) reaction rate and CuCl2 concentration can also fitted well.

In ethylene oxychlorination, both the solid phase and gas phase are likely mobile on the catalyst surface. Especially for the co-feeding steady-state, it will create a more complicated surface environment than the transient reduction and oxidation reactions separately. All the above results of the simulation and experimental fit well, showing the accuracy of the kinetic model. This model can be used to predict and analyze the reaction rate and Cu oxidation state during the steady-state experiments.

4. Conclusions

Kinetic study of ethylene oxychlorination, a vital process involved in VCM production, was performed at 483–513 K, atmospheric pressure on the K-doped CuCl2/γ-Al2O3 catalyst. A new approach for kinetic modeling of the MvK-type process was developed taking into account the dynamic changing characters of the active sites in the redox cycle. The new approach includes detailed kinetic modeling at three levels, including the transient kinetic model for half-reactions in the redox cycle of reduction of CuCl2 by \(C_2H_4\) and oxidation of CuCl by \(O_2\), a transient kinetic model of the whole redox cycle by combining the kinetic models of the half-reactions, and the steady-state reaction, to study and evaluate the reaction kinetics. A kinetic model describing the transient and steady-state behaviors combining the reactant gas-phase and catalyst solid-phase in the reaction including the reaction rate and Cu oxidation state has been developed with the best fitting. The transient reaction rates fit the corresponding experimental results for a variety of temperatures and partial pressures. The simulated steady-state reaction rate is also in good agreement with the analogous experimental reaction rates. Furthermore, the simulated evolution of CuCl2 concentration during the steady-state is also fittingly matched with the experimental result. This kinetic model can accurately predict the gas- and solid-phase catalytic behaviors during the steady-state without doing any complicated computation. This model can be used to predict the conversion and spatial-time CuCl2 concentration decently well, which are the two most important factors for this...
industrial process. It has been implied that applying the transient experiments to extract the correlated kinetic parameters for building the model to further describe the steady-state is a reliable and efficient method to study the kinetics of the MVK-type of catalytic reactions. Therefore, the industrial application of this kinetic model can be expected as it is easy to perform. It is also expected that this method can be exploited to other catalytic reaction systems, in which redox cycles are involved, especially for MVK-type reactions in general.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data

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