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Understanding of potassium promoter effects on oxychlorination of ethylene by operando spatial-time resolved UV–vis–NIR spectrometry

K.R. Rout [a], M.F. Baidoo [a], E. Fenes [a], J. Zhu [a], T. Fuglerud [b], D. Chen [a],*

[a] Chemical Engineering Department, Norwegian University of Science and Technology, Sem sælands vei 4, Norway
[b] INOVYN, Herøya Industrial Park, Norway

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Obtaining the comprehensive kinetics of elementary reaction steps in catalytic redox cycles remains a challenge. We report here an operando study by combined mass and UV–vis–NIR spectrometry to obtain kinetic data for reduction and oxidation steps in the catalytic cycle of ethylene oxychlorination on potassium-promoted $CuCl_2/Al_2O_3$ catalysts and understand the catalytic consequences of potassium promotion for ethylene oxychlorination through a comprehensive kinetic analysis of the catalytic cycle. The results demonstrate that the Cu^{2+} and Cu^{1+} concentration, the number of active sites, and the activity of the active sites are highly dynamic, depending on the catalyst composition and the operating conditions. A pseudo-steady-state approach was applied to deconvolute the effect of promoters on the oxychlorination reaction into the effects on the individual reduction and oxidation steps, as well as their consequences in steady state in terms of the active site number and the site activity. It has been found that the rate of oxidation of Cu^{1+} by oxygen is much lower than the rate of reduction of Cu^{2+} by ethylene at relatively high Cu^{2+} content. This resulted in CuCl dominating at the surface and thus a low rate in the steady state on the neat $CuCl_2$ catalyst. Potassium promotion increased the reducible Cu^{2+} content from 0.61 mol/mol_{Cu} of the neat $CuCl_2$ catalyst to 0.8 mol/mol_{Cu} by reducing the interaction between Cu and the alumina support. Further increasing the potassium loading from 0.92 to 1.54 wt.% decreases the reducible Cu^{2+} from about 0.8 to 0.7 mol/mol_{Cu}. Potassium promotion significantly increased the site activity of the Cu^{1+} oxidation, but decreased the site activity of the Cu^{2+} reduction by ethylene. The positive effect of potassium promotion is due to the increase in the number of Cu^{2+} active sites, which was more significant than the negative impact on turnover frequency (TOF); thus, potassium promotion increased the steady-state reaction rate. In addition, owing to the kinetic balance between the higher Cu^{1+} oxidation rate and the lower Cu^{2+} reduction rate, potassium promotion yielded an increased Cu oxidation state with Cu^{2+} dominating the steady-state catalyst surface. This led to remarkably improved stability of $CuCl_2$ catalysts.

1. Introduction

Ethylene oxychlorination is one of the most important routes for producing 1,2-dichloroethane (EDC), a key step in polyvinyl chloride (PVC) production [1]. In the PVC manufacturing industry, PVC is produced by vinyl chloride monomer (VCM) polymerization, obtained by EDC cracking following the reaction

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl. \tag{1}$$

EDC, in turn, is produced by either a gaseous mixture of ethylene, HCl, and air on a $CuCl_2$-based catalyst via oxychlorination,

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O, \tag{2}$$

or direct chlorination of ethylene [2–4],

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2. \tag{3}$$

Recently, a bifunctional ceria catalyst for the production of VCM in a single step has been proposed by Scharfe et al. [5]. The redox centers on the catalyst are said to convert ethylene to EDC, which is subsequently dehydrochlorinated to VCM on strong acid sites.

However, the oxychlorination process provides two significant economic benefits to the chemical industry: first, it uses cheap and abundant feedstock, and second, it consumes waste HCl produced during EDC cracking (Eq. (1)) [2,3,6]. Commercial ethylene oxychlorination reactors typically operate in temperature and

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* Corresponding author.
E-mail address: de.chen@ntnu.no (D. Chen).

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pressure ranges of 217–257 °C and 5–6 atm, respectively [2–4]. It is generally agreed that ethylene oxychlorination involves a redox mechanism in which copper cycles between Cu^{2+} and Cu^{1+} states [7–9]. In the literature [8,10–16], by feeding the three reactants separately, it has been demonstrated that the oxychlorination reaction is catalyzed by a highly dispersed $CuCl_2$ phase following a three-step redox mechanism:

Step 1. Reduction of $CuCl_2$ to CuCl:

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 2CuCl. \quad (4)$$

Step 2. Oxidation of CuCl to form an oxychloride, Cu_2OCl_2:

$$2CuCl + \frac{1}{2}O_2 \rightarrow Cu_2OCl_2. \quad (5)$$

Step 3. Hydrochlorination of the oxychloride using HCl to form $CuCl_2$ and H_2O:

$$Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O. \quad (6)$$

The oxychlorination reaction mechanism is not yet fully understood, despite more than 30 years of research and commercial application, although knowledge of it has recently been significantly improved [7–9,15–22]. However, most of the preceding work related to the oxychlorination reaction qualitatively studied the $CuCl_2$ catalyst oxidation state during the reaction. This is due to one of the main challenges of this process, that Cu^{1+} deposits on the catalyst surface during the reaction, thereby causing aggregation and loss of Cu active materials due to the high volatility of cuprous copper [23]. To alleviate this problem, industrial $CuCl_2$-based catalysts are generally promoted with different promoters. Therefore, compounds of alkali metals, such as K and Na, and/or rare earth metals such as La, are often used as promoters to increase the activity, selectivity, and stability of $CuCl_2$-based catalysts in industrial reactors [24–27].

Effects of promoters on catalytic activity and stability have been studied by several researchers [1,17,18,20,21], including the role of the dopants and the nature, reducibility, and dispersion of active Cu phases. However, detailed quantitative kinetic effects of the dopants on the catalyst activity, selectivity, and stability are still not known. Owing to the great importance of a space–time quantitative prediction of the Cu^{2+} profile in industrial reactors, predictive kinetics for not only product formation but also the evolution of catalyst composition is essential. Therefore, a detailed kinetic study of all three reactions involved in the redox cycle of ethylene oxychlorination is necessary.

K, being the most common promoter of the oxychlorination catalyst [1,17,28], has been reported to influence the $CuCl_2$-based oxychlorination catalyst in several ways: (i) replacing inactive copper atoms located in the alumina surface vacancies, effectively increasing the number of Cu active sites on the catalyst [19,28,29]; (ii) forming a mixed copper–potassium salt (CuK_xCl_{2+x}), retarding ethylene adsorption and/or Cl migration on the catalyst surface [1,18,19,28], so that the overall reaction rate eventually decreases when the potassium content becomes high enough, making hotspot formation more manageable; (iii) shifting the rate-determining step from the oxidation (Eq. (5)) in the nonpromoted catalyst to the ethylene reduction, decreasing the concentration of volatile Cu^{1+} species [1,18,28]; and (iv) limiting the number of Lewis acid sites, decreasing the number of chlorinated byproducts [17,20,30]. All the results suggest that the reaction could be highly dynamic. The knowledge of dynamic changes of the active Cu sites during the reaction and their dependence on the catalyst composition, including the dopants, is of significant importance. It thus requires in situ measurement of Cu oxidation state changes during the reaction.

Operando spectroscopy is often used to monitor the oxidation state changes of the catalyst [31–36]. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) have been used to study the Cu^{2+} to Cu^{1+} transformation of the $CuCl_2$-based oxychlorination catalyst [1,18,19,28,37]. Unfortunately, this requires complicated data treatment. In addition, the thin catalyst layer and high space velocity of transition mode XANES and EXAFS complicate gas composition analysis. UV–vis–NIR spectrometry has been demonstrated as a relatively simple approach to quantitatively follow the Cu^{2+} concentration in zeolites with dilute amounts of Cu [38]. However, obtaining the required UV–vis–NIR absorbance range of 0.05–1 [39] in the oxychlorination catalyst would require inert dilution with uniform diluent distribution throughout the reactor where significant dilution could reduce the conversion and thus complicate the analysis.

Avoiding these pitfalls of dilution, UV–vis–NIR spectrometry was applied on undiluted $CuCl_2$-based catalysts in this study similarly to previous studies, quantitatively following coke formation in catalytic propane dehydrogenation [35,36]. To the best of our knowledge, such a space–time resolved systematic in situ quantitative kinetic study of the Cu^{2+}/Cu^{1+} ratio of the undiluted $CuCl_2$-based oxychlorination catalyst in a fixed-bed reactor using UV–vis–NIR spectrometry has not been carried out previously. It will provide information vital in determining the influence of K on Cu reducibility, steady-state site activity, and stability.

In the present work, we utilize a relatively simple operando method compared with XANES and EXAFS, namely combined mass and UV–vis–NIR spectrometry to study the kinetics of the reaction in a fixed bed, where the flow is well defined and mass and heat transport limitations were eliminated to ensure intrinsic kinetics. Both transient and steady-state kinetic studies are carried out to elucidate the effects of the K promoters on the catalyst performance. The evolution of the reaction rates and the oxidation state in the redox reaction steps and the transient process approaching the steady state are coupled in the operando kinetic study. This method has contributed to a more nuanced view of the Cu^{1+} oxidation state as the more relevant kinetic step governing the Cu oxidation state. Furthermore, the new method makes it possible to deconvolute the effect of the promoters on the steady-state rate into the effects on the number of active sites and the site activity, namely turnover frequency (TOF). The application of this strategy to the K-promoted $CuCl_2$-based catalysts could further be used as a basis for rational design of heterogeneous catalysts where the catalyst undergoes oxidation state changes, in particular in redox reactions [40].

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by the incipient wetness impregnation method, where precursors ($CuCl_2 \cdot 2H_2O$ and KCl) were co-impregnated on γ-Al_2O_3 and then dried for 10 h at 25 °C, and after that it is held at 120 °C for 6 h [7]. The catalyst named Cu5.0 contains only 5 wt.% Cu, whereas the catalysts K0.92Cu5.0 and K1.54Cu5.0 contain 0.92 and 1.54 wt.% K, respectively, along

Table 1
Physical properties of the oxychlorination catalysts.

Catalyst	Surface area [m^2/g]	Pore volume [cm^3/g]	Pore size [nm]
γ-Al_2O_3	164	0.45	10.9
Cu5.0	150	0.40	10.6
K0.92Cu5.0	137	0.37	8.7
K1.54Cu5.0	136	0.36	8.7