

## Descriptors for Alkali Metal Promotion in Redox Catalysis: Ethylene Oxychlorination

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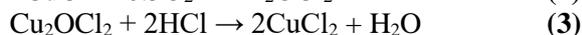
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### Highlights

- Catalyst optical band gap a proper descriptor for catalyst redox site activity.
- Alkali metal first ionization energy tunes Cu optical bandgap.
- The methodology is applicable to redox catalyst in general.

### 1. Introduction

Ethylene oxychlorination is an industrial process with worldwide application, providing 1, 2- ethane-dichloride (EDC), a raw material in polyvinylchloride (PVC) production. The overall reaction is comprised of reduction (Eq.1) of the CuCl<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> based catalyst to form EDC followed by catalyst regeneration through oxidation (Eq.2) and hydro-chlorination (Eq.3) [1];



Previously, promoters have been partially grouped based on their apparent effect [2] while the fundamental principle(s) have eluded discovery. For the first time, we demonstrate how the optical band gap ( $E_g$ ) of the solid phase determines the activity of the two kinetically significant steps (Eq.1-2) and how the alkali promoter first ionization energy ( $IE_1$ ) tunes the band gap. Preliminary results from our group indicate that the alkali metal effect is directly transferrable to other catalytic redox systems. In combination with our previous work [3-5], this enables a targeted approach to rational catalyst design of catalytic redox systems in general.

### 2. Methods

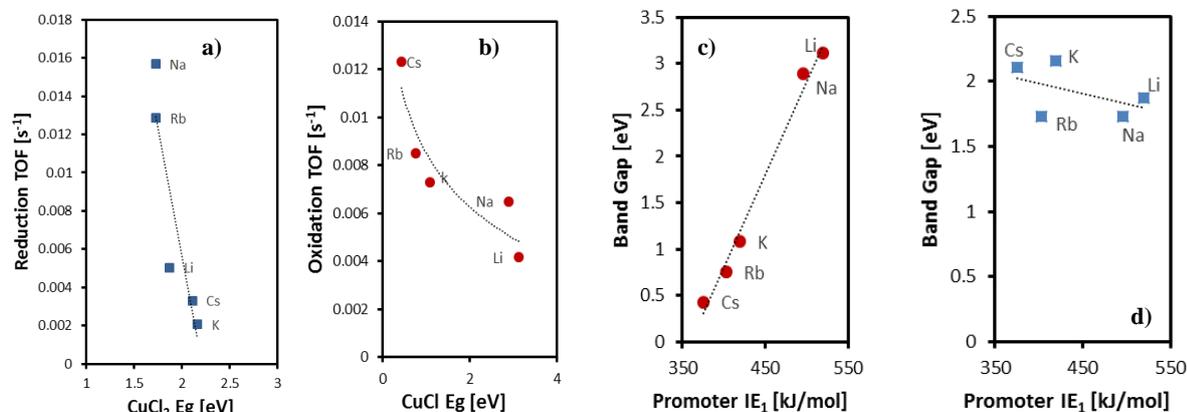
All CuCl<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were made according to the incipient wetness impregnation method from the chloride salts, contains 5wt% Cu and a promoter: Cu molar ration of 0.4. The catalyst physical properties was obtained with BET, catalyst characterization with *ex situ* XRD, XPS and Raman spectroscopy while the  $E_g$  was obtained by *in situ* UV-Vis-NIR spectroscopy. Reactants were fed at 230°C one by one in step transient experiments and effluent gasses monitored by an online mass spectrometer and gas chromatograph.

### 3. Results and discussion

The initial turnover frequency was estimated from the initial reaction rate based on the total active sites obtained by the titration or reduction of CuCl<sub>2</sub> by ethylene. The initial TOF during the respective transient reduction and oxidation steps is reported in Figure 1 a) and b) as a function of the catalyst band gap ( $E_g$ ). In both cases, the TOF decreases as  $E_g$  increases but where the oxidation TOF follows the periodical order of Cs > Rb > K > Na > Li promotion, the reduction step is slightly more complicated.

For the oxidation, Figure 1c demonstrates how the alkali promoter first ionization energy ( $IE_1$ ) tunes the optical band gap of these reduced catalysts. The  $IE_1$  describes the ease of which the outermost electron is removed from the alkali metal. The more electron donating the alkali promoter is the lower catalyst  $E_g$ . As  $E_g$  decreases, one interpretation is that the alkali metal transfers its outermost electron to a reduced Cu site, increasing the electron density of the existing site and promoting the adsorption and/or dissociation of oxygen. It has also been reported that alkali metals can act as an independent active site in oxygen adsorption

and dissociation which subsequently transfers to and reacts with reduced Cu species. Distinguishing the relative contributions of these two hypothesis is attempted by XPS and synchrotron XRD analysis.



**Figure 1.** Initial reduction a) and oxidation b) turnover frequency (TOF) as a function of the respective CuCl<sub>2</sub> and CuCl copper phase band gap (E<sub>g</sub>). Correlation between the promoter IE<sub>1</sub> (literature values) and E<sub>g</sub> of the respective Cu<sup>1+</sup> and Cu<sup>2+</sup> phases are presented in c) and d).

Within the reduction step, the E<sub>g</sub> dependency on IE<sub>1</sub> is less pronounced in Cu<sup>2+</sup> phases as shown in Figure 1d and while increasing the band gap has a negative impact on the TOF in Figure 1a, Na and Rb promoted catalysts have significantly higher activity than Li, Cs and K. In the latter group, especially K and Cs form mixed CuAlCl<sub>3</sub> (A=Alkali) salts upon precipitation of an aqueous solution of CuCl<sub>2</sub> and AlCl<sub>3</sub>, while Na and Rb appears unable. Additionally, peaks related to CuCsCl<sub>3</sub> appear in synchrotron XRD profiles when Cu related phases are generally not visible due to the high dispersion of CuCl<sub>2</sub> nanocrystals. Combined with XPS analysis of K promoted catalysts, which indicate e<sup>-</sup> donation from K to Cu via a bridging Cl atom, CuAlCl<sub>3</sub> formation appears to result in an increased significance of Cl diffusion in the larger particles and increased Cu electron density, reducing the interaction between the active site and the e<sup>-</sup> rich ethylene pi orbitals. Both effects having a negative impact on the reduction TOF.

Ongoing work includes systematically changing promoter loading and additional promoters such as alkali earth and lanthanide chlorides to further elucidate the presented relationships. Finally, the promoter effect on the selectivity at steady state will be explored.

#### 4. Conclusions

The optical band gap appears to be a proper descriptor for both the reduction and oxidation of the CuCl<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> based oxychlorination catalysts where a decreased band gap increases the site activity. In particular, during the oxidation, the band gap is tuned by the first ionization energy of the promoter while additional CuAlCl<sub>3</sub> salt formation appears to have a detrimental impact on the reduction of the oxidized catalyst. Preliminary results indicate that the effects of alkali promotion are general to redox catalysis and additional work on unrelated redox systems are in preparation.

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**Keywords:** Redox catalysis, Reaction kinetics, Catalyst design, Descriptor