

## Variations in Activity and Selectivity for Supported KCl/CuO and KCl/CuCl<sub>x</sub> Catalysts

### INTRODUCTION

Supported liquid-phase (SLP) catalysts, typically containing equimolar amounts of an alkali metal salt such as potassium chloride (KCl) and copper chloride (a CuCl<sub>2</sub>/CuCl mixture hereafter referred to as CuCl<sub>x</sub>) have been utilized commercially for some time in the manufacture of chlorine (via the Deacon reaction) and in the preparation of chlorinated organics (via oxychlorination) (1). By itself, solid CuCl<sub>x</sub> readily sublimates at reaction temperatures ( $\leq 500^\circ\text{C}$ ), but with addition of KCl a low volatility eutectic melt is formed which significantly improves catalyst stability. The mechanisms for the Deacon and oxychlorination reactions and the rather complex role of the catalysts have been studied extensively (1-4) but are still not entirely understood.

Much less consideration has been given to the potential dynamic conversion of the chloride form of this catalyst (CuCl<sub>x</sub>) to the oxide form (CuO) and vice versa, as previously found by X-ray diffraction measurements under appropriate conditions of temperature and oxygen/HCl concentrations (5). At  $500^\circ\text{C}$ , 1:1 KCl/CuCl<sub>x</sub> is a liquid (melting point  $320^\circ\text{C}$ ), while KCl and CuO are both solids (melting points 760 and  $1360^\circ\text{C}$ , respectively). Thus two separate catalytic phases would be anticipated on the support under conditions when both catalyst forms coexist.

This paper examines the effects of changes in catalyst form (i.e., copper oxide versus copper chloride species) on activity and product selectivity for vapor-phase

conversion of methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) in excess air at  $500^\circ\text{C}$ .

### EXPERIMENTAL

Reactions were carried out with the SLP copper salt catalyst systems supported on low surface area ( $\sim 0.4 \text{ m}^2/\text{g}$ ) silica monoliths (0.6 cm i.d.  $\times$  1.6 cm o.d.  $\times$  22.9 cm long, each weighing approximately 60 g) obtained from the Norton Co., Akron, Ohio. The KCl/CuO catalyst was formulated by the method of incipient wetness using an aqueous solution containing equimolar concentrations of KCl and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>). Calcination for 8 h in air at  $500^\circ\text{C}$  yielded the final monolith containing 1.97 wt% KCl/CuO with a BET surface area of  $0.36 \text{ m}^2/\text{g}$ . Preparation methods for the supported KCl/CuCl<sub>x</sub> catalyst were similar except that CuCl<sub>2</sub> was substituted for Cu(NO<sub>3</sub>)<sub>2</sub> during the formation step; a monolith containing 2.10 wt% KCl/CuCl<sub>x</sub> with surface area of  $0.38 \text{ m}^2/\text{g}$  was thus obtained.

Mixtures of CH<sub>2</sub>Cl<sub>2</sub> in concentrations ranging from 2900-3500 ppm by volume in dry air were passed through each monolith at flow rates which gave a reactor residence time of 0.4 s at  $500^\circ\text{C}$ . Reactor inlet and outlet vapors were periodically sampled and analyzed using a Hewlett-Packard Model 5890 gas chromatograph with Model 5970B mass selective detector to identify as well as quantify all detectable products. Product HCl was monitored by aqueous trapping and subsequent titration; no interfering formic acid was detected. Product carbon monoxide (CO) and chlorine (Cl<sub>2</sub>) were analyzed separately using MSA

Draeger tubes. For CO, this was necessary because of interference by N<sub>2</sub>, while for Cl<sub>2</sub> a sharp GC peak could not be obtained.

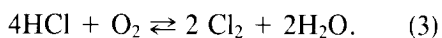
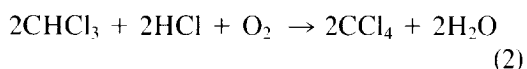
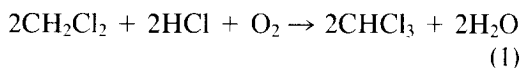
For the KCl/CuO catalyst runs, material balances on chlorine and carbon averaged 97.4 and 98.1%, respectively, while for the KCl/CuCl<sub>x</sub> catalyst runs, they averaged 102 and 97.5%, respectively. Details of the experimental apparatus and analytical procedures are reported elsewhere (5, 6).

## RESULTS AND DISCUSSION

### Chemical Reactions

At 500°C, the homogeneous reaction of CH<sub>2</sub>Cl<sub>2</sub> in air was found to be negligible (<5%). However, under identical reaction conditions on the catalyst monoliths, three types of heterogeneous chemical changes are anticipated: Type I changes (oxychlorination and Deacon reactions) where the primary products are more highly chlorinated species; Type II changes where C-Cl bonds are broken to yield deep oxidation products primarily consisting of CO<sub>2</sub> and HCl; and Type III changes involving the SLP catalyst itself (CuCl<sub>x</sub> ⇌ CuO). The Type III changes in catalyst composition from oxide to chloride forms over time are believed responsible for corresponding shifts in selectivity from deep oxidation to oxychlorination products.

In the present study with CH<sub>2</sub>Cl<sub>2</sub> feed and with the catalyst largely in the CuCl<sub>x</sub> form, selectivity to Type I reactions should be primary:



The Deacon reaction is included here because Cl<sub>2</sub>, not HCl, may be the actual chlorinating agent (4). The real mechanism for these reactions most likely involves the lattice copper cation which oscillates between the +2 and +1 oxidation states,

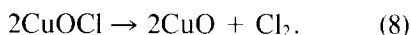
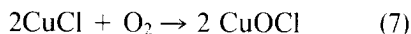
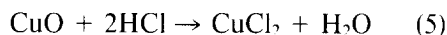
thereby catalyzing both the oxychlorination and Deacon reactions. Several detailed mechanisms for these Type I reactions have been proposed (1, 2, 4), but no general agreement on their correctness exists.

With the catalyst in the oxide form, a Type II deep oxidation reaction for CH<sub>2</sub>Cl<sub>2</sub> is expected:



The term "deep oxidation" is used to categorize Type II reactions because more oxygen-catalyst bonds must be broken to form these products than for Type I (mild oxidation) reactions (1).

Experiments on the mechanism of Type III conversion of the catalyst itself have shown that when vapor-phase HCl concentrations are appreciable, the oxide catalyst is substantially converted to the chloride form, whereas when O<sub>2</sub> concentration is high and HCl negligible, the catalyst remains in the oxide form. These catalyst transformations were previously documented to occur over a period of 5–30 h at 500°C as a function of HCl concentration (5) as shown stoichiometrically below:



Based on previous arguments, variation in catalyst composition may be expected to produce substantial changes in catalyst selectivity.

### Catalyst Conversion and Selectivity

#### Results

Figures 1–7 show comparisons of catalyst activity and selectivity with time for the initially pure KCl/CuO or KCl/CuCl<sub>x</sub> catalyst forms. Catalyst selectivity in the present discussion is defined as the ratio of moles of a given product actually formed to moles of the product which could have been formed at that level of conversion.

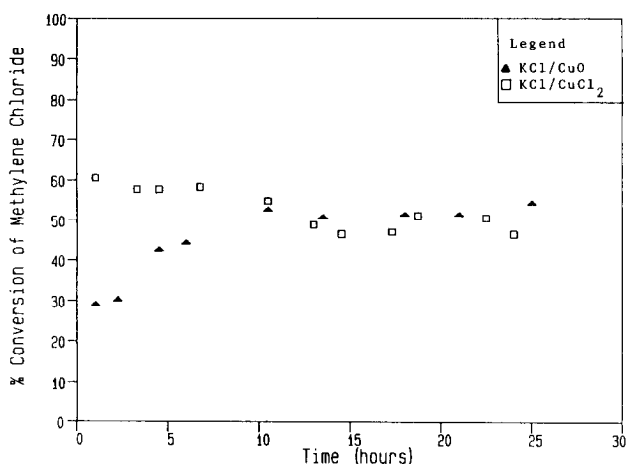


FIG. 1. Conversion of methylene chloride with time.

Figure 1 shows an initial conversion level of about 60% for  $\text{CH}_2\text{Cl}_2$  with the  $\text{KCl}/\text{CuCl}_x$  catalyst, while with  $\text{KCl}/\text{CuO}$  it is initially less than 30%. Over a run time of 8–10 h conversion levels for the two catalysts tend to converge to a steady-state value of about 50%. This scenario is consistent with the partial conversion of  $\text{CuCl}_x$  to  $\text{CuO}$  as a function of time in the former case and substantial conversion of  $\text{CuO}$  to  $\text{CuCl}_x$  in the latter, when reactor  $\text{HCl}$  concentrations averaged about 950 ppm. These catalyst changes were visually confirmed after cooling by observation of small gray "islands" of  $\text{CuO}$  in the initially reddish brown

$\text{K}_2\text{CuCl}_4$  complex salt formed between  $\text{KCl}$  and  $\text{CuCl}_x$ . The presence of  $\text{K}_2\text{CuCl}_4$  was confirmed by X-ray diffraction techniques (5). Conversely, reddish brown  $\text{K}_2\text{CuCl}_4$  regions were observed in the initially gray  $\text{KCl}/\text{CuO}$  surface after operation.

Selectivities to  $\text{CHCl}_3$  and  $\text{CCl}_4$ , both oxychlorination products, are shown in Figs. 2 and 3. The most noticeable trend is the steady increase in oxychlorination selectivities for the  $\text{KCl}/\text{CuO}$  catalyst during the initial 8- to 10-h run period, as this catalyst is substantially converted to the chloride form.

Figures 4 and 5 show the initial high

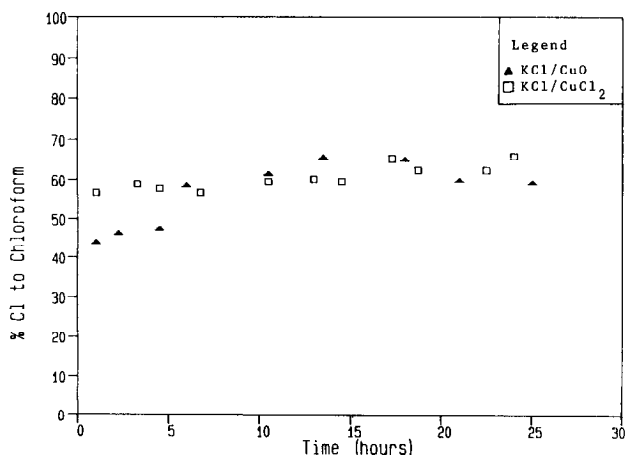


FIG. 2. Selectivity to chloroform with time.

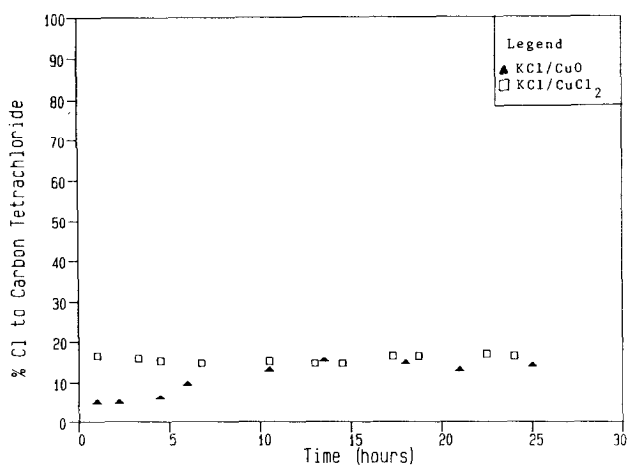


FIG. 3. Selectivity to carbon tetrachloride with time.

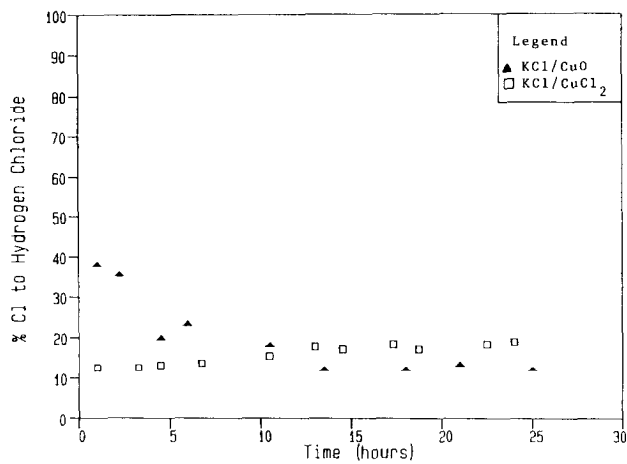


FIG. 4. Selectivity to hydrogen chloride with time.

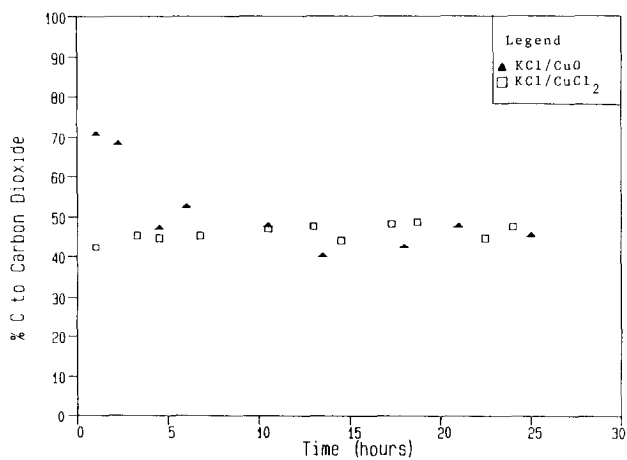


FIG. 5. Selectivity to carbon dioxide with time.

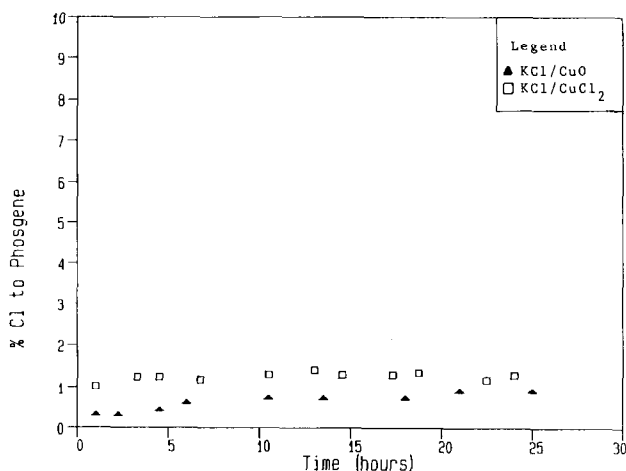


FIG. 6. Selectivity to phosgene with time.

selectivity values of the KCl/CuO catalyst for deep oxidation products ( $\text{CO}_2$ , HCl) as anticipated. Again, convergence of selectivities for the two catalysts occurs after 8–10 h of operation. No product CO was detected for either catalyst.

Figures 6 and 7 show selectivities to phosgene ( $\text{COCl}_2$ ) and  $\text{Cl}_2$  for each catalyst. Higher values for both  $\text{COCl}_2$  and  $\text{Cl}_2$  were noted with the KCl/CuCl<sub>x</sub> catalyst which is in agreement with this catalyst's ability to facilitate the oxychlorination and Deacon reactions. Although concentration levels

for these products are lower than with most others (making accurate analysis more difficult), it appears that the two sets of selectivities do not converge until about 20 h of operation. One might speculate that these two reactions occur significantly in the melt phase (not just on the surface) of the KCl/CuCl<sub>x</sub> catalyst and that it requires about 20 h of operation under these reactor conditions to substantially convert the entire KCl/CuO layer to molten KCl/CuCl<sub>x</sub>. Conversely, the other reactions may occur primarily on or near the catalyst surface,

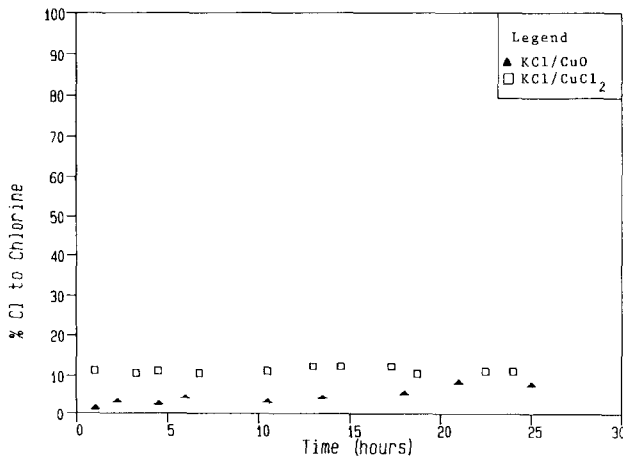


FIG. 7. Selectivity to chlorine with time.

which presumably requires only 8–10 h under reactor conditions for conversion from the oxide to chloride form.

#### ACKNOWLEDGMENTS

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