JOURNAL OF MATERIALS SCIENCE **32** (1997) 1479–1482

# Redistribution of copper in KCl-promoted $CuCl_2/\Upsilon$-$Al_2O_3$ catalyst during oxychlorination of ethylene

P. S. SAI PRASAD, K. B. S. PRASAD*, P. KANTA RAO
*Indian Institute of Chemical Technology, Hyderabad 500 007, India*
V. K. KAUSHIK
*Research Centre, Indian Petrochemicals Corporation Ltd, P.O. Petrochemicals, Vadodara 391 346, India*

In a study on oxychlorination of ethylene using KCl-promoted $CuCl_2/Al_2O_3$ catalyst having a composition similar to that of a commercial catalyst, steady-state catalyst composition was determined over a wide range of temperature after identifying the surface copper species by X-ray photoelectron spectroscopy (XPS). The data show a marked shift in the steady-state catalyst composition at about the same temperature at which structural change had been previously reported for similar catalysts. This is confirmed in a separate study of the $CuCl_2$–ethylene reaction which is considered to be the key intermediate step in the overall oxychlorination reaction network.

## 1. Introduction

KCl-promoted $CuCl_2$catalysts are used in oxychlorination of hydrocarbons. The study of these catalysts has evoked considerable interest in characterization [1–4], salt–support interaction [5–7] and kinetics of oxychlorination [8–13]. Structural change is reported in KCl–$CuCl_2$/ fumed silica catalyst [14] and in KCl–$CuCl_2/Al_2O_3$ catalyst [15]. In general, oxychlorination of hydrocarbons on $CuCl_2$-based catalysts occurs by a cyclic mechanism involving $CuCl_2$ which is constantly regenerated *in situ.* Hence, the composition of the catalyst is expected to change significantly with temperature during the reaction. Any structural change in the catalyst may also be reflected in its temperature–composition behaviour. A study of this aspect of the oxychlorination catalyst is particularly important with reference to the commercial oxychlorination of ethylene (to produce dichloroethane, a valuable intermediate in the balanced vinyl chloride monomer process) in a fixed-bed reactor, because of the presence of a large temperature gradient in such reactors [16]. The catalyst in different temperature zones in the reactor may be structurally different and may behave differently with regard to reaction kinetics. The redistribution of copper in the catalyst during oxychlorination is rarely reported in literature. Even less attention has been given to the study of any possible relation between composition and the structure of the catalyst. This paper examines the change in copper distribution during oxychlorination of ethylene over a wide range of temperature in the light of the reported structural change in the catalyst.

Oxychlorination of ethylene was carried out on a catalyst similar to that used in oxycholorination of methane, except that the K/Cu ratio in case of the former is considerably smaller. In this work, the stable intermediate copper species were first identified by X-ray photoelectron spectroscopy (XPS) after exposing the catalyst to oxychlorination. The steady-state solid composition is then determined in separate experiments. The reaction of copper (II) chloride with ethylene, which is the main component reaction of the oxychlorination reaction network, is also carried out on the same catalyst. Both sets of the composition data show a dramatic change in the pattern of copper distribution at the temperature at which the structural change had been previously reported.

## 2. Experimental procedure

### 2.1. Sample preparation

Commercial $Al_2O_3$ (Harshaw, Al-111-61 E), crushed and sieved to a particle diameter of 0.5 mm, was chosen as the support. The pellets were then activated in air at 823 K for 12 h. An aqueous solution of $CuCl_2 \cdot 2H_2O$ and KCl (both B.D.H. Analar grade) was used to impregnate the support by the incipient wetness method. The sample was dried at 393 K for 8 h in air and stored in a desiccator. It has 18% wt/wt copper (II) chloride and 2% wt/wt KCl on $\gamma$-$Al_2O_3$, which corresponds to the commercial Stauffer-C catalyst [16].

---

*Author to whom all correspondence should be addressed.

0022–2461

## 2.2. Technique

A vacuum Generator's ESCALAB MKII spectrometer with Mg$K_\alpha$ radiation (1253.6 eV) was used for measurement of copper state spectra. The X-ray anode was operated at 10 kV, 10 mA, and the vacuum in the analysis chamber was ensured to be better than $5 \times 10^{-8}$ mbar. The catalyst sample, which had been collected under an inert atmosphere after the reaction, was dusted on to double-sided adhesive tape and mounted on a sample holder. The catalyst sample was transferred to the fast-entry lock of the spectrometer and was kept overnight in the preparation chamber before being transferred to the analyser chamber for XPS analysis. C(1s) BE at 285 eV from pump oil contamination was used as a standard for the correction of the charging effect. The data were collected and analysed on an Apple IIe (48k) microcomputer interfaced with the spectrometer.

An adiabatic fixed-bed differential reactor was used for carrying out the overall oxychlorination reaction. Spatial isothermality was ensured by keeping the gas phase conversion below 5%. Attainment of a constant bed temperature indicated that steady- state had been attained. It was found that 4–5 h exposure of the catalyst to the reactants was sufficient to establish the steady-state. The analysis of the used catalyst for copper species was carried out by a standard method based on quantitative conversion of CuCl to $CuCl_2$ by ferric ammonium sulphate [17]. However, because the target chemical was lodged within the pores of the alumina support, the mixture was slightly warmed to hasten the reaction.The total amount of cupric chloride was then estimated gravimetrically as equivalent silver chloride after correcting for chlorides not containing copper. The balance copper was distributed in the light of the XPS analysis. The catalyst composition was not allowed to change during discharge before subsequent analysis. This was ensured by carefully transferring the catalyst in the presence of 99.999% pure nitrogen (IOLAR-1, India). The effluent gas was analysed chromatographically [18] to ensure low gas-phase conversion.

A pulsed micro-catalytic reactor was employed for studying the $CuCl_2$–ethylene reaction using 10% ethylene in helium. The pulse size was 0.5 – 1.0 cm$^3$. The product was analysed by an on-line gas chromatograph equipped with a flame ionization detector using a stainless steel SE-30 on chromosorb column, 3 mm diameter and 12 m long. A new sample of catalyst was taken for each pulse.

# 3. Results and discussion

## 3.1. Identification of copper species by XPS

The XPS of the used catalyst between 925 and 950 eV given in Fig. 1a, shows Cu($2p_{3/2}$) photoelectron line with a strong satellite structure indicating the absence of CuO and $Cu_2O$ [19]. In any case, formation of $Cu_2O$ under the present conditions is unlikely. If that were to happen, chlorine would be a coproduct. But no free chlorine is detected in the present study. As the line shape of this photoelectron line indicates the presence of at least two copper species on the surface of this catalyst, deconvolution of the peak due to different copper species was essential. Kaushik [20] has recently reported binding energy (BE) and full-width at half-maxima (FWHM) values for different copper standards and his data are used as a starting point in peak synthesis and their fitting to the observed Cu($2p_{3/2}$) envelope. Line positions and FWHM values for fitted photoelectron lines are given in Table I and different lines are shown in Fig. 1b. The synthesis of these photoelectron lines is carried out after linear background subtraction using a symmetrical line shape with a flat tail on a VGS-1000 data system.

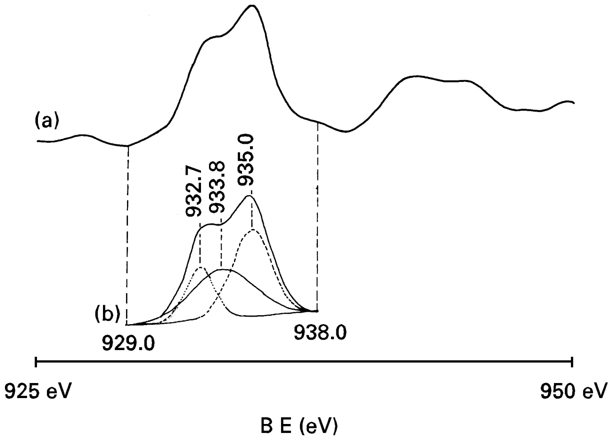

*Figure 1* (a) Cu ($2p_{3/2}$) photoelectron spectrum with satellite structure of the catalyst run at 513 K. (b) Synthesized Cu($2p_{3/2}$) photoelectron lines showing contributions from $Cu^+$ and $Cu^{2+}$ species.

TABLE I Line positions and full-width at half-maxima (FWHM) of synthesized lines of Fig. 1b

| Identified species | Line position (eV) | FWHM (eV) |
|---|---|---|
| $Cu^+$ (CuCl) | 932.7 | 1.6 |
| $Cu^{2+}$(CuO) | 933.8 | 3.4 |
| $Cu^{2+}$($CuCl_2$) | 935.0 | 2.2 |

Fontana *et al.* [21], who investigated the $CuCl_2$–CuCl–KCl phase diagram, reported no binary or ternary phase under the conditions used in the present study. The presence of these double salts in the $Cu^{2+}$ state is expected to exhibit satellites which will differ in intensity from that of CuO and $CuCl_2$ and hence fitting of the photoelectron line envelope and satellite intensity composition corresponding to (CuO + $CuCl_2$) intensity will not be possible in such a case. Our recent study has shown that the intensities of CuO and $CuCl_2$ are 41% and 61% of the main line intensity [19]. Strohmeier *et al.* [22] have also shown that $Cu^{2+}$ from $CuAl_2O_4$ appears at different FWHM and satellite intensity ratios. The formation of copper aluminate is quite unlikely at the temperatures of the present investigation [23]. Thus Table I and Fig. 1 together indicate the presence of CuCl, CuO and $CuCl_2$ on the catalyst.

## 3.2. Temperature–composition behaviour

Fig. 2 is a ternary diagram showing the steady-state catalyst composition obtained by chemical analysis.

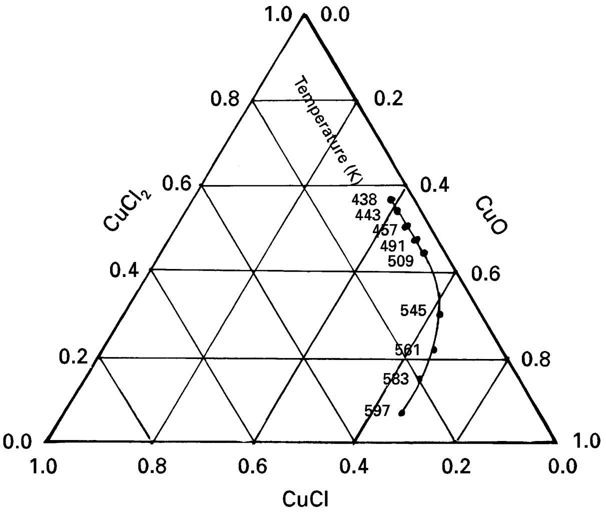

*Figure 2* Ternary distribution of copper species in the bulk at various steady states.

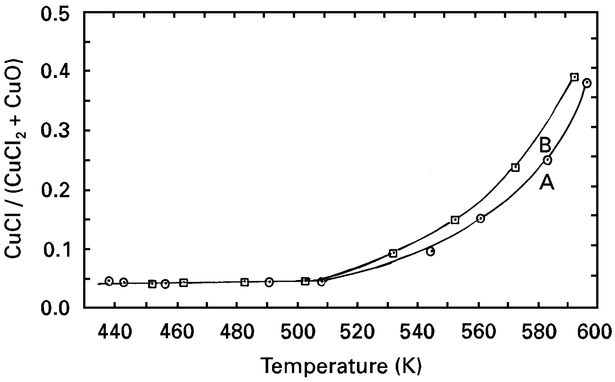

*Figure 3* Effect of temperature on $Cu^+/Cu^{2+}$ based on bulk composition.

Each point on the line corresponds to a steady-state value reached as a result of oxychlorination under isothermal conditions. The initial composition in each case is 100% $CuCl_2$ represented by the apex. At first glance, it is clear that the reaction causes redistribution of copper, whose pattern changes with temperature. Up to about 509 K, there is no net increase in the CuCl content and CuO is formed only at the expense of $CuCl_2$. Above this temperature, there is a gradual change until about 561 K, beyond which CuCl is formed exclusively at the expense of $CuCl_2$, leaving CuO substantially constant.

It is convenient to represent the distribution of copper by the ratio $CuCl/(CuCl_2 + CuO)$. This is plotted against temperature in Fig 3. Curve A refers to the data obtained for the overall oxychlorination reaction in the continuous flow reactor, and curve B refers to the data obtained for the $CuCl_2$–ethylene reaction in the pulsed reactor. The curves appear to merge up to about 510 K and thereafter a sudden change in the pattern of distribution begins to occur, which is shown by both the curves. We have observed that change in pulse residence time has no significant effect (not shown here) on the general shape of curve B except that a higher residence time has resulted in a steeper change at the same temperature of 510 K. It appears, therefore, that both the $CuCl_2$–ethylene reaction and the overall oxychlorination reaction occur somewhat slowly up to a temperature of about 510 K beyond which the rate in each case picks up rather quickly. This leads to the belief that some physical change rendering the catalyst more active may be occurring on the surface at this temperature. Indeed, literature evidence, based on differential scanning calorimetry [14], suggests that at about 513 K, all the crystalline phases disappear in KCl–$CuCl_2$ catalysts. Further, an endothermic DTA peak has also been reported for KCl–$CuCl_2$ catalysts at about 515 K [15]. The sudden change in the pattern of copper distribution observed in the present work seems to reflect the chemical side of this physical behaviour. However, it must be noted that the catalyst used in the present study has a low K/Cu ratio compared to the catalysts used in the above cited studies. It was pointed out by Heinemann [24] that the initial presence of some CuCl together with $CuCl_2$ on the alumina support is necessary in order to avoid long induction times in oxychlorination of ethylene. Thus, the observed temperature–composition behaviour corroborates with the literature evidence, and considering all available information including the present study, it is quite reasonable to conclude that a threshold temperature of about 510 K exists for vigorous oxychlorination reaction to set in.

## 4. Conclusions

1. XPS analysis of reacted $CuCl_2$ oxychlorination catalyst has indicated the presence of CuCl, CuO and $CuCl_2$ compounds of copper.
2. Oxychlorination of ethylene, or even exposure of the catalyst to ethylene alone, is found to cause redistribution of copper, which is found to be a strong function of temperature.
3. A sudden change in the pattern of copper redistribution has been observed at a temperature at which structural change had been previously reported for similar catalysts.

## Acknowledgements

The authors thank the Director, Indian Institute of Chemical Technology, Hyderabad, India, for permission to publish this work. Financial assistance provided by M/s Indian Petrochemicals Corporation Limited, Vadodara for the catalyst development project is gratefully acknowledged.

## References

1 P. G. HALL, M. PARSLEY and D. R. ROSSEINSKY, J. Chem. Soc. Farad. Trans. 1 **79** (1983) 343.
2. P. G. HALL, P. HEATON and D. R. ROSSEINSKY, *ibid.* **80** (1984) 2777.
3. P. G. HALL, R. A. HANN, P. HEATON and D. R. ROSSEINSKY, *ibid.* **81** (1985) 69.
4. P. A. SERMON, K. ROLLINS, P. N. REYES, S. A. LAWRENCE, M. A. MARTIN LUENGO and M. J. DAVIS, *ibid.* **83** (1987) 1347.

5. P. AVILA, J. BLANCO, J. GARCIA-FIERRO and S. MENDIOREZ, in "New Horizons in Catalysis", edited by T. Seiyama and K. Tanabe, Vol. 7B (Elsevier, Amsterdam, New York, 1982) p. 1031.
6. J. VALLE, A. VARGAS, J. FERRIERA and A. FLORES, *ibid*., p. 1040.
7. E. M. FORTINL, C. L. GARCIA and D. E. RESASCO, *J. Catal.* **99** (1986) 12.
8. R. V. CARUBBA and J. L. SPENCER, *Ind. Eng. Chem. Proc. Des. Dev.* **9** (1970) 414.
9. R. P. ARGANBRIGHT and W. F. YATES, *J. Org. Chem.* **27** (1962) 1205.
10. M. L. SPECTOR, H. HEINEMANN and K.D. MILLER, *Ind. Eng. Chem. Proc. Des. Dev.* **6** (1967) 327.
11. H. D. EICHHORN, C. JACKH, W. D. MROSS and H. SCHULER, in "Proceedings of the 8th International Congress on Catalysis", Berlin (Dechema, Frankfurt-am-Main, 1984) p. IV-647.
12. E. CAVATERRA, *Hydrocarbon Processing* **67** (1983) 63.
13. A. SARAF, H. L. GREENE, M. S. KOSUSKO and S. NARAYANAN, *J. Catal.* **120** (1989) 478.
14. Wm. C. CONNER Jr, W. J. M. PIETERS and A. J. SEGNORELLI, *Appl. Catal.* **11** (1984) 59.
15. C. L. GARCIA and D. E. RESASCO, *ibid.* **46** (1989) 251.
16. J. S. NAWORSKI and E. S. VELEZ "Applied Industrial Catalysis", Vol. 1, (Academic Press, San Diego, 1983) p. 239.
17. A. I. VOGEL, "Quantitative Inorganic Analysis", (Longmans, London, 1961 p. 323).
18. A. ARCOYA, A. CORTES and X. L. SEONE, *Ind. Eng. Chem. Proc. Res. Dev.* **19** (1980) 77.
19. V. K. KAUSHIK, *Z. Phys. Chem. Neue Folge* **168** (1990) 161.
20. V. K. KAUSHIK, *Spectrochim. Acta* **44B** (1989) 581.
21. C. M. FONTANA, E. GORIN, G. A. KIDDER and C. S. MERIDITH, *Ind. Eng. Chem.* **44** (1952) 363.
22. B. R. STROHMEIER, D. E. LEYDENO, R. SCOTTFIELD and D. M. HERCULES, *J. Catal.* **94** (1985) 514.
23. C. ZIPELLI, J. C. J. BART, S. GALVAGNO and C. CIMINO, *Z. Anorg. Allg. Chem.* **502** (1983) 199.
24. H. HEINEMANN, *Chem. Tech.* **1** (1971) 286.

*Received 16 February
and accepted 20 May 1996*