Low Temperature Ethylene Chemisorption (L.T.E.C.): A Novel Technique for the Characterisation of $CuCl_2$–KCl/γ-Al_2O_3 Oxychlorination Catalysts

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Low temperature ethylene chemisorption (l.t.e.c.) by promoted and unpromoted copper chloride catalysts supported on γ-alumina is described and the ethylene uptake correlated with copper loading and Cu/K atomic ratio.

The selective adsorption of gases on metal and metal oxide and sulphide catalysts has been used extensively to evaluate surface area, particle size, and the degree of metal dispersion. While chemisorption of carbon monoxide, hydrogen, and oxygen have been widely used, nitrous oxide decomposition and hydrogen–oxygen titration are less commonly employed.[1] Recently, attempts have been made to characterise unsupported and supported copper chloride catalysts by adsorption of ethylene using transient gas adsorption chromatography and temperature programmed desorption mainly to calculate heats of adsorption from isotherms.[2] Although low temperature adsorption of oxygen is available to characterise the catalysts used in oxidation,[3] hydrodesulphurisation *etc.*, it has not been possible to characterise those used in the oxychlorination of ethylene to give 1,2-dichloroethane using this technique. We now report the development of low temperature ethylene chemisorption (l.t.e.c.) at −78 °C using two adsorption isotherms to determine the extent of irreversible adsorption as a function of copper(II) chloride loading.

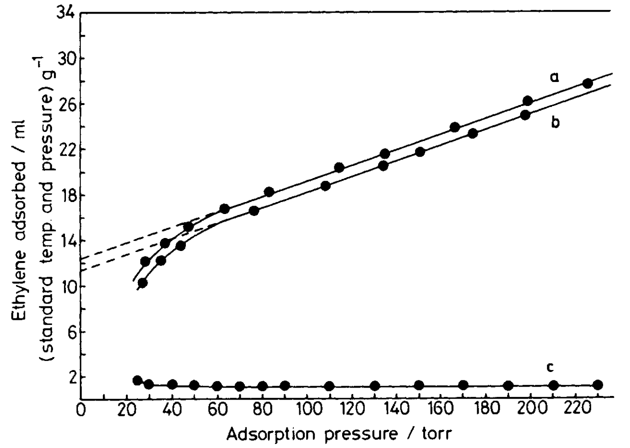

Figure 1. Low temperature ethylene adsorption isotherms at −78 °C. Catalyst: $CuCl_2$–KCl/γ-Al_2O_3 (Cu = 6.68 wt %, K = 1 wt %). (a) Physisorption + chemisorption; (b) physisorption; (c) difference between (a) and (b).

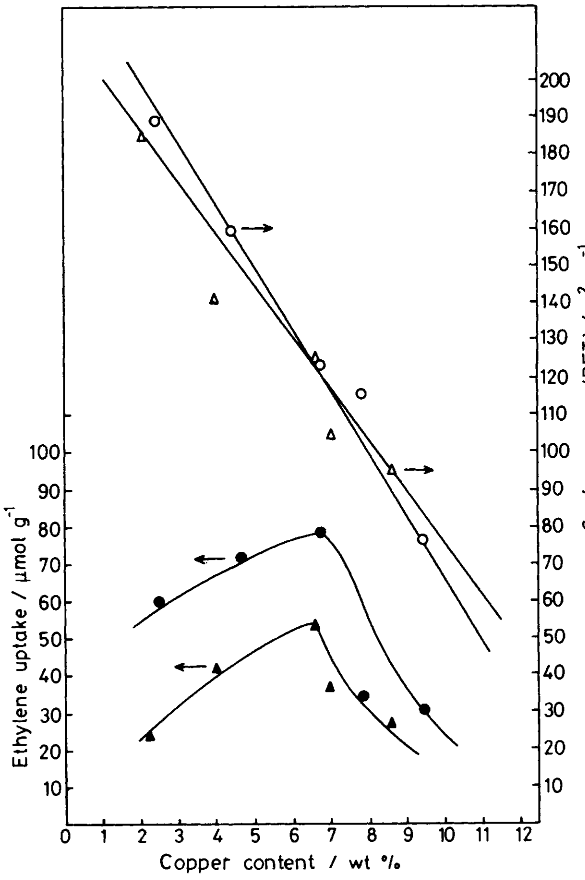

Figure 2. Variation of ethylene uptake and BET (Brunauer–Emmett–Teller) surface area with copper loading. △,▲: promoted catalyst; ○,●: unpromoted catalyst.

Unpromoted and KCl-promoted $CuCl_2$ catalysts were prepared by an incipient wetness method using commercial γ-alumina (Harshaw Al-111-61E) as a support. They were first dried overnight at room temperature and then at 110 °C for 6 h. The loading of $CuCl_2$ on the support varied between 2 and 10% by weight of Cu and the atomic ratio of Cu/K ranged between 2 and 11. The promoted catalysts were further calcined at 250 °C for 2 h under pure N_2 gas. They were then selectively extracted with acetone in a soxhlet to remove unreacted $CuCl_2$ from the support. In addition a sample of KCl supported on γ-alumina (*ca.* 1 wt % of K) and one of pure $CuCl_2$ (by heating $CuCl_2 \cdot 2H_2O$ under N_2 at 250 °C for 2 h) were also prepared.

The conventional high vacuum glass system was used for the l.t.e.c. experiments. The samples were evacuated at room temperature under 10^{-6} torr for 2 h. The first adsorption isotherm representing the sum of physisorbed and chemisorbed ethylene was determined at −78 °C. After evacuation at 10^{-5} torr for 1 h at the same temperature a second isotherm representing only physisorbed ethylene was generated in an identical manner. All the isotherms so obtained exhibited non-linearity up to an adsorption pressure of 60 torr in the pressure range studied (20—200 torr). By extrapolating the parallel linear portions of these isotherms (Figure 1) the chemisorbed ethylene could be determined from the difference of their intercepts on the *y*-axis.

Plots of ethylene uptake and of Brunauer–Emmett–Teller (BET) surface area *vs.* copper content are given in Figure 2. At a copper loading of *ca.* 7 wt % the two curves showed maximum chemisorption values. However, addition of KCl

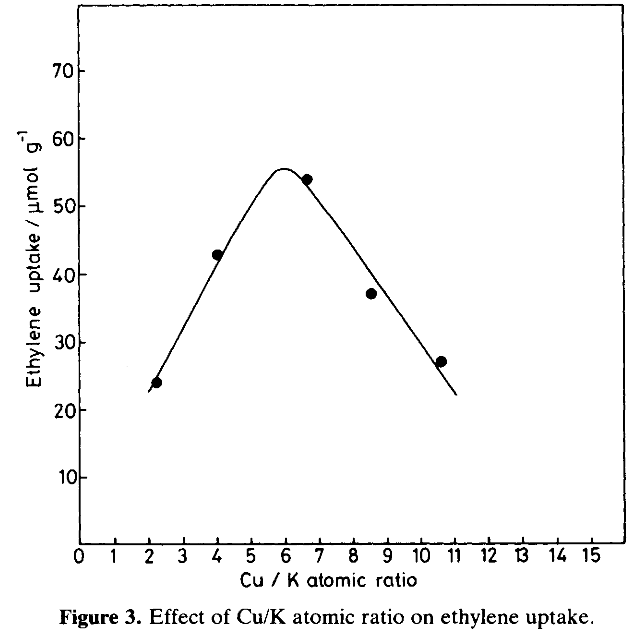

Figure 3. Effect of Cu/K atomic ratio on ethylene uptake.

Table 1. Adsorption data on acetone-extracted catalysts.

	Cu content/ wt%	Volume of ethylene chemisorbed/μmol g⁻¹	BET surface area/ m² g⁻¹
1	1.72	25	161
2	3.22	42	171
3	4.74	75	160
4	4.78	71	144
5	4.40	62	138

decreased the adsorption to some extent. A plot of ethylene uptake *vs.* Cu/K atomic ratio is given in Figure 3. At a Cu/K atomic ratio of *ca.* 6 the curve exhibited a maximum.

It was reported that with $CuCl_2$–KCl impregnated on α-Al_2O_3[4] and γ-Al_2O_3[5] the activity maximum was a function of $CuCl_2$ loading in the oxychlorination of ethylene and the maximum rate of reaction was observed at a copper loading of *ca.* 8 wt % and at a Cu/K atomic ratio of *ca.* 6. Thus our results of l.t.e.c. show a similar trend to those previously reported.

From the data on acetone extracted catalysts (Table 1) we found that the extent of the salt–support interaction initially increases with increase in the $CuCl_2$ loading and then remains constant, forming a monolayer. It can be concluded that ethylene chemisorbs on the interacting species as the chemisorption of ethylene on pure $CuCl_2$ was very low (5 μmol g^{-1}). γ-Al_2O_3 also contributes to ethylene uptake (40 μmol g^{-1}). Potassium chloride reduces the concentration of acid sites on the γ-Al_2O_3 surface decreasing the ethylene uptake due to the support. The chemisorption of KCl-doped γ-Al_2O_3 (20 μmol g^{-1}) confirmed this observation. The non-interacting $CuCl_2$ inhibits ethylene chemisorption on the interacting species probably by blocking the pores with crystallites of $CuCl_2$, because of the decrease in BET area.

L.t.e.c. may thus be related to the active sites on the oxychlorination catalysts.

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