

EFFECT OF DISPERSION ON THE KINETICS OF REDUCTION OF CUPRIC CHLORIDE BY ETHYLENE^{*}

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Kinetics of reduction of cupric chloride by ethylene using (i) KCl-CuCl₂- γ -Al₂O₃, (ii) CuCl₂- γ -Al₂O₃ and (iii) unsupported CuCl₂ has been studied. It is observed that the activation energy of the reaction is less sensitive to dispersion when KCl is not present. However KCl promotion has the effect of substantially reducing the activation energy.

1. Introduction

Reduction of cupric chloride to cuprous chloride is an important component reaction in the overall mechanism of oxychlorination of ethylene to ethylene dichloride [1]. It is found that the progress of a topochemical reaction such as this one can be conveniently described by Avrami-Erofeev equation [2], which has been applied successfully to many reacting systems [3-6]. The present work aims to show that the title reaction follows this model even when the solid reactant is dispersed on alumina which is the form in which it is generally used as oxychlorination catalyst; also an attempt is made to explain the role of potassium chloride as promoter with reference to this model

2. Experimental

Commercial γ -Al₂O₃ (Harshaw, Al-III-61E, sieved to 18/25 BSS mesh) was chosen as the support. It had a BET surface area of 264 m²/g. Aqueous solution of cupric chloride (BDH, Analar) alone and in combination with potassium chloride (BDH, Analar) were used to prepare the unpromoted and promoted catalysts respectively. The impregnation was done by the incipient wetness method. The catalysts

were dried at 393 K for eight hours in air. The unpromoted catalyst contained 18 wt% CuCl₂ and the promoted catalyst had 2 wt% KCl in addition to 18 wt% CuCl₂. Pure cupric chloride powder was dried at 393 K for eight hours and used for the reactivity studies.

A tubular reactor of 8 mm inner diameter with a facility to quickly discharge the catalyst was used. The catalyst bed (about 1 g) was heated electrically under flowing nitrogen (IOL, AR, 3 ℓ /min) to the required temperature with an accuracy of ± 1 K and was allowed to remain at the same temperature for one hour. Then ethylene was admitted by means of a 4-way stop-cock at a flow rate of 3 ℓ /min which was sufficient to eliminate mass transfer effect. Nitrogen flow was stopped at the instant of ethylene admission. Several runs were performed by changing the temperature and the time of exposure of the catalyst bed to ethylene. In each run a fresh sample of catalyst was used and after the required time had elapsed, the catalyst was quickly discharged into a standard ferric ammonium sulphate solution under flowing nitrogen. The resultant ferrous species was then titrated with standard ceric sulphate [7] using ferroin as the indicator and the extent of CuCl₂ conversion was calculated. The blank analyses for Cu₂Cl₂ after heating the catalyst at various temperatures in the inert medium did not give any significant conversions of CuCl₂.

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3. Results and discussion

Avrami-Erofeev equation has the following form:

$$[\ln 1/(1-x)]^{1/m} = kt, \quad (1)$$

where x is the conversion of solid reactant at time t and m and k are constants; it is expected that m is independent of temperature and k follows Arrhenius dependence.

Fig. 1 is a log-log plot of eq. (1) for three sets of data presented in linearised form, showing the applicability of Avrami-Erofeev model to reduction of cupric chloride by ethylene when the solid is present either as bulk or as dispersed phase or when the dis-

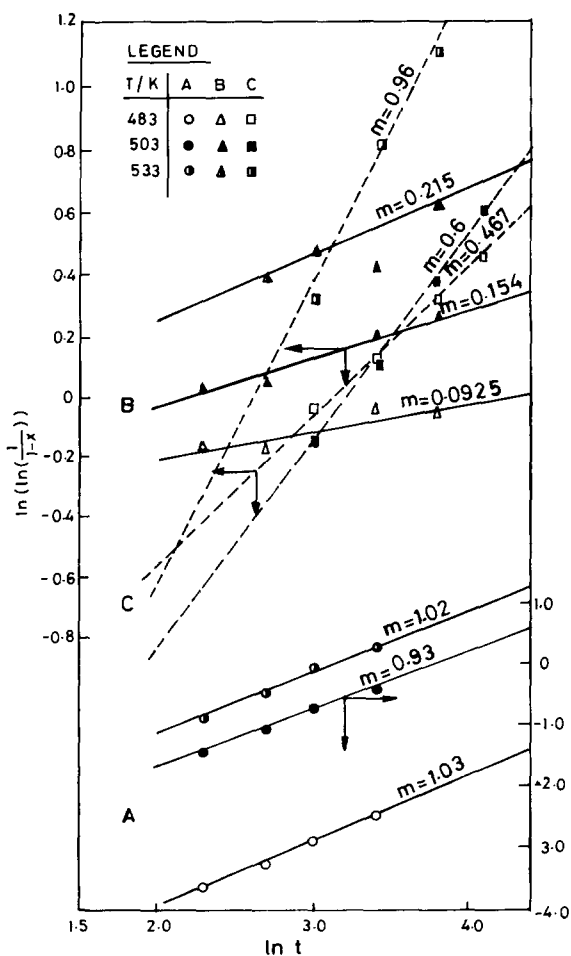


Fig. 1. Log-log plots for the unsupported and supported cupric chloride.

persed phase is doped with KCl. Curves shown at A refer to bulk or unsupported CuCl_2 . The lines are nearly parallel with slope equal to unity ($m \approx 1$). This indicates that the reduction proceeds via a well-defined single step transformation and that it is a case of one dimensional growth of nucleus. The nucleation has probably occurred already in the adjoining lateral areas, permitting the growth only along the inward drawn normal. It may be concluded that the nucleation has probably not occurred in the interior of the solid crystallite, for, then, the resulting three-dimensional growth would have yielded a value of 3 for m . It may be noted that for $m=1$, eq. (1) also represents the first order rate model, although in this case the order is with respect to conversion.

On the other hand, dispersed CuCl_2 , while following Avrami-Erofeev equation, has yielded a remarkably low value for m as depicted by curves shown at B. Dispersion has probably hindered growth of nucleus in the only direction it could grow, because the nucleus encounters alumina support almost as soon as it forms. However, unlike the case of unsupported CuCl_2 , curves at B are not parallel, but register a two-fold increase in slope from 0.0925 at 483 K to 0.215 at 533 K. Such temperature dependence of m indicates lowering of the intrinsic reaction rate at higher temperature, perhaps due to increased diffusion resistance or perhaps due to unaccounted increase in surface area following opening of hitherto blocked pores caused by loss of chlorine from CuCl_2 . The later explanation seems to be more plausible as indicated by the measured BET surface areas of fresh and reacted samples; a fresh sample has a BET surface area of $111 \text{ m}^2/\text{g}$ whereas the samples completely reacted at 483 K and 533 K have $128 \text{ m}^2/\text{g}$ and $137 \text{ m}^2/\text{g}$ respectively showing an increase of about 20%. In the case of unsupported CuCl_2 , which is not porous, the surface area is unlikely to change, leaving m a constant.

Curves shown at C in fig. 1 refer to the case when KCl is added to CuCl_2 . It is generally believed that KCl acts as a promoter in oxychlorination. As will be explained below, its role at least in the title reaction, seems to be that of a moderator. Curves at C are similar to those at B except that the slope m at each temperature is larger than the corresponding one at B. This indicates that the presence of KCl reduces the extent of dispersion probably by forming a double

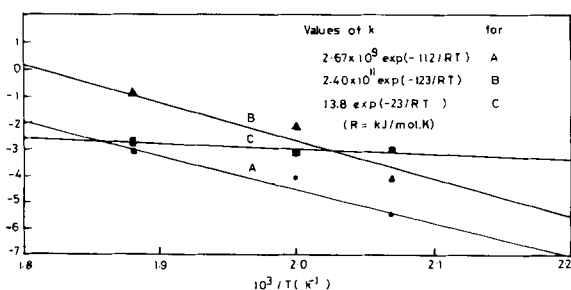


Fig. 2. Arrhenius plots for the unsupported and supported CuCl_2 .

salt [8] or a complex [9] or even by changing phase [10]. The temperature behaviour of m is similar to that of KCl-free supported CuCl_2 and could be corroborated by a similar trend in observed BET surface area.

Arrhenius plot of the rate constant k is shown in fig. 2. Using the same legend as in fig. 1, the activation energy for case A is close to that for case B, which perhaps indicates that dispersion has not changed the basic reaction mechanism. However, the frequency factor increased from case A to case B by about 100 times, which is the same order of magnitude of increase in surface area of supported CuCl_2 . Presence of KCl (lines at C), however, caused a tremendous decrease in activation energy presumably due to the change in reaction mechanism; there is also a loss of active surface area as indicated by the low value of frequency factor. The role of KCl thus appears to be a moderator as it has reduced the degree of difficulty of reaction by lowering the activation energy at the same time masking a great deal of hitherto active surface. Blocking of active surface by KCl in CuCl_2 catalysts has also been suggested earlier in the kinetic study of oxychlorination of ethylene [7]. More recently in a study of low temperature chemisorption of ethylene reported from this laboratory [12] it has been observed that KCl promotion has led to a lower uptake of ethylene for

CuCl_2 catalysts indicating a decrease in active site concentration. The present observation of decrease in the frequency factor due to KCl promotion which also indicates a decrease in active site concentration is thus corroborated. Exactly how this is achieved is a matter of speculation at this stage. One may put forward an argument that the free energy change in the double-salt formation is highly negative and that the double salt is taking part in the reduction reaction losing chlorine much more readily than cupric chloride. Further investigation, particularly, into the effect of support which is under way at the authors' laboratory, may throw more light on the system. We propose to publish the results of our studies on the role of KCl in a subsequent paper.

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