

A Microstructural Study of a Supported Liquid Phase Oxychlorination Catalyst

J. A. LITTLE* AND C. N. KENNEY†

*Department of Metallurgy and Materials Science, and †Department of Chemical Engineering,
University of Cambridge, Cambridge, England

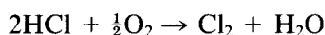
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A supported liquid phase catalyst consisting of a copper chloride/potassium chloride mixture with or without cerium chloride and supported on either alumina or titania has been investigated using X-ray diffraction and transmission electron microscopy both with and without a heating stage. Catalysts used in an oxychlorination experiment have also been examined. X-Ray and TEM studies confirmed the existence of small clusters of active phase which were mobile at high temperatures and could coalesce to a greater or lesser extent depending upon the addition of cerium chloride. The X-ray studies also indicated the presence of a $K_2CuCl_4 \cdot 2H_2O$ phase in the used catalyst. © 1985 Academic Press, Inc.

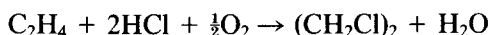
INTRODUCTION

Supported liquid phase (SLP) catalysts find industrial application in various organic reactions (e.g., chlorination, selective oxidation and dehydrogenation, and akylation) and in SO_2 oxidation. Despite many published data on the thermodynamics and kinetics of these reactions there are but few references to the microstructures of these catalysts, and these mostly refer to the vandanium oxide—potassium sulphate system (1-3).

This work concerns the SLP catalyst (alumina- or titania-supported copper chloride) used in the Deacon process reactions



and



whose thermodynamics and kinetics have been much investigated (4, 5). Chlorides of the alkali metals and rare earth metals are often added.

Fontana *et al.* (6) give the phase diagram of the $CuCl-CuCl_2-KCl$ system and show that at the operating temperature (300-400°C) the catalyst is always partly liquid. The penetration of the pores of the oxide

support by liquid and its redistribution during the reaction profoundly affect the liquid and gas-phase diffusion resistance, and hence the catalytic effect. In the $V_2O_5-K_2S_2O_7/SiO_2$ system (300-nm pore-diameter silica) contact of the catalyst with unimpregnated silica for a few minutes at 500°C is sufficient to extract most of the melt (7), illustrating the high mobility of the liquid. Sharma *et al.* (1, 2) have investigated the microstructure in $V_2O_5-K_2SO_4/SiO_2$ by various methods both before and after use in methanol oxidation. Although certain distinct crystalline structures were observed, X-ray diffraction showed no evidence of interaction between the V_2O_5 and K_2SO_4 .

We report in this paper on the microstructural changes occurring as a result of the Deacon reaction on a supported copper-potassium chloride catalyst. The work includes an *in situ* study in the transmission electron microscope of the effect of heating on the catalyst microstructure.

EXPERIMENTAL

Catalyst preparation. The catalysts used consisted of mixed copper and potassium chloride (BDH analytical grade) on supports of alumina (SAEHS-33, 4 m^2g^{-1}) and titania (CLDD-1362, 5.2 m^2g^{-1}) with cerium

chloride (BDH analytical grade) added to some preparations as a promoter. All catalysts were prepared using standard impregnation techniques with subsequent grinding. Compositions were chosen to give molar ratios of 2Cu/8K or 2Cu/0.2Ce/8K on both supports.

X-Ray analysis. X-Ray powder diffraction spectra were recorded on a Philips 1011 vertical diffractometer using $\text{CuK}\alpha$ radiation.

Electron microscopy. Samples for transmission electron microscopy were prepared using conventional techniques for powders with chloroform as the suspension medium and supported on a holey carbon film. A Philips 400T STEM/TEM microscope was used for analytical measurements and a Philips 300 EM for the heating experiments.

RESULTS AND DISCUSSION

Catalyst Preparation

The supports used were characterized for specific surface area and mean pore size using gas absorption and mercury porosimetry. As catalysts they were used to investigate the kinetic parameters in the Deacon reaction and these results will be reported elsewhere (8). Low surface area supports were used to prevent excessive formation of CO and CO_2 . Values in Table 1 show a mean pore size of approximately 200 nm, a value compatible with the BET surface area measurements using simple models assuming spherical particles. Thus there is no porosity inside the carrier particles and the only existing porosity is as visualized in the TEM micrographs.

TABLE 1

Properties of Titania and Alumina Supports

	Surface area (BET) (m^2g^{-1})	Porosity (ml g^{-1})	Mean pore size (nm)
TiO_2 (CLDD-1362)	5.2	0.43	225
SAEHS-33 (Al_2O_3)	4.0	0.32	193

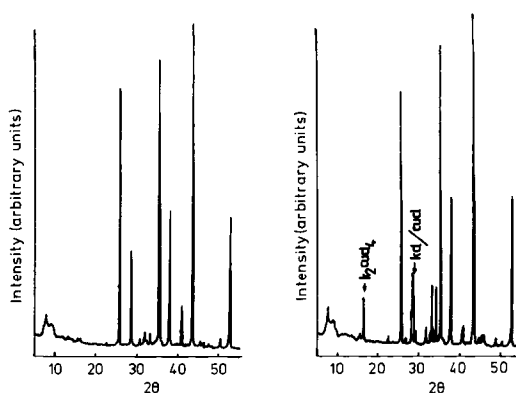


FIG. 1. X-Ray diffraction pattern from nonreacted and reacted alumina-supported catalyst.

X-Ray Studies

X-Ray diffraction was used to examine the bulk catalyst both before and after reaction. Samples of the raw catalyst show intense peaks characteristic of the support used and smaller peaks corresponding to potassium, copper and cerium chlorides. Figure 1 shows results for the alumina-supported catalyst. Line-broadening studies gave the support crystallite size as approximately $1 \mu\text{m}$ in good agreement with TEM studies. The small concentration of active phase makes analysis of peak profiles less rigorous but certain differences are apparent between the reacted and nonreacted catalyst. The (200) KCl peak and the (111) CuCl peak overlap on the unused catalyst due to small crystallite size estimated at approximately 30 nm. This is in good agreement with the average size of dark clusters seen in the TEM before a heating experiment which was 10–20 nm. After reaction the two diffraction peaks narrowed due to particle coarsening and could be resolved into separate components giving an average cluster size of approximately 40 nm. Also the relative intensity of the dual KCl/ CuCl peak decreased with respect to the alumina and a peak representing the phase $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ appeared with a cluster size of approximately 100 nm. Thus there appeared to be interaction between chlorides forming

this compound although some KCl and CuCl still remained.

In the titania-supported samples no equivalent reaction was seen, although one strong potassium chloride reflection disappeared.

ELECTRON MICROSCOPY

In Situ Heating

A group of sufficiently electron transparent particles were chosen and bright-field micrographs with their associated diffraction patterns were taken at the beginning of the run. Due to the small volume of sample examined in diffraction no evidence for diffraction due to CuCl, CuCl₂, or KCl was observed. Heating was begun and observations were made using a nonfocused electron beam. During the heating thermal currents caused image drift and the chosen area was manually centered using the specimen translation controls. Stability was achieved after about 5 min and thus this was the time that the specimen remained at each temperature.

It has been shown (9) that for a good thermally conducting metallic specimen a small temperature rise (<10°C) may occur on the specimen where the stationary electron beam is impinging. However, for a poor thermal conductor the rise may be appreciably greater, and using the data from Hobbs (9) could be as much as 60°C in an alumina foil and 200°C in an amorphous carbon film. In the results presented, the electron beam was under-condensed to drastically reduce such heating whilst keeping photographic time to approximately 1 s. Thus in the following micrographs it has been assumed that there has been a further heating of 50°C above the furnace temperature at each setting.

Figure 2 shows a sequence from a heating run on the catalyst consisting of copper and potassium chlorides on the titania support. The approximate temperature is given for each photograph. The bright-field image at room temperature shows no major indica-

tion of discrete chloride clusters on the support although a higher magnification image of one of the titania particles (Fig. 3) does show some small dark spots, the largest of which is approximately 5 nm in diameter. This may represent some initial clustering of the chlorides although only a few of these dark spots are seen at the beginning of a reaction. By 400°C many more dark spots have appeared than at room temperature with a size range between 5 and 40 nm and on one support particle two spots can be seen to be merging. Such effects could be caused by a change of tilt of the specimen particle causing foreshortening and thus apparently a merging, or a change in diffraction conditions. However, careful examination of the support/dark phase geometry, careful tilting experiments, and the comparison of succeeding images confirm that the dark spots are indeed, on average, moving together and agglomerating into larger entities. At 500°C further relative motion has occurred between spots although the average size remains at approximately 40 nm in good agreement with X-ray studies. The highest temperature of 600°C shows that there appears to be an upper limit on the size to which the spots grow as, although a little relative translation appears to have occurred, no further coarsening of cluster size is apparent.

Figure 4 shows a similar sequence of micrographs from the alumina-supported catalyst plus cerium chloride. The initial support now shows more evidence of some preexisting clusters of chlorides, a feature evident in both cerium-containing catalysts, but not those without cerium. The sequence in Fig. 4 shows a much slower development of the clustered phase and it was not until approximately 500°C that some clusters did appear to have grown and some evidence of merging could be seen. Similar results were obtained using both of the other catalyst formulations. It must be stressed that these reactions are not occurring under reaction conditions and are occurring under a moderate vacuum, but in all

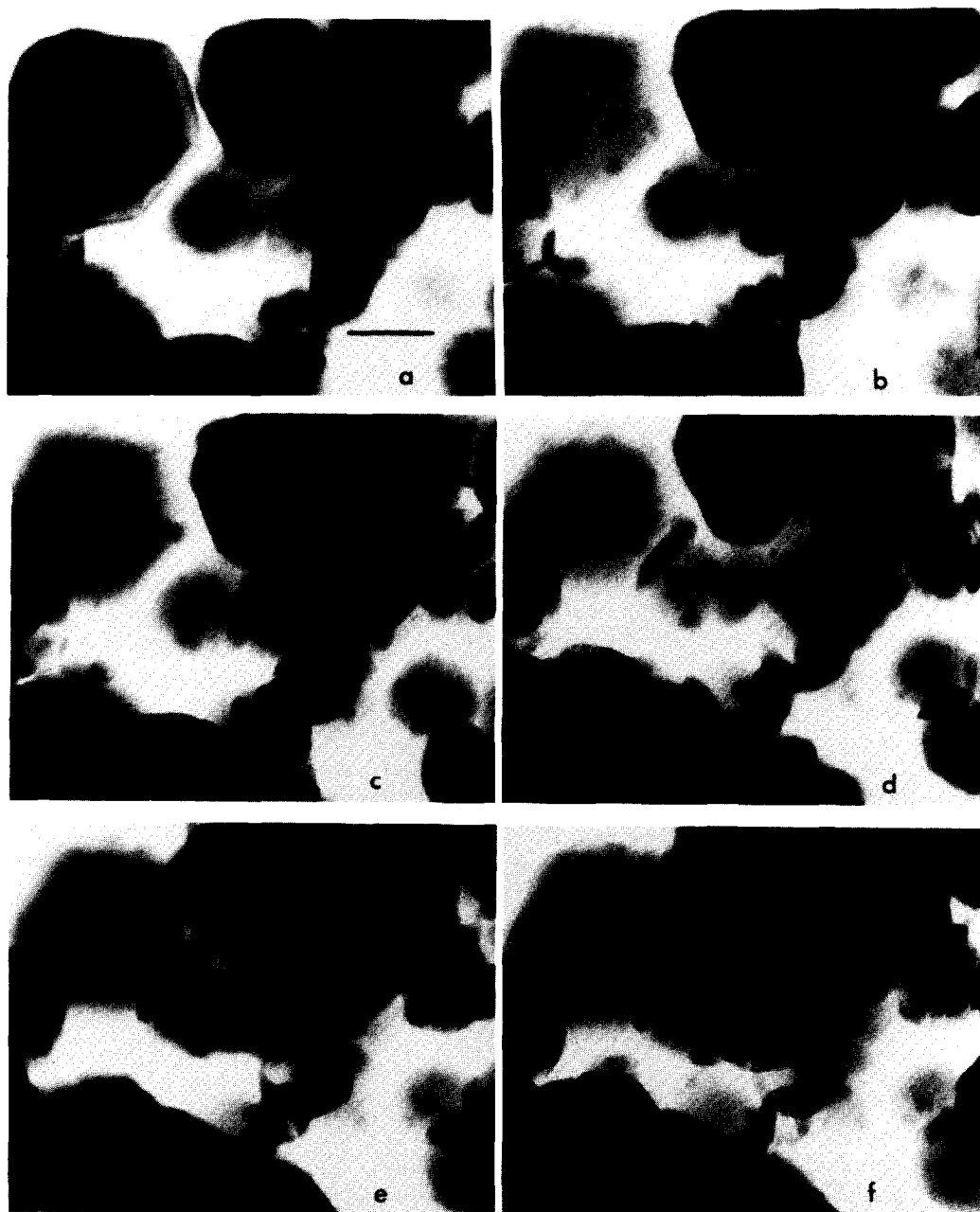


FIG. 2. Electron micrographs during a heating run on copper and potassium chlorides on titania. (a) Room temperature, (b) 416°C (c) 457°C, (d) 500°C, (e) 550°C, (f) 650°C. Bar = 0.5 μm .

cases examined in this way the cerium chloride-containing catalyst had a decreased tendency to show agglomeration of the clusters as the temperatures were raised and this may thus act as an additional pro-

moting factor to any chemical promoting effects. In the accompanying kinetic measurements (8) the activity of the catalysts for the oxidation of hydrogen chloride was found to be dependent upon the support

and decreased in the order

silica > alumina > titania

and this is also in good agreement with the increased tendency to agglomeration in the titania-supported catalysts, both with and without cerium.

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM)

All catalysts used were examined by STEM utilising energy dispersive X-ray analysis (EDX) with a LINK computer. All samples gave results very similar to those in the heating runs and thus a titania-supported copper/potassium chloride will be used as an example. It was possible to obtain information from two distinct areas on the specimen, as both the small black clusters on the titania were again evident and also some particles were seen on the carbon grid, these probably being areas of active phase which had become detached during the grinding of the powder and had settled out on the carbon support film.

The range of concentrations found in the small clusters varied enormously for both types of site. When analysing particles supported on the carbon the copper/potassium ratios varied from 19:1 to 1:1 while for the clusters on the titania the ratios of copper to potassium showed an equally wide variation with wholly potassium-containing clusters being found.

To overcome this inhomogeneity, a series of analyses of clusters on both used and unused catalysts were carried out and although still showing a wide variation the average weight percentage of copper to potassium on the unused catalyst was found to be approximately 1.3 wt% copper and 0.3 wt% potassium which corresponds to a molar ratio of approximately 1:1 copper to potassium. These results show the inhomogeneity of the active phase as formed by this method although the overall composition does approach the expected initial composition.

Results from the titania specimen after use in a catalytic run showed that the aver-

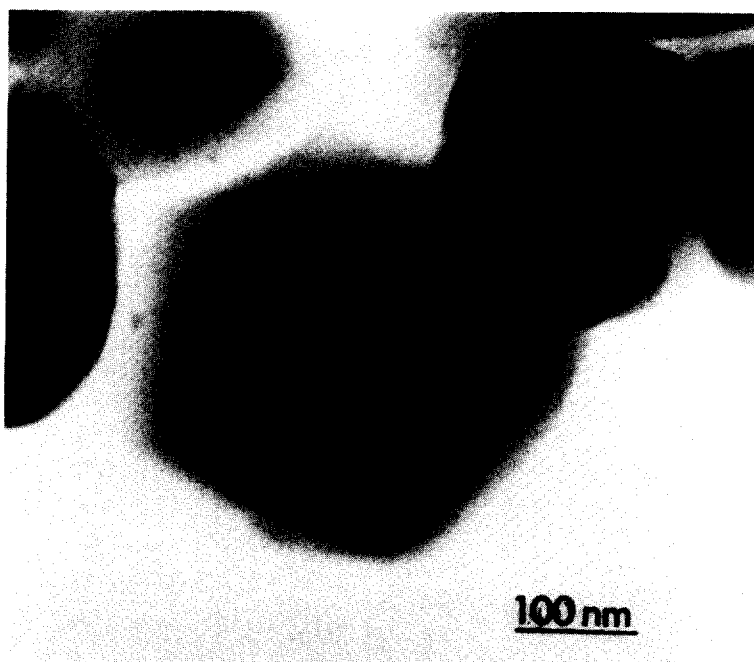


FIG. 3. Higher magnification of one grain from Fig. 2 (room temperature). Bar = 100 nm.

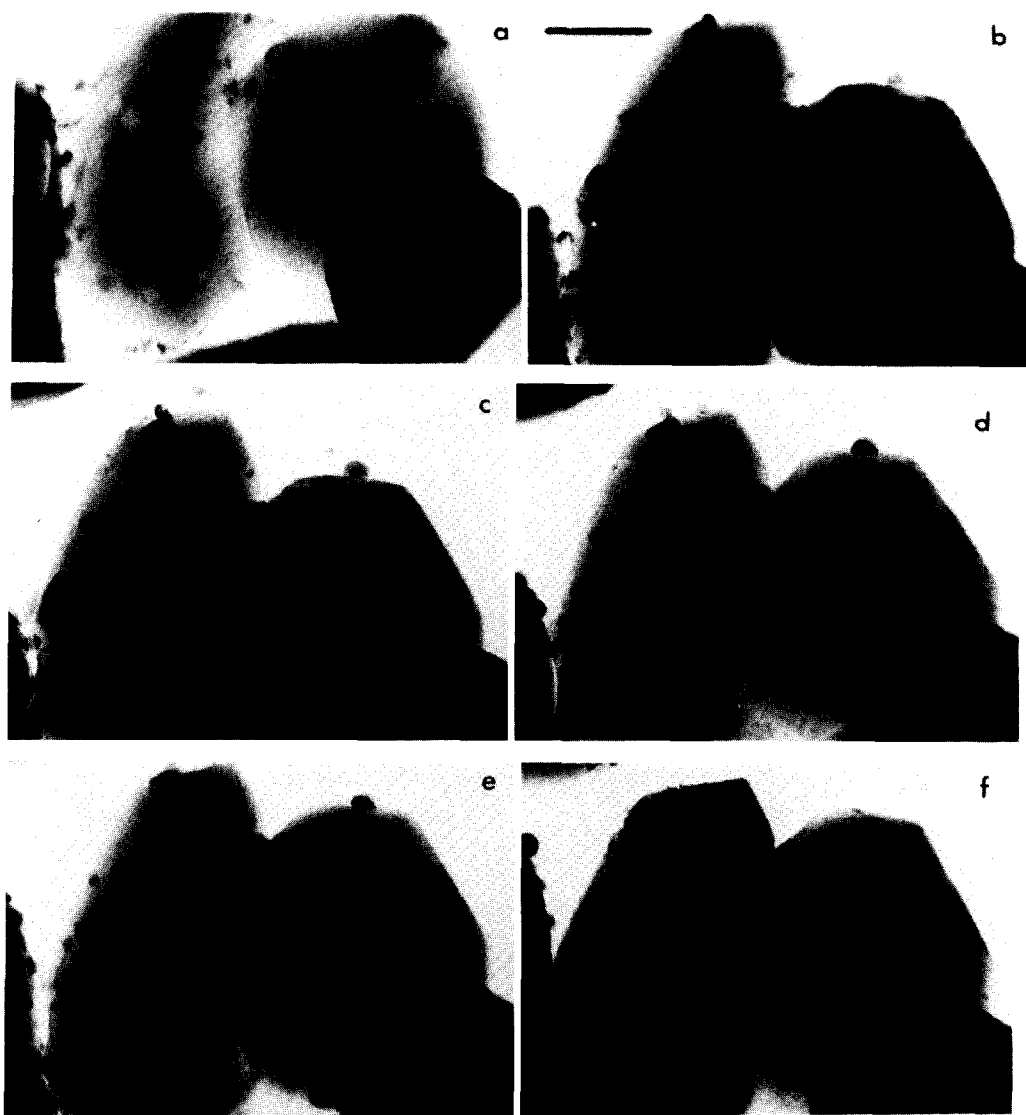


FIG. 4. Heating run on copper, potassium, and cerium chlorides on alumina. (a) 90°C, (b) 320°C, (c) 380°C, (d) 500°C, (e) 550°C, (f) 700°C.

age copper concentration in the clusters increased reaching approximately 4 wt% copper on titania. The potassium level decreased to approximately 0.1 wt% in agreement with the disappearance of the diffraction peaks associated with potassium chloride. This result also correlates well with the lesser activity in the titania-supported catalyst (8).

These analyses are given to show a general trend between the used and unused cat-

alysts as indicated by many experimental determinations. However, they must be used as a general guide and indicate the difficulty of using X-ray measurements on a microscale to investigate a highly heterogeneous dispersion.

CONCLUSION

Supported liquid phase catalysts are a class of industrially important materials which depend upon a high dispersion of the

active phase and thus a suitable microstructure. In this study copper, potassium and cerium chlorides distributed on alumina and titania have been examined, both before and after a catalytic test reaction and during an *in situ* heating run. X-Ray studies have confirmed the existence of clusters of a similar size to those seen in the TEM and indicated the presence of a $K_2CuCl_4 \cdot 2H_2O$ phase in the used catalyst. Although spectrochemical data from the TEM investigation confirmed that such a phase could be present it highlighted the existence of a wide range of chemical composition in the observed clusters. During the *in situ* heating experiment the clusters were seen to move over the support and merge as the temperature was increased although those samples containing the cerium chloride did not appear to merge and form as large a cluster size as did the samples without cerium chloride. Thus in addition to its "promoting" behaviour, the cerium chloride may have further effects, possibly on the surface energies of the small clusters,

which hinder coalescence and thus maintain higher values of active surface area. The support material is also important in determining activity. In particular titania may produce a significant clustering effect.

REFERENCES

1. Sharma, R., Rai, K., and Srivastava, R. D., *J. Catal.* **63**, 271 (1980).
2. Sharma, R., and Srivastava, R. D., *J. Catal.* **65**, 481 (1980).
3. Livbjerg, H., Jensen, K., and Villadsen, J., *J. Catal.* **45**, 216 (1976).
4. Kenney, C. N., *Catal. Rev.-Sci. Eng.* **11**, 197 (1975).
5. Michalska, Z., and Webster, D., *Chem. Technol.* **5**, 117 (1975).
6. Fontana, C., Gorin, E., and Kidder, G., *Ind. Eng. Chem.* **44**, 363 (1952).
7. Jensen-Holm, H., Ph.D. thesis [reported in J. Villadsen and H. Livbjerg, *Catal. Rev.-Sci. Eng.* **17**, 203 (1978)].
8. Puga, Y., and Kenney, C. N., in preparation.
9. Hobbs, L., in "Introduction to Analytical Electron Microscopy" (Hren, Goldstein, and Joy, Eds.). Plenum, New York, 1979.
10. Fisher, S., *Radiat. Eff.* **5**, 239 (1970).