X-ray photoelectron spectroscopy studies on ethylene oxychlorination catalysts†

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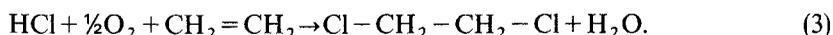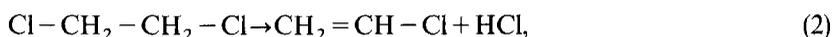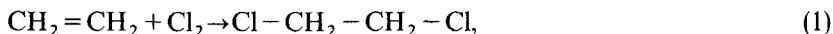**Present address: Department of Chemistry, University of Keele, Staffordshire, UK

Abstract. Copper chloride on alumina catalyst used for oxychlorination of ethylene represents a typical system where copper is in a dynamic equilibrium between Cu^+ and Cu^{++} oxidation states. Surface studies on redox, structural and compositional properties have been undertaken to monitor the changes that occur on the catalyst during use and pinpoint causes for its deactivation. For this, a fresh and a spent catalyst were been chosen for characterization. A core consisting of copper in Cu^+ state and present as $CuAlO_2$ is formed at the centre of the catalyst sphere. Formation of such a nonreversible phase under reaction conditions upsets the redox equilibrium. XPS also shows the absence of potassium in the core and its precipitation as a new phase on use, probably KCl, formed by the decomposition of active component $KCuCl_3$. These factors facilitate deactivation.

Keywords. Oxychlorination; deactivation; x-ray photoelectron spectra; $CuAlO_2$; $KCuCl_3$.

1. Introduction

The major reactions that take place in an industry producing vinyl chloride are

$$CH_2 = CH_2 + Cl_2 \rightarrow Cl - CH_2 - CH_2 - Cl, \tag{1}$$

$$Cl - CH_2 - CH_2 - Cl \rightarrow CH_2 = CH - Cl + HCl, \tag{2}$$

$$HCl + \tfrac{1}{2}O_2 + CH_2 = CH_2 \rightarrow Cl - CH_2 - CH_2 - Cl + H_2O. \tag{3}$$

Of these, reaction (3) is an oxychlorination reaction and is an adoption of the classical Deacon reaction

$$2HCl + \tfrac{1}{2}O_2 \rightarrow Cl_2 + H_2O \tag{4}$$

catalysed by a $CuCl_2/Al_2O_3$ system (Buckley 1966). This reaction takes care of the by-product HCl formed in reaction (2) and economizes the process. Reaction (3) is basically an oxychlorination of ethylene (Allen and Clark 1971).

Fundamentally, oxychlorination is a redox reaction in which the active component copper is in a dynamic equilibrium between 1+ and 2+ oxidation states.
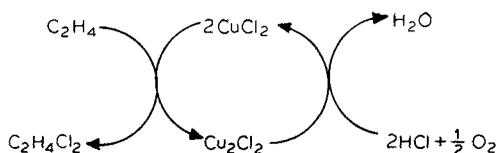
An optimum balance of Cu^+ and Cu^{2+} population and their presence in easily interchangeable environments is essential for smooth functioning of the catalyst. Addition of alkalihalides (KCl for e.g.) is known to improve the Cu^+/Cu^{2+} ratios (Conner et al 1981).

The present investigation aims at finding out transformations that cause activity loss of the catalyst. The focal point is to monitor the oxidation states of copper which directly influences the effectiveness in the redox catalyst system. The choice of x-ray photoelectron spectroscopy (XPS) for such a study, is based on the characteristic spectra exhibited by Cu^+ and Cu^{2+} states; the Cu^{2+} species show typical shake-up satellites associated with the $2p\,1/2$ and $2p\,3/2$ energy levels, whereas these satellites are absent for Cu^+ species. The satellite structure of Cu^{2+} compounds has been attributed to the simultaneous $3d{\to}4S$ transition. Such transitions are not seen for Cu^+ compounds or Cu^0 (d^{10}) (Strohmeier et al 1985). The absence of satellites indicates the absence of Cu^{2+} whereas their presence indicates copper to be in a mixture of $2+$ and $1+$ oxidation states or in $2+$ state only. XPS, therefore, is a useful method to identify the fluctuations in the Cu^+/Cu^{2+} redox system and to help understand the mechanism of deactivation.

2. Experimental

X-ray photoelectron spectra of fresh and spent catalysts have been recorded on a spectrometer (VG ESCALAB III). The catalysts have also been subjected to a thorough characterization using standard techniques.

3. Results and discussion

A cross-sectional view of a fresh and spent catalyst is shown in figure 1. It is seen that the catalyst on use develops a block core, which could be easily separated physically from an outer shell. While studying the used catalyst, the inner core and the outer shell have therefore been analysed separately. What forms this core? Table 1 gives
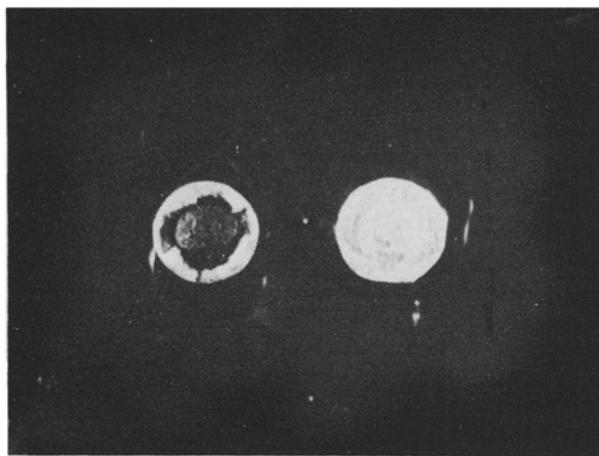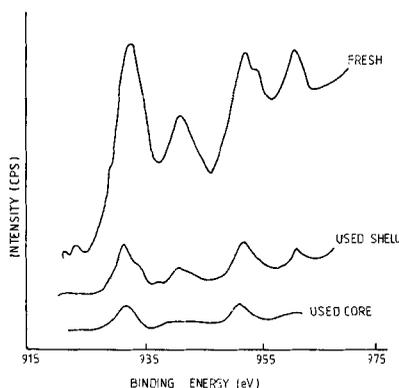

Figure 1.   Cross-sectional view of fresh (right) and used (left) oxychlorination catalysts.

Table 1. Phases indentified in the catalysts.

Sample	Phases
Fresh catalyst	γ-Al_2O_3, $KCuCl_3$ $CuCl_2 \cdot 2H_2O$
Spent catalyst	
Shell	γ-Al_2O_3, $KCuCl_3$, KCl $CuCl_2 \cdot 2H_2O$
Core	Al_2O_3, $CuAlO_2$

Figure 2. XP spectrum of oxychlorination catalyst (region of copper).

the phases that could be identified in the different samples by x-ray diffraction measurements. Fresh catalyst consists of the support Al_2O_3, the impregnated active component $CuCl_2 2H_2O$ and its double salt with KCl, $KCuCl_3$. The shell of used catalyst additionally contains free KCl, obviously formed by the decomposition of the double salt on use. Interestingly no KCl was observed in the core, which contained a new Cu^+ compound, $CuAlO_2$. This can only be formed by the reaction

$$Cu_2O + Al_2O_3 \rightarrow 2\,CuAlO_2. \tag{5}$$

Is this really possible under reaction temperature of around 250°C?.

A look at the spectrum of catalysts (figure 2) in the region of Cu $2p$ 1/2 and $2p$ 3/2 binding energies provides some confirmation. The binding energy values for the catalysts and that of some pure compounds for comparison, given in table 2, make it very clear that the core contains only a Cu^+ phase as indicated by the absence of satellite, whereas the shell consists of both Cu^{2+} and Cu^+ phases. Presence of the satellites and proximity of binding energy values render deconvolution of the main peaks into Cu^+ and Cu^{2+} peaks a difficult proposition and hence no attempts were made to derive any Cu^+/Cu^{2+} ratios from these curves. Temperature-programmed reduction did indicate a two-stage reduction for fresh catalyst and shell of used catalyst corresponding to reduction of different species namely Cu^{2+} and Cu^+ (Vetrivel *et al* 1987). Likewise in the case of core, a reduction maxima was observed at 710 K which has been attributed to the stable spinal phase $CuAlO_2$ undergoing reduction. The copper binding energies of 932·8 eV ($2p$ 3/2) and 952·8 ($2p$ 1/2), therefore, correspond to Cu^+ from the compound $CuAlO_2$.

Table 2.   XPS data on the catalysts.

| Sample | Binding energy (eV) | | | | |
	2p 3/2	Satellite	2p 1/2	Satellite	References
Cu	932·5	—	951	—	a
CuCl	934·6	—	954·5	—	b
Cu_2O	932·5	—	954·7	—	a
$CuCl_2$	936·4	944·9	956·2	964·8	b
CuO	933·8	944·0	956·3	964·8	a
Fresh catalyst	932·2	940·0	952·2	962·2	
Spent catalyst					
Shell	932·8	942·0	952·2	962·0	
Core	932·8	—	952·2	—	

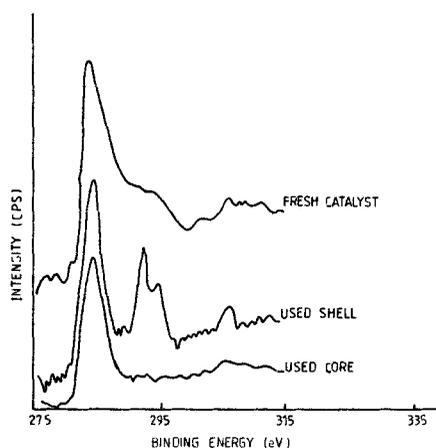*a*, McIntyre and Cook (1975);   *b*, Frost *et al* (1972).

Figure 3.   XP spectrum of oxychlorination catalysts (region of potassium).

The XP spectrum showing the state of the promoter potassium in the catalyst is shown in figure 3. Potassium in KCl is expected to show a doublet corresponding to 2p 1/2 and 2p 3/2 at 297 and 294 eV respectively.

In the case of a fresh catalyst the potassium 2p 1/2 and 2p 3/2 peaks appear to have shifted to a lower binding energy and hence it merges with the C_{1s} peak (285 eV). In the case of shell of the spent catalyst, potassium appears as a doublet as expected at 294 and 297 eV respectively. A shift towards a lower binding energy, in case of potassium, compared to the case of KCl is possible only if K is attached to a lesser electro-negative group. Comparison of KCl with the potassium compound present in the fresh catalyst i.e. $KCuCl_3$ shows that this is only to be expected because, in $KCuCl_3$, potassium is attached to a bulky $(CuCl_3)$ group whose charge is distributed over a larger volume than in the case of Cl on KCl and hence, the former has less electro-negative influence on K than Cl.

It is surprising to note that potassium is absent in the core of the sample. Concentration profiling by energy dispersive x-ray analysis (EDXA) also indicated a migration of potassium from the bulk to the periphery of the catalyst pellet on use

(Vetrivel *et al* 1987). These observations are consistent with phase identification obtained earlier from x-ray diffraction measurements.

Figure 4 shows the XP spectra of oxychlorination catalysts in the region of chlorine. Qualitatively, the spectra of the fresh catalyst may be indicative of a bound chlorine in two different environments as shown by the doublet. The origin of two chlorine states could be attributed to the presence of two chlorine containing compounds in the fresh catalyst i.e. $CuCl_2 \cdot 2H_2O$ and $KCuCl_3$ (table 1). Further, an enrichment of the chlorine in the outer shell is evident from figure 4. This has also been confirmed by the concentration profiling of the catalysts by EDXA which showed chlorine migration from the centre to the periphery of the sphere on use.

The oxygen states in these compounds are shown in figure 5. First, the oxygen species are similar in all samples (fresh, shell core), showing a peak at 530 eV. However there appears to be an enrichment of surface oxygen in the shell compared to the fresh catalyst. This enrichment of oxygen is higher in the shell than that of the core. This is in agreement with the observation that the shell contains both +2 and +1 copper states while copper in the core is present exclusively in +1 state as $CuAlO_2$.

A very stable compound like $CuAlO_2$ is an inactive phase for the redox oxychlorination catalysts. This is because of the prime requirement that copper should be available in an optimum Cu^+/Cu^{++} ratio and an easily interchangeable environment does not hold good once the difficultly reducible or oxidisable phase like $CuAlO_2$ is formed. What is the cause of its formation? Being an oxidation reaction, improper intraparticle heat transfer can cause sufficiently high local temperature and help a reaction of the type $Cu_2O + Al_2O_3 \rightarrow 2CuAlO_2$ otherwise known to occur around 1270 K. The presence of copper as Cu^+ in the core could be due to oxygen diffusibility limitations in the interior of the core. There is tremendous porosity loss in the core indicated by the values of total pore volume (shell 0·43 ml/g) and core
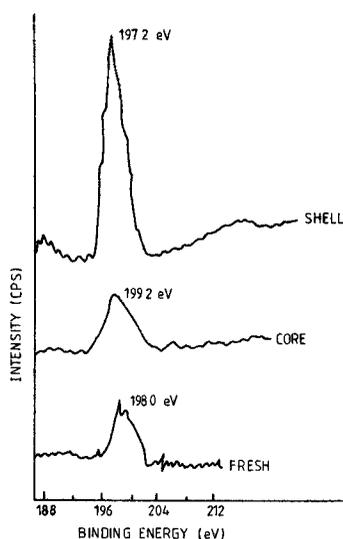

Figure 4. XP spectrum of oxychlorination catalyst (region of chlorine).
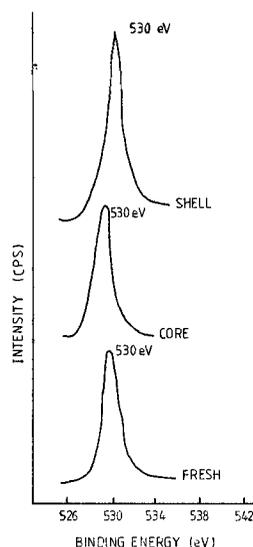
Figure 5. XP spectrum of oxychlorination catalyst (region of oxygen).

(0·09 ml/g)). This is to be expected because of the formation of a crystalline compound like $CuAlO_2$ and its sintering and growth to larger crystallites caused by the high local temperatures. In order to confirm these limitations to oxygen diffusivity, temperature-programmed oxidations were carried out and it was observed that oxidation was relatively easier when the core was crushed to a very fine powder in comparison to the situation when the core was taken as it was, proving that it is difficult for oxygen to penetrate the core due to its reduced porosity.

4. Conclusion

Deactivation in oxychlorination catalysts seems to be facilitated by preferential formation of a Cu^+ phase, $CuAlO_2$, in the core of the catalyst, on use, upsetting the Cu^+/Cu^{++} redox equilibrium. This is a thermally stable phase and formed as a solid solution between Cu_2O and Al_2O_3 due to the high oxothermicity of the reaction resulting in high local temperatures and the oxygen diffusibility limitations to the core caused by the reduction in porosity due to sintering of the core. Such a stable $CuAlO_2$ phase cannot be active for oxychlorination catalysts, where easy changes in oxidation states of copper are essential. Deactivation is also facilitated by decomposition of the active double salt $KCuCl_3$ and precipitation of free KCl followed by migration of potassium and chlorine from the core to periphery. There is also an enrichment of oxygen in the shell compared to the core obviously due to the diffusion limitations to the core.

References

Allen J A and Clark A J 1971 *Rev. Pure Appl. Chem.* **21** 145
Buckley J A 1966 *Chem. Eng.* **73(24)** 102
Conner Wm.c, Pieters W J M and Signorelli A J 1981 *Appl. Catal.* **11** 59
Frost D C, Ishitani A and McDowell C A 1972 *Mol. Phys.* **24** 861
McIntyre N S and Cook M G 1975 *Anal. Chem.* **47** 2208
Strohmeier B R, Leyden D E L, Field R S and Hercules 1985 *J. Catal.* **94** 514
Vetrivel R, Seshan K, Rao K V, Krishnamurthy K R and Prasada Rao T S R 1987 (to be published)