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Studies of the Surface Behavior of Oxide Catalysts by Secondary Ion Mass Spectrometry (SIMS)

1. The Surface Composition of Copper-Containing Spinel Catalysts and Their Precursors

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A series of powdered catalysts MgO, Al_2O_3, $MgAl_2O_4$, and $Mg_{1-x}Cu_xAl_2O_4$ were studied by secondary ion mass spectrometry (SIMS). It is evident from the spectra that the identity of the sputtered ion is dependent on the geometry and bonding in the lattice, a simple ionic compound such as MgO giving a very simple spectrum. The effect of these factors on relative sputtering rates is also discussed.

Investigation of one of these samples, $Mg_{0.9}Cu_{0.1}Al_2O_4$, which had been used as an oxychlorination catalyst, showed the surface changes which had occurred in use. Many stable surface species were observed but depth of attack on the catalyst was known to be minimal.

INTRODUCTION

A study of the catalyst parameters important in the catalysis of the oxychlorination reaction of ethylene to 1,2-dichloroethane over copper-containing spinel catalysts is being pursued in this laboratory. An understanding of the mechanism of this reaction would be facilitated by a knowledge of the basic surface structure of the catalysts, the effect of use, and the manner in which reactants and products adsorb on the surface. Recently the importance of SIMS as a technique for investigating the surface behavior of catalysts has been demonstrated (*1,2*). In the first part of this paper the results of a SIMS study of the basic spinels $Mg_{1-x}Cu_xAl_2O_4$ ($x = 0$–1) together with various precursors (MgO, Al_2O_3, $Mg_{0.95}Cu_{0.05}O$) are presented. The second part contains details of a SIMS investigation of adsorption on the spinel catalysts.

Earlier SIMS studies have concentrated on metal surfaces (*3–5*) but it has been shown in this and other laboratories that an insulator single crystal can also be studied (*6*). In these papers the feasibility of investigating a powdered insulator by secondary ion mass spectrometry is demonstrated. The choice of solids has also enabled us to determine the effect of changing crystal structure on the production of secondary ions, a field which has hitherto been little studied.

EXPERIMENTAL

Catalyst preparation. The powder samples were prepared by making slurries of MgO with the appropriate sulphates, heating at 400°C, compressing and firing at 900–1000°C. ANALAR reagents were used throughout. The absence of phases other than spinel was shown by X-ray diffraction.

SIMS procedure. The secondary ion mass spectrometer was constructed by Vacuum Generators Ltd., and basically consisted of two isolable chambers through which the sample could be moved on a horizontal probe. The first chamber is used for sample preparation and is separately pumped to base pressures of 10^{-9} Torr. The sample can be cleaned by argon ion sputtering and can be treated with adsorptives at pressures of up to 1 atm. Incorporated in this chamber is the UHV bellows mechanism for sample transport.

The second, or analysis, chamber can be separately pumped to 10^{-10} Torr and contains a Vacuum Generator AG3 ion gun as a source of primary ions. This is inclined at 20° to the sample plane and produces a flux of 10^{-10}–10^{-8} A cm^{-2} of argon ions having energies of 2–3 keV (capable of removing a monolayer in $\sim 10^5$ sec. assuming unity sputtering coefficients.) Emitted secondary ions are collected and analyzed by a V.G. Q8K quadrupole mass spectrometer set vertically above the sample. Since there is a distribution of secondary ion kinetic energies, energy filtering is used to improve resolution of the mass spectra.

The powdered sample was pressed into a special holder which was clamped to the heatable (25–600°C) probe. By means of the UHV bellows system the sample can be transferred from the preparation chamber to the analytical chamber. It is also possible to introduce adsorptives directly into this chamber at low pressure, $<10^{-5}$ Torr, by means of a gas handling system, and to take SIMS spectra during adsorption. The problem of charging which occurs with insulators, resulting in peak broadening, has been overcome by flooding the surface of the sample with electrons of low energy (typically <10 eV).

RESULTS

MgO and $Mg_{0.95}Cu_{0.05}O$. The SIMS spectrum of clean magnesium oxide is very simple and contains only peaks at mass numbers 24, 25, 26, and 41. These can be ascribed to Mg^+ and $MgOH^+$. In the $MgOH^+$ case the magnesium isotope pattern is less clear due to the lower intensity. Incorporation of a significant amount of divalent copper in the magnesium oxide leads to some interesting effects. Mg^+(24) and $MgOH^+$(41) are again present while Cu^+(63,65) is clearly visible. In addition, $MgO_2H_2^+$(58) and $MgO_2H_4^+$(60) become visible as also do peaks at mass numbers 82 and 84, ascribable to $CuOH_3^+$. On heating to 200°C the latter peaks (82–84) disappear and MgO^+(40) increases at the expense of $MgOH^+$(41), presumably because of dehydration of the surface.

α-Al_2O_3. The spectrum of α-alumina was found to be a little more complicated than that of MgO, containing peaks which we have ascribed to Al^+(27), $AlOH^+$(44), AlO_2^+(59), $AlO_2H_2^+$(61), and a small Al_2OH^+(71).

$MgAl_2O_4$. As can be seen from Fig. 1, the SIMS spectrum of $MgAl_2O_4$ is more detailed. Mg^+(24,25,26), Al^+(27), $MgO(H)^+$(40,41), and $AlO(H)^+$(43,44) are all clearly visible, as are $MgO_2H_2^+$(58) and $AlO_2(H)_2^+$(59,61). Multi-cation peaks such as $MgAlO(H_2)^+$-(67,69) and $Al_2OH_3^+$(73) are also present. Interestingly, on heating to 200°C, Al_2OH^+(71) and $MgAlOH^+$(68) become dominant in this region, $MgO_2H_2^+$(58) disappearing completely. In common with all other catalyst systems investigated, fairly intensive peaks due to Na^+ and K^+ impurities were observed. The intensity of these signals is due to the high sputtering rate of these species (where sputtering rate is defined as the probability of a particular positive secondary ion being produced by a given primary ion flux, typically $\sim 10^9$ A cm^{-2}).

$Mg_{0.9}Cu_{0.1}Al_2O_4$. Figure 2 shows the effect of the partial substitution of magnesium by copper ($x = 0.1$ in $Mg_{1-x}Cu_xAl_2O_4$). M^+ and MO^+ peaks are visible even for copper, which is not present in large amounts. Apart from this the spectrum is somewhat similar

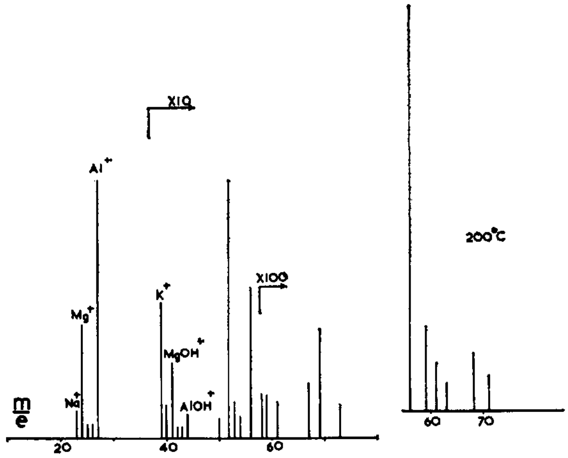

FIG. 1. $MgAl_2O_4$.

to that of $MgAl_2O_4$, except that AlO_2^+ species are not in evidence.

$Mg_{0.5}Cu_{0.5}Al_2O_4$. It can be seen from Fig. 3 that when x is increased to 0.5 the spectrum again changes, the copper peaks becoming more prominent. M^+ and MO^+ species are present except for CuO^+. $MgO_2H_2^+(58)$ has greatly decreased, while $MgAlOH^+(68)$ is not visible. The aluminium species $Al_2OH^+(71)$ and $Al_2O_2H_2^+(88)$ are observed but AlO_2^+ is not. $Cu_2^+(126)$ is also observable in the low-resolution spectrum. There was little change on heating the catalyst to 200°C.

$CuAl_2O_4$. The $CuAl_2O_4$ spectrum (Fig. 4) contains peaks which can be ascribed to $AlO_2H^+(60)$ and $Al_2O(H)^+(70)(71)$ and the copper species $CuAlOH_2^+(108)$, $Cu(OH)_3^+$-(114), $CuAlO_2^+(122)$, and $Cu_2^+(126)$.

$Mg_{0.9}Cu_{0.1}Al_2O_4$ catalyst sample. This specimen was studied after it had been used as a catalyst in the oxychlorination of ethylene to 1,2-dichloroethane at 200°C. The sample was transferred from the reactor to the SIMS apparatus, and the surface composition investigated. Thereafter it was heated to 200°C and the spectral changes were monitored. Figure 5 shows

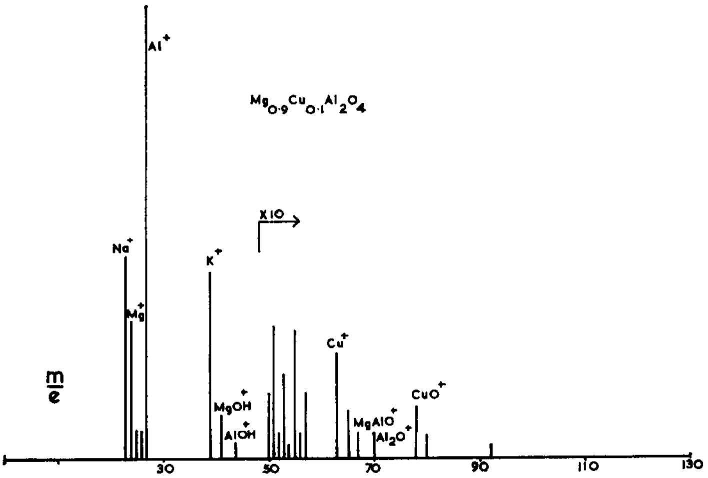

FIGURE 2

the principal features of the spectrum of the used catalyst above mass 63. The presence of carbon species is evident from mass numbers 14, 15 (CH_2^+ and CH_3^+) and mass numbers 24, 25, 26, 29 (C_2^+, C_2H^+, $C_2H_2^+$, and $C_2H_5^+$). As well as the Mg^+(24,25,26), Al^+(27), and Cu^+(63,65) signals, there are a large number of other peaks. By comparing the isotopic ratios expected for species containing Cl (35:37 = 3:1), Cu (63:65 = 7:3), and Mg (24:25:26 = 8:1:1) and by observing the temperature stability of the peaks, the following species are believed to be present at the surface. Masses 52 and 56 appear to be quite stable and appear on all samples; they can be attributed to the carbon residues C_2O_2,C_3H_4O(56) and C_3O or C_4H_4(52). C_4H_8 is an alternative explanation for mass 56 but it might be expected to be removed from the surface under the heating treatment. A broad signal at masses 68 and 69 which disappears at 200°C suggests an $MgAlOH_2$ species. $MgCl^+$(59,61) is found and is relatively stable, although $AlCl^+$(62,64) is not observed.

In the mass range 74–80 there are four signals whose relative intensities change markedly after heating. It is concluded that the species represented are $Al_2OH_4^+$(74), $AlCH_2Cl^+$(76,78), and $MgOH_2\cdot HCl^+$-(78,80). $Al_2OH_4^+$ and $MgOH_3Cl^+$ are greatly reduced on heating to 200°C; a transient OH_2^+ peak is also observed.

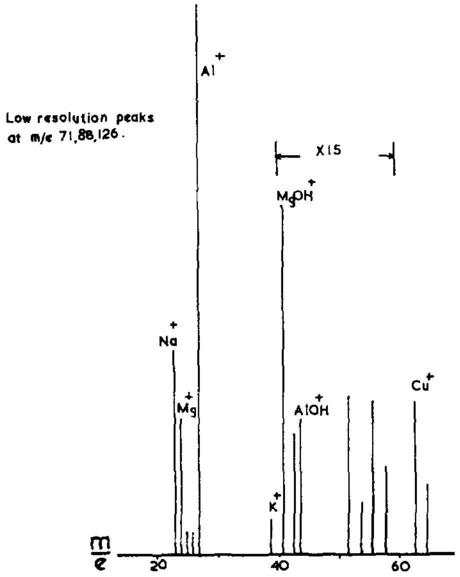

FIG. 3. $Mg_{0.5}Cu_{0.5}Al_2O_4$.

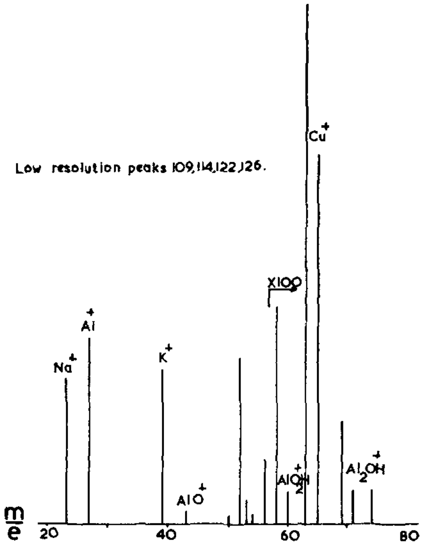

FIG. 4. $CuAl_2O_4$.

There are two possible assignments for masses 82 and 84, namely, $AlClOH_4^+$ and $CuOH_3^+$. $AlC_2H_2Cl^+$ is observed at 88 and 90, and $AlOCH_2Cl^+$ at 92, 94. The ratio of 98 to 100 changes from 2.5:1 to 1.9:1 after heating at 200°C, suggesting that there are two species contributing to the spectrum of the unheated sample, probably $CuCl^+$

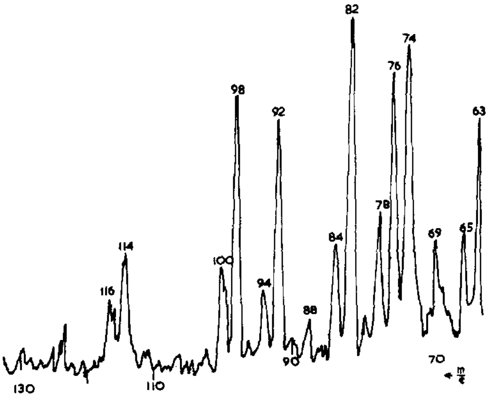

FIG. 5. Partial spectrum of catalyst $Mg_{0.9}Al_2Cu_{0.1}O_4$.

TABLE 1

Species Observed on the $Mg_{0.9}$ $Cu_{0.1}$ Al_2O_4 Catalyst Surface after Use

Mg	Al	Cu	C
MgO^+	AlO^+	$CuOH_3^+$	$C_2O_2^+$
$MgCl^+$	$Al_2OH_4^+$	$CuC_2H_5^+$	$C_3H_4O^+$
$MgOH_3Cl^+$	$AlCH_2Cl^+$	$CuCl^+$	C_3O^+
$MgAlOH_2^+$	$AlC_2H_2Cl^+$	$CuO \cdot Cl^+$	
	$AlO \cdot CH_2Cl^+$	$CuO_2H_3^+$	

and $CuO_2H_3^+$, $CuCl^+$ being the more stable. Finally, we find $CuOCl^+$ at 114, 116, and 118.

In Table I we summarize the most likely species formed on the surface of the spinel catalyst.

DISCUSSION

The process of secondary ion generation in SIMS is dependent on the transfer of kinetic energy from the primary ion to the lattice of the sample. This occurs in a series of collisions as the primary ion enters the surface layers.

If the series of energy transfers initiated by the primary ion results in the transfer of sufficient energy from a subsurface atom to a surface atom (i.e., $E > E_{\text{binding}} + E_{\text{ionisation}}$), then a charged species will be emitted. The composition of the species obviously must depend on the geometry of the lattice. The particular bonds broken will depend on the bonding in the solid, and therefore an investigation of a series of compounds such as the MgO, Al_2O_3, $MgAl_2O_4$ system should provide insight into the relation between chemical structure and the type (or identity) of ions sputtered. The validity and usefulness of this type of approach has recently been demonstrated by Preisinger and Buhl (*2*). Furthermore, the sputtering rate of species is dependent on their chemical identity. In a study of oxides of known composition it is possible to compare the sputtering rates of different ions. We will discuss this latter topic first.

Sputtering Ratios

In Table 2 the observed sputtering ratios of various simple ions are compared; absolute values are not obtained. In calculating these theoretical ratios it is assumed that changes in crystal structure and bonding will not materially affect the sputtering rate. This is clearly a rather crude assumption, but the results demonstrate a certain internal consistency which suggests that sputtering rates in this set of related oxides are relatively constant.

TABLE 2

Observed and Theoretical SIMS Sputtering Ratios of Various Powdered Insulators

	Al^+/AlO^+	Mg^+/MgO^+	Mg^+/Al^+	Al^+/Cu^+	Mg^+/Cu^+
Al_2O_3	56:1	—	—	—	—
MgO	—	15:1	—	—	—
$Mg_{0.95}Cu_{0.05}O$	—	31:1	—	—	20:1 Theor. 19:1
$MgAl_2O_4$	56:1	17:1	1:1.8 Theor. 1:2	—	—
$Mg_{0.9}Cu_{0.1}Al_2O_4$	60:1	18:1	1:2 Theor. 1:2.2	100:1 Theor. 20:1	40:1 Theor. 9:1
$Mg_{0.5}Cu_{0.5}Al_2O_4$	200:1	18:1	1:4.5 Theor. 1:4	20:1 Theor. 4:1	5:1 Theor. 1:1
$CuAl_2O_4$	190:1	—	—	12.5:1 Theor. 2:1	—

The SIMS spectra of $MgAl_2O_4$ suggest that the sputtering rates of Mg^+ and Al^+ ions are very similar (Table 2). Earlier work on oxidized metal surfaces (*3*) has shown that the sputtering rates for these ions are normally very different (Mg^+:Al^+ = 0.65:2.00). Obviously, in a semi-ionic oxide matrix such as $MgAl_2O_4$, the cations Mg and Al behave toward sputtering in very similar manners.

It is interesting that the sputtering rates for Mg^+, Al^+, and Cu^+ in spinel are in the ratio 5:5:1, while in $Mg_{0.95}Cu_{0.05}O$ the Mg^+:Cu^+ sputtering rates appear to be the same. This anomaly could be explained on several gounds, by assuming a high surface copper content in $Mg_{0.95}Cu_{0.05}O$, by a sputtering rate difference between octahedral and tetrahedral copper, by changing covalency or by reference to the strained environment of Cu^{2+} in magnesium oxide. With regard to the internal self-consistency of the spinel ratios, surface enrichment seems to be the most likely explanation. This conclusion is supported by a recent Auger investigation of Cu_xMg_yO catalysts by Goldobin and Savchenko (*7*), which shows substantially higher copper contents than would be expected from bulk measurements. Schiavello *et al.* have also demonstrated that CuO–MgO catalyst show segregation (*8*).

MgO

MgO has a simple cubic lattice where one would expect a homogeneous electronic structure and bonding. The α-Al_2O_3 structure is a little more complicated and so the surface environment of the metal ions will vary from one crystal plane to another. The spinel is again more complex both structurally and electronically, containing two different cation sites, octahedral and tetrahedral. Clearly both the bonding and the structure will be affected by the inclusion of dopent ions.

The SIMS spectrum of MgO is very simple, as one would expect from the geometric regularity of the sample, yielding only M^+ and $MO(H)^+$ ions. It is significant that a fair proportion of the MgO^+ species have hydrogen attached, suggesting extensive hydroxylation of the surface. That the electronic regularity or perhaps ionicity of the sample is important in determining the identity of the ion is shown by the lack of further multiple ions. The occurrence of MO^+ species themselves could lead to speculation that a small degree of surface covalency exists in the supposedly ionic structure of magnesium oxide, although a study of the sputtering characteristics of a truly ionic solid would be required to substantiate this suggestion.

α-Al_2O_3

The presence of MO_2^+ and M_2O^+ species in addition to M^+ and MO^+ makes a striking contrast between α-Al_2O_3 and MgO. The appearance of $AlOH^+$, Al_2OH^+ again gives evidence of surface hydroxylation. These multiple atom species may be evidence of greater covalency within the Al_2O_3 structure; nevertheless, their appearance can also be understood by considering the nonuniformity of O^{2-} bonding in the likely surface planes (*9*).

Examination of the corundum structure suggests that on the (001) and (111) planes, low-coordinate (i.e., 3- or 4-coordinate) Al^{3+} would be exposed. If it is assumed that bare Al^{3+} will not appear at the surface then the possibility of AlO_2 species is explained. The structure is such that the Al^{3+} ions are present as pairs with three bridging O^{2-} ions. The environment of each atom is the same in the bulk solid, but at the surface the exposed Al_2 pair will have bridging O^{2-} ions which are nonequivalent. It is possible that one of these O^{2-} ions is attached only to the Al_2 pair. This would indicate a possible route for the formation of the Al_2OH^+ ions seen in the spectrum.

$MgAl_2O_4$

The structure of bulk normal spinel is such that each ion is in the same environment; e.g., each O^{2-} ion has three Al^{3+} and one Mg^{2+} nearest-neighbor ions. It is known that artificial spinel (*10*) is approximately 10–15% inverse, but this should not greatly affect the following discussion.

The most usual cleavage planes in the spinel crystal are (100), (110), and (111). Examination of these planes indicates that on a proximity basis Mg_2-containing species would be very unlikely to occur as secondary ions. A similar argument applies to Al_2 if one assumes no direct interaction between Al^{3+} ions. Mg^+ and Al^+ are obviously possible species, as also are $MgO(H)^+$ and $AlO(H)^+$ if one considers hydroxylation of the surface.

In the (110) plane there are MgOAl groups exposed where the bridging O^{2+} ion has only one Al^{3+} attached to it, the other surrounding O^{2-} ions having more metal ion nearest neighbors. Thus there exists a simple explanation for the formation of this species. Al_2O^+ ions could be easily formed from the rows of Al^{3+} ions which are characteristic of the spinel structure. The amount of hydrogen in these species indicates that there is a fair degree of hydroxylation and hydration of the surface. It is interesting that heating causes the loss of $MgO_2H_2^+$, presumably $MgO \cdot H_2O^+$, but not of $AlO_2H_2^+(AlO \cdot H_2O^+)$.

The Effect of Cu^{2+} Incorporation

In MgO. The incorporation of small quantities of Cu^{2+} into the MgO lattice has a very remarkable effect on the structure and bonding of the surface layer. There is a large change in the MgO^+/Mg^+ ratio. On a simple probability basis this ratio should remain constant as Cu^{2+} is added. Simultaneously, with the change in MgO^+/Mg^+ ratio, the MgO_2^+ species appears. Thus the incorporation of Cu^{2+} decreases the incidence of MgO^+ and increases the MgO_2^+. It could be argued that the appearance of MgO_2^+ reflects an increased covalency or stronger bonding of oxygen to the Mg^{2+} ions in the surface layers. On a probability basis the MgO_2^+ species is more likely than MgO^+, although the sputtering coefficients will be in the reverse order since MgO_2^+ is a three-atom entity. If the bonding of oxygen to Mg is increased in strength, then the incidence of MgO_2^+ may be increased relative to MgO^+. There are a number of interrelated mechanisms whereby the presence of copper ions may increase the bonding in the surface layer. First, the presence of copper could lead to reduction and nonstoichiometry resulting in oxygen vacancies. Second, Cu^{2+} is a Jahn–Teller ion, so repulsion of some of the oxygen ligands could lead to closer bonding with neighboring Mg^{2+} ions. Third, it is known that dopent ions exert an electronic influence, presumably through bonding orbitals, far beyond their actual radius (*11*). It is interesting and significant that this effect is not observed for Mg in the spinel samples. This is presumably a function of the isolation of these ions in tetrahedral sites.

In spinel. Replacement of Mg^{2+} by Cu^{2+} in the spinel system leads to changes in the sputtering ratios, as well as in the ions produced. In the $x = 0.1$ case ($Mg_{1-x}Cu_xAl_2O_4$), Cu^+ and CuO^+ species are clearly visible but the $AlO_2^+(H)$ peaks are lost. This could be due to a loss of surface oxygen or water from the sample, or it marks a fundamental change in surface properties due to the copper ion. Since the $AlO_2^+(H)$ peaks are absent in the $x = 0.5$ case but reappear in copper aluminate ($x = 1.0$), a possible explanation would be that the degree of inversion plays an important part in the formation of this ion. Both $CuAl_2O_4$ and $MgAl_2O_4$ are known to be partially inverse (*10,12*) and it would not be unreasonable to suppose that the incorporation of Cu^{2+} ions in the spinel would lead at first ($x = 0.1$) to a return to the normal structure; in practice, copper is known to favor tetrahedral site symmetry. This is shown by diffuse reflectance spectroscopy of the solid solutions, which indicates that the majority of Cu^{2+} ions are in sites of tetrahedral symmetry (*13*). An increase of copper content ($x = 0.5$) would lead to inversion until the partially inverse structure of $CuAl_2O_4$ was reached. In this scheme, if $AlO_2^+(H)$ were associated with Al in tetrahedral sites, these peaks would appear in $MgAl_2O_4$, $CuAl_2O_4$, and, only weakly, in $Mg_{0.5}Cu_{0.5}Al_2O_4$.

Some support for the above theory comes from the incidence of the Cu_2^+ peaks which are just detectable in the $x = 0.5$ case and stronger in the $CuAl_2O_4$ spectrum. The occurrence of these peaks must imply direct interaction and we believe that this can only occur though occupation of octahedral sites by Cu^{2+} ions. This gives evidence for the increase in inversion when proceeding from $x = 0.5$ to $x = 1.0$.

A distinct decrease in the AlO^+ sputtering rate occurs at high copper contents (Table 2). This could be due to (a) occupation of octahedral sites by copper ions where they have an effect on the AlO^+ sputtering rate for reasons similar to those advanced for the Mg^+/MgO^+ effect in copper-doped or MgO (b) lack of surface oxygen. These factors could of course both operate (a) on lattice oxygen removal and (b) on adsorbed oxygen participation in AlO^+ sputtering. It is known that the heat of formation of $CuAl_2O_4$ is substantially lower than that of $MgAl_2O_4$ (*14*), also that surface oxygen in chromite and cobaltite spinels (*15*) is less strongly held by copper than by magnesium compounds.

In conclusion, there are clearly a number of factors that need further study, for example, the influence of the matrix on the sputtering rate of dopent ions, etc. Nevertheless, the foregoing data demonstrate the power of SIMS in the study of the composition and structure of surfaces. In this initial study we have observed the following.

(a) There is a marked contrast between the secondary ions observed from MgO, Al_2O_3, and $MgAl_2O_4$, demonstrating the increasing complexity and varying bonding of the surfaces exposed.

(b) The incorporation of Cu in MgO clearly has a fundamental effect on the surface behavior and bonding even within the Mg–O part of the lattice.

(c) The incorporation of Cu in spinel has a varying effect as the concentration of Cu increases, the most marked effect being that at low contents of Cu, the surface Cu seems to be mainly in tetrahedral sites, whereas at high Cu contents some Cu is in octahedral sites. The incorporation of Cu also affects surface bonding of oxygen.

(d) There is a varying hydration of surfaces before and after heating. With increasing experience with the technique it is clear that greater definition will be given to the conclusions that can be drawn from the SIMS data.

Used Catalyst $Mg_{0.9}Cu_{0.1}Al_2O_4$

After use as a catalyst the spectral changes were very marked. Chlorination and hydration of the surface had occurred (Table 1). In addition there is evidence of adsorbed hydrocarbon species. It may be questioned whether these species are real surface entities or merely fragments that result from the SIMS process. An absolutely categorical answer cannot at present be given to this question but two points should be borne in mind. First, the SIMS process is relatively gentle, several hours being required to remove a monolayer. Second, our studies of simple adsorption systems such as CO on Ni and C_2H_4 on Ni strongly suggest that no surface fragmentation of adsorbed species takes place due to the SIMS process (*16*).

It must be realized that the history of the sample, since its use as a catalyst, makes it unlikely that unstable reaction intermediates will be detected (Table 1). Table 1 indicates very clearly that the three surface cations perform rather different functions. Chlorination occurs at the Mg^{2+} and Cu^{2+} ion *but not* at Al^{3+}. The chlorohydrocarbons formed during reaction adsorb at the Al^{3+} or $Al \cdot O$ but not on Mg^{2+} and Cu^{2+}. Ethylene appears to adsorb on the Cu^{2+} ion while there is little or no evidence of hydrocarbon attachment at the Mg^{2+}. Extensive hydration of the surface has occurred, the OH and H_2O species attaching at Mg, Cu, *and* Al_2. The appearance of peaks pertaining to aluminum–chlorocarbon species can be explained by assuming strong adsorption of hydrogen on an oxygen, and of chlorine on an aluminum of an Al–O site. The resultant weakening of the carbon–carbon bond gives rise to the observed species. This would provide a possible explanation for the $AlOC_2H_2^+$, $AlCH_2Cl^+$, $AlC_2H_2Cl^+$, $AlO \cdot CH_2Cl^+$ species if differing numbers of atoms in the molecule had bonds with the surface. The associations of copper with a hydrocarbon, i.e., $Cu \cdot C_2H_5^+$ or perhaps $H \cdot Cu \cdot CH_2 = CH_2^+$, indicate that on this catalyst copper acts as an adsorption site for ethylene which is subsequently chlorinated by mobile chlorine ions. Vinyl chloride is a by-product in this reaction. The appearance of hydrocarbon fragments (*52,56*) provides further evidence that dehydrogenation occurs at the surface.

This is a complex catalyst system, and as a result there are uncertainties in the interpretation of the spectra. Nevertheless, the data obtained on the surface species demonstrate the power and versatility of SIMS for the investigation of adsorbate–adsorbent interactions. In addition to its apparent ability to study the identity and reactivity of adsorbing centers, its applicability to all types of catalyst materials, metals and insulators, single crystals, and powders makes it particularly useful.

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Note added in proof. Further work utilising X.R.D. indicates that our previous conclusions on the copper site occupancy need modification. At low copper contents Cu is mainly in octahedral sites. As a result the observed sputtering patterns are more easily explained in terms of varying adsorption activity towards oxygen, which parallels the general adsorption behavior. AlO_2^+ is only observed on $MgAl_2O_4$ and $CuAl_2O_4$ and can be attributed to oxygen adsorbed on aluminum. Al_2O^+ is observed on all samples, and can arise from octahedral Al joined by a *lattice* oxygen. CuO^+ only appears on $CuAl_2O_4$ and on $Mg_{0.9}Cu_{0.1}Al_2O_4$. By analogy this can be attributed to oxygen adsorbed at a Cu site.

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