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Surface Characterization of Copper–Silicon Catalysts[1]

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X-Ray photoelectron spectroscopy has been employed to examine copper–silicon catalysts used in the synthesis of methylchlorosilanes. A freshly prepared catalyst shows the eixstence of copper silicide on the surface along with some oxidized silicon. Partial use of the catalyst results in surface enrichment of silicon on the copper silicide, in which copper exists in the Cu^{2+} state as evidenced by the characteristic shake-up satellite peaks. This supports an earlier proposed mechanism which involves an intermediate complex of methyl chloride with Cu^{2+} as the active state. Zinc, as an additive in the catalyst, segregates on the surface of the freshly prepared catalyst, but is reduced significantly during the course of the reaction. Storage of the catalyst under ambient conditions has been found to produce a surface coating of cupric oxide. © 1985 Academic Press, Inc.

INTRODUCTION

Silicones achieved prominence as unique inorganic polymers as early as 1945 (*1*, *2*). The basic precursors to these polymers usually are substituted chlorosilanes, such as mono-, di-, and trichloromethylsilanes which have normally been synthesized from the reaction between metallic silicon and methyl chloride. Copper has invariably been used as the major catalyst along with certain other elements as activators or promoters. Efforts have also been made as early as 1964 in the utilization of an easily available and cheap raw material, ferrosilicon, as the source of silicon in the synthesis of precursors (*3*, *4*).

Considerable work has been reported on various aspects of these basic reactions, e.g., the role of a specific phase of copper silicide, such as Cu_3Si (η-phase) as the active catalyst, and the effect of various additives such as Ca, Zn, and Fe as promoters to influence the mode and selectivity of the reaction (*3*). Based on some of these results, various mechanisms have been postulated to explain the role of copper and additives in the synthesis, but, as yet, the reaction mechanism is not fully understood (*3*, *5–11*). Apparently, further work is required in this direction.

It is toward that particular aim that the present work has been undertaken with X-ray photoelectron spectroscopy (XPS), popularly known as ESCA. Successful utilization of XPS as a surface characterization technique has been reported for a number of catalytic processes (*12–14*).

EXPERIMENTAL

The basic starting material used in the preparation of the chloromethylsilanes mixture is a silicon–iron alloy with about 4 wt% of iron and is commonly termed ferrosilicon. As described in the patent (*4*) ferrosilicon is treated with cuprous chloride to produce what is termed the "contact mass" which functions both as a catalyst as well as a source of silicon in the reaction. The next step involves its reaction with gaseous methyl chloride in the temperature range 300–400°C. The various samples for the present XPS work were kindly supplied by Rajiv Yadav and Hans Raj of this laboratory who are actively engaged in investiga-

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TABLE 1

Percentage Atomic Concentration of Surface Constituents[a]

	Fresh contact mass		Spent contact mass	
Element	As received	Sputtered	As received	Sputtered
Cu	2.3	1.3	0.2	3.1
Si	3.7[b]	3.8	16.7	9.0
	0.85[c]	0.46	3.3	5.5
Zn	7.9	7.7	0.2	0.6
Fe	[d]	[d]	[d]	[d]
O	34.5	32.2	55.0	43.6
C	31.8	32.1	24.8	38.1
Cl	11.3	9.5	0.9	3.4
S	[d]	[d]	1.8	0.2
Na	8.5	13.2	0.3	1.7

[a] Estimated uncertainty is ±40%.
[b] Total content including SiO_2.
[c] Excluding SiO_2.
[d] Below detection limit.

tions of this particular synthesis using the ferrosilicon-based method reported elsewhere (*3*, *4*). These samples corresponded to various stages of the reactions.

The XPS studies were conducted on pelletized samples using Mg K_α X rays with the Physical Electronics, Perkin–Elmer, ESCA/SAM Model 550 instrument. An argon ion beam was used for sputter cleaning the top surface. Data acquisition was accomplished with a dedicated PDP 11/04 computer which also enabled other treatments such as curve deconvolution. Energy was calibrated using the ubiquitous carbon C 1*s* peak at 284.6 eV. Published relative photoelectron sensitivities referred to the C 1*s* signal served as a basis for calculations of the relative concentrations of the different surface constituents which are presented in Table 1 (*15*). The values of the electron inelastic mean free path (IMFP) for solids recommended by Seah and Dench were used for consideration of depth analysis (*16*).

The as-received samples were pelletized in a KBr pellet-making device at pressures of ~30 tons. Surface cleaning to an extent of ~30 Å by sputtering was normally done using Ar^+ ions with an energy of 5 keV and a surface current of 1.4 $\mu A/cm^2$. The sputtering rate of tantalum oxide has been used for this estimation. Thus, throughout the text the sputtered sample refers to ~30 Å surface cleaning. Sample charging was generally quite insignificant.

Figure 1 displays the spectra of the starting ferrosilicon material. Partial surface oxidation of silicon is evident from the Si $2p_{3/2}$ peaks at 102.2 and 98.1 eV, separately depicted as an inset in Fig. 1. Iron is not detected although its sensitivity is higher by a factor of ~15 compared to that of silicon. The Al signal arises from the aluminum foil in which the sample pellet is wrapped for mounting purposes. The Ca signal on the top seems to be due to impurities. XPS spectra of both the fresh and partly spent catalysts are compared in Fig. 2.

RESULTS AND DISCUSSION

Fresh Contact Mass

XPS spectra depicted in Figs. 3a and b show a surface oxidation layer of SiO_2 on the catalyst which on surface cleaning only decreased slightly (Table 1). The observed chemical shift, ΔE_1, of 5.4 and 5.2 eV in the binding energy (BE) value of the Si $2p_{3/2}$ peak as presented in Table 2 is larger than the 4.2 eV reported for Si to SiO_2 (*17*), and in fact our present data yield 3.9 eV for this latter shift. Moreover, the BE values of

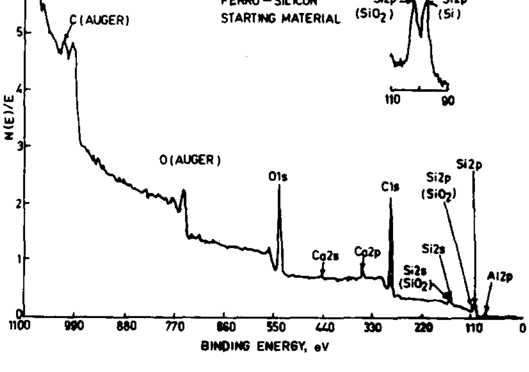

FIG. 1. XPS spectra of the starting material, ferrosilicon. The inset depicts expanded spectra of Si $2p_{3/2}$.

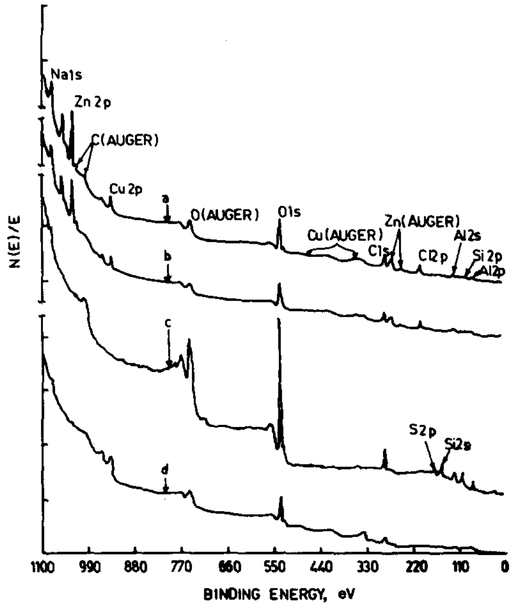

FIG. 2. Comparison of XPS spectra of the fresh contact mass (a) as received and (b) sputtered and partly spent contact mass (c) as received and (d) sputtered with and without sputter cleaning to ~30 Å.

98.0 and 97.7 eV are also lower than the 99.2 eV reported for pure silicon (*17*). This suggests the presence of some kind of chemical bonding with Cu which is more electropositive than Si and, consequently, a lowering of the Si $2p_{3/2}$ value is expected. A similar decrease observed in the BE of Se $3d$ in cadmium selenide has been attributed to the electronegative nature of selenium (*18*). The presence of copper and silicon on the surface in approximately 3 : 1 ratio (Table 1) also suggests the existence of the Cu_3Si phase which has been generally associated with the catalytic activity of copper in the chlorosilane synthesis (*19*). Recent Auger spectroscopic work of Frank and Falconer on Cu_3Si and other copper silicides also indicated similar changes in the Si $2p_{3/2}$ binding energy value (*20*). Such changes in binding energy due to alloying have also been reported in other systems (*21–30*). Noteworthy among these and somewhat related to the present system, for example, is the observed catalytic enhancement of ambient oxidation of silicon in the

TABLE 2

Observed Si 2*p* Binding Energy Data (in eV)[a]

Systems	SiO_2	Si	Cu_3Si	ΔE_1^b	ΔE_2^c
Fresh contact mass					
As received	103.4 (3.4)	—	98.0 (1.7)	5.4	—
With sputtering	103.0 (3.8)	— —	97.2 (1.8)	5.2	—
Partly spent contact mass					
As received	101.9 (3.1)	98.2 (2.7)	—	—	3.7
With sputtering	104.0 (3.5)	100.7 (2.7)	97.7 (2.3)	6.3	3.3
Published values[d]	103.4 (2.1)	99.2 (1.3)	—	—	4.2
Present work[e]	103.2	99.3	—	—	3.9

[a] *FWHM* values in parenthesis. Estimated error in BE is ±1 eV.

[b] Difference of binding energy of Si 2*p* in SiO_2 and Cu_3Si.

[c] Difference of binding energy of Si 2*p* in SiO_2 and Si.

[d] Ref. (*17*).

[e] These are averages of five separate measurements on the starting material, ferrosilicon. Standard deviation is 0.5 eV.

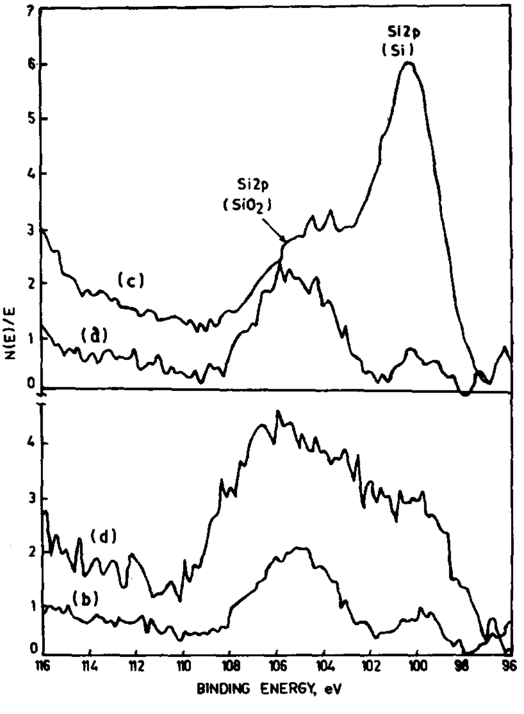

FIG. 3. Comparative Si 2*p* XPS spectra of the fresh contact mass (a) as received and (b) sputtered and partly spent contact mass (c) without sputtering and (d) with sputtering indicating the effect of sputter etching.

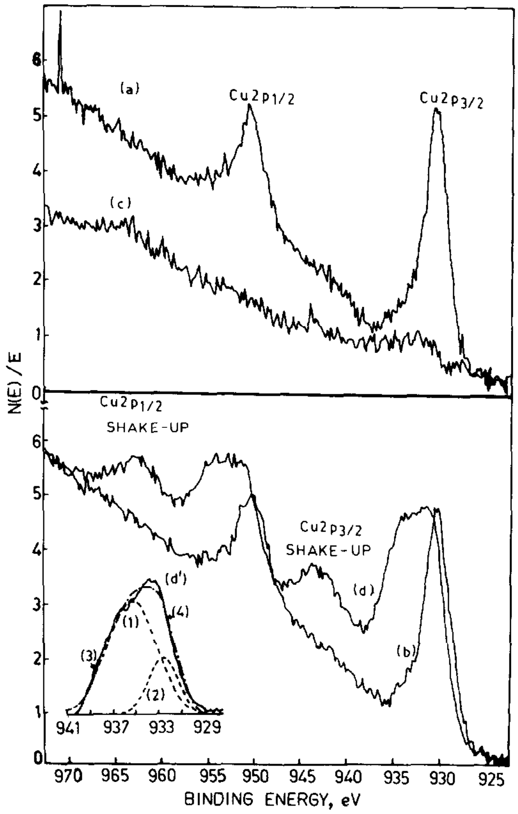

FIG. 4. Comparative Cu 2*p* XPS spectra of contact mass. Fresh: (a) without sputtering and (b) with sputtering. Partly spent: (c) without sputtering, (d) with sputtering, and (d′) with sputtering (deconvoluted segment).

presence of gold, silver, nickel, palladium, and chromium, which has been attributed to either a silicide formation or an associated modification of the silicon sp^3 hybridization state (*21–23, 27–30*).

The associated data on copper from Figs. 4a and b give the Cu $2p_{3/2}$ BE at 931.6 eV, compared with reported value of 932.4 eV for pure copper as given in Table 3 (*31*). Sputtering has virtually no influence on the energy value although the atomic concentration of Cu decreased slightly (Table 1).

Partly Spent Contact Mass

The results refer to the contact mass after approximately 20% consumption of silicon in the synthesis. Figure 3c clearly shows Si segregation to the surface as its concentration increased to 16.7 at.% from a mere 2.6% in fresh contact mass with a corresponding sharp decline in copper concentration (Fig. 4c and Table 1). Deconvolution of the mixed peak as depicted in Fig. 5a gives for Si $2p_{3/2}$ BE values at 98.2 and 101.9 eV which are tentatively assigned to Si and SiO_2 phases respectively. Upon sputter cleaning the spectra change markedly to a predominance of higher BE peaks and reduction of the lower BE signal (Fig. 5b). Deconvolution gives 104.0, 100.7, and 97.7 eV values, which are assigned to SiO_2, Si, and Cu_3Si, respectively. Some discrepancies in BE values compared to the reported values for the pure systems, as presented in Table 2, may be due to localized differential charging; this is believed to arise due to gross differences in electrical conduction properties of the materials (*15*). Especially for insulating samples, BE values are difficult to pinpoint due to such problems (*32*). Hence, a much larger uncertainty has been assigned to these BE values (Table 2). The chemical shifts in BE values, however, seem to agree quite well and have therefore been given more emphasis in these assignments.

Thus, it appears that during the synthesis, silicon diffusion to the surface is quite

TABLE 3

Observed Cu $2p_{3/2}$ Binding Energy Data[a]

Systems	Energy (eV)	*FWHM* (eV)	Shake-up (eV)	Valence state
Fresh contact mass				
As received	931.6	3.2	—	Cu^0
With sputtering	931.6	3.0	—	Cu^0
Partly spent contact mass				
As received	933.2	6.5	943.2	Cu^{2+}
With sputtering	933.1	6.5	943.0	Cu^{2+}
Published data				
Copper[b]	932.4	1.8	—	
Cupric oxide[c]	933.7	4.0	943.1	

[a] Estimated error in BE is ±0.5 eV.
[b] Ref. (*17*).
[c] Ref. (*31*).

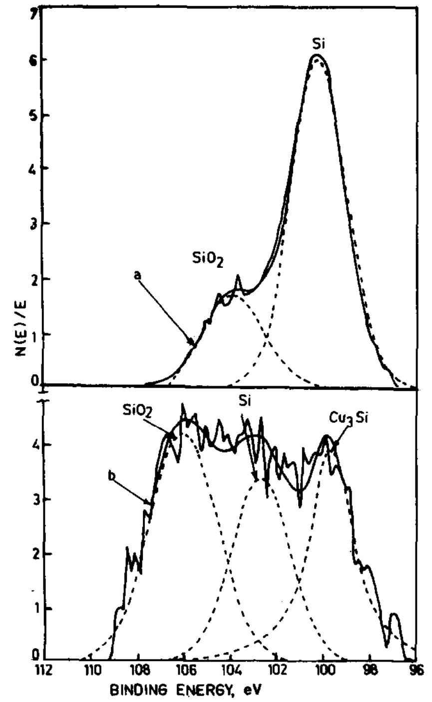

FIG. 5. Deconvoluted spectra of Si 2*p* peaks of partly spent contact mass. (a) As received and (b) sputtered.

rapid, i.e., faster than the rate of consumption by reaction. This observation is in agreement with that of Frank and Falconer who also observed, on thermal treatment, surface enrichment of Si on Cu_3Si (*20*). The presence of surface SiO_2 does not appear to be affected by the reaction. The surface segregation of silicon is also substantiated by the presence of a very small Cu $2p_{3/2}$ signal (Fig. 4c) which increases dramatically after sputter cleaning of the top surface (Fig. 4d). The Si $2p_{3/2}$ data also indicate the presence of Si along with Cu_3Si at these depths, which leads to a Cu:Si stoichiometry much different from that of silicide (Table 1).

The Cu 2*p* spectra (Fig. 4d) at 30 Å depth are most interesting by virtue of the strong presence of shake-up peaks, typically associated with the Cu^{2+} state (*15*). In addition, there is the usual shift and broadening of the main peak, viz. the $2p_{3/2}$ peak shifting from 931.6 eV (*FWHM* = 3.2 eV) to 933.2 eV (*FWHM* = 6.5 eV). In view of the reported range of 4.2 ± 0.2 eV for the *FWHM* of the $2p_{3/2}$ peak of the most Cu^{2+} compounds (*13*, *31*, *33*), this peak in Fig. 4d may be assigned to at most two constituents. For this purpose, it has been deconvoluted and depicted as Fig. 4d′. The lower BE peak at 930.5 eV (*FWHM* = 3.0 eV) has been assigned to Cu_3Si and the higher value at 933.2 eV (*FWHM* = 5.0 eV) to Cu^{2+} species. These BE values from deconvolution cannot be given much significance except as assistance in assignments. The primary BE data are summarized in Table 3.

Further analysis of these data can be undertaken with the calculation of shake-up in relation to the main peak (*15*). Reported shake-up probability data of a few Cu^{2+} compounds are, e.g., CuO 0.58, $CuCl_2$ 0.69, and $Cu(OMe)_2$ 0.50 (*33*). In the present case the peak area related to only Cu^{2+} species from Fig. 4d′ has been used to yield a shake-up probability of 0.18 which seems to indicate bonding to a weak electronegative group or element and definitely not elemental oxygen or chlorine. This would seem to corroborate the ionic mechanism proposed by Klebanskii and Fikhtengolts in which $CH_3^{\delta+}Cl^{\delta-}$ during the course of the reaction is visualized to form a transition complex with Cu in the Cu^{2+} state (*5*, *6*).

It has been established that specific valence states of elements act as active sites in a number of catalyst systems (*12–14*). For example, in copper chromite catalysts used for isomerization and hydrogenation of conjugated dienes, the most active states are reported to be Cu^{1+} and Cu^0, respectively (*13*). In other cases, Rh^{3+} for hydrogenation of olefinic bonds (*14*) and V^{5+} in V_2O_5 for oxidation of alkyl pyridines have been cited (*12*). It is noteworthy that no such formation of the Cu^{2+} state was detected in the fresh contact mass, although it did show a definite presence of a copper silicide phase, most likely the Cu_3Si η-phase. Hence, Cu^{2+} as the active state of copper is believed to participate in the reaction with CH_3Cl, perhaps to form an intermediate complex (*5*, *6*).

Effect of Storage

The contact mass on storage under ambient conditions has been found to develop a film of cupric oxide which is removed on sputtering ~50 Å. The shake-up spectral features typical of cupric oxide with a shake-up probability value of 0.48 are observed. Since copper oxides have been reported to give rise to different selectivities of the product (*34*), the stored catalyst must be used only with appropriate caution. The influence of oxygen studied by De Cooker *et al.* (*35*) is also supportive of this contention.

Other Elements

Although iron is a constituent of the starting materials (Table 1), its presence on the catalyst surface was well below the detection limit in either the fresh or the partly spent contact mass (Fig. 2). Iron is known to be a catalyst for the synthesis of chlorosilanes, but mostly at temperatures above 500°C, which are higher than those used in the present case and, additionally, it has selectivity toward trichloromethylsilane (*9*, *11*). Perhaps, at these elevated temperatures, iron may diffuse to the surface. Further work along these lines is planned to verify this suggestion.

Zinc is added as an additive to the catalyst mass to the extent of about 0.4 wt% but as may be seen from Fig. 2 and Table 1, its surface presence in the contact mass starts at a fairly high level (7.9 at.%), and reduces significantly to 0.2 at.% in the partly used state. Detailed spectra clearly show this effect. Its role in the reaction is not understood, but it certainly does not reduce surface SiO_2 as has been postulated by earlier workers (*30*).

The presence of sulfur in the partly spent mass was well established, which suggests its most likely origin to be impurities in the reactants. The existence of sodium is not too surprising as it is a common impurity.

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