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Characterization of Reactive Areas in the Direct Process for the Production of Methylchlorosilanes

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The surface of silicon reacting with methyl chloride in a laboratory fluidized bed via the direct process is characterized at several stages. In the first activation stage, the CuCl catalyst reacts with the Si, resulting in a decrease in the Cu surface concentration. Once reaction with methyl chloride has begun the Cu catalyst, the promoters (Zn, Sn) are found only on reactive sections of the silicon. The regions where reaction occurred had high Cu levels with Cu/Si ratio near 1. XPS determined the oxidation state of Cu on the surface to be zero. Zn is found to remain at higher surface concentrations than those of Cu during the course of reaction.

INTRODUCTION

The direct reaction of silicon with methyl chloride forms the basis for the silicone industry (*1*, *2*). The desired product is mainly dimethyldichlorosilane but, as is common with any catalytic reaction, a variety of compounds is produced. The goal of most research is to maximize the selectivity of the reaction for dimethyldichlorosilane. It is remarkable that, with very little understanding, the literature reports many reaction conditions and catalysts that produce greater than 70% dimethyldichlorosilane (*2*).

The interesting chemistry, combined with the commercial importance of the direct process, has generated a tremendous amount of literature (*2*). The direct process is a heterogeneous reaction, but only recently have studies of the fundamental surface reactions been performed (*3–10*). It has been shown that silicon particles do not react uniformly over their surface (*6*). The reaction to form methylchlorosilanes occurs only at discrete sites, unless the surface SiO_2 layer is removed. This paper describes work characterizing the surface of a silicon bed at several points in a batch reaction. The intent is to provide information of the changes that occur at the surface during a typical reaction. Improved knowledge of silicon reacting in a laboratory-scale fluidized bed reactor is of value in relating more fundamental high-vacuum experiments to conditions present under typical reaction conditions.

EXPERIMENT

The laboratory-scale fluidized bed reactor, analysis procedures, and silicon/catalyst preparation used were previously described in detail (*11*) and will only briefly be outlined here. Metallurgical grade Si (analysis in Ref. (*11*)) was ground and aerodynamically classified, and the fractions were recombined to produce a mixture with a BET surface area of 0.27 m^2/g. Cu was added as CuCl, Puratronic grade purchased from Alfa. Sn and Zn metal (99.99 metal basis, −325 mesh) were added as promoters such that the mixture contained 7.5 wt% Cu, 0.75 wt% Zn, and 87 ppm Sn. The formation of a reactive Si mass was carried out in two steps. First, the Si, CuCl, and Sn powders were combined in hexane, forming

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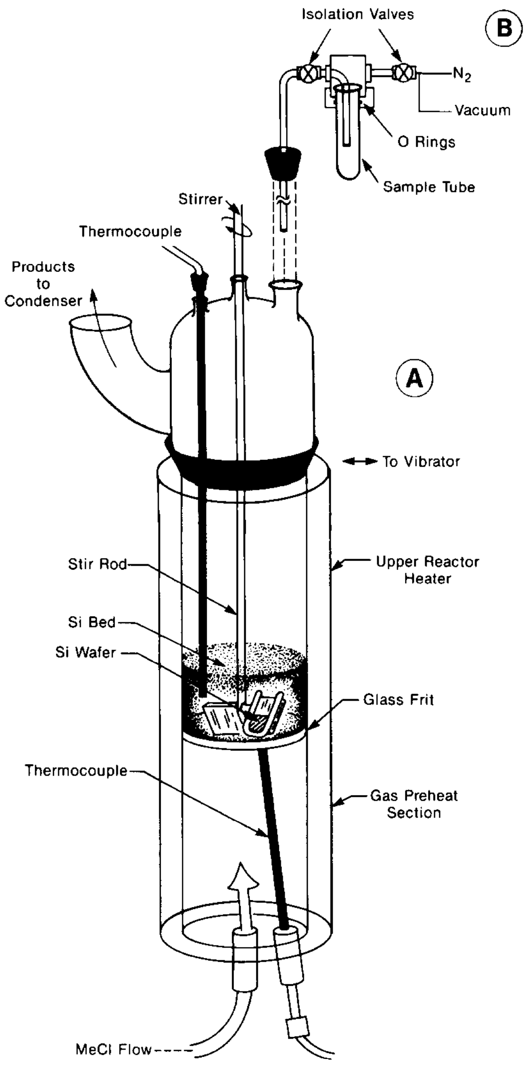


FIG. 1. (A) Schematic of laboratory scale fluidized bed reactor; (B) schematic of device used to remove bed samples from reactor without exposing them to air.

a slurry to improve dispersion. The hexane was removed in a vacuum oven. The Si, CuCl, and Sn mixture was then heated to 380°C in Ar for 2 h. This step reacted the CuCl and Si, forming $SiCl_4$ and Si_2Cl_6 (details in Ref. (*6*)). The resulting Si, Cu, Sn mixture is commonly referred to as "contact mass," and the process is referred to as "activation," or "contact mass formation." During contact mass formation, there is some vapor transport of the CuCl (*6*). Following activation, the Zn metal was added to the contact mass and the entire mixture placed into the laboratory fluidized bed reactor.

The reaction with CH_3Cl was performed at 300°C. The fluidized bed reactor was constructed of glass and consisted of two zones. Zone 1 preheated the CH_3Cl to 300°C and was separated from zone 2 by a glass frit. The frit supported the Si bed and served as a gas distributor. Figure 1A is a schematic of the reactor system. The products were condensed on a cold trap (−20°C) and were periodically analyzed by GC analysis.

Samples of the bed during the reaction were taken under inert conditions by inserting a tube, attached to a powder trap, into the bed (Fig. 1B). The sampling apparatus was continually purged with N_2 that had been passed through a liquid N_2 trap and an activated Ridox bed. To take a bed sample, the sampling tube (purge with N_2) was introduced through an opening in the reactor top and immersed in the fluidized bed. The N_2 purge was stopped, and a vacuum was drawn to force powder up the sample tube and into the glass sampling vial. The sample vial was then isolated from the sampling tube and gas lines by isolation valves. The sample vial was transported to a glovebox, in which the powder was removed and pressed into In foil. The sample was then transferred into either a Surface Science Labs SSX-100 small spot ESCA or a Phi 600 scanning Auger microprobe using inert introduction accessories.

The above procedure minimized artifacts introduced by exposing the samples to air.

The XPS data were taken using a 600-μm X-ray spot; thus the spectra represent an average taken over a large number of particles. The analyzer pass energy was 50 eV and, under the conditions used, the resolution of analyzer was 0.8 eV on the Au $4f_{7/2}$ line. The samples occasionally charged during analysis so that, in all the detailed spectra, the binding energies were corrected

TABLE 1

Product Distribution vs Si Utilization

Utilization	% Di	% Tri	% Mono	% MH	% TMS	% Res
4.1	59.9	26.5	3.8	0.5	5.9	3.3
9.5	62.3	25.1	3.0	0.4	6.2	2.9
16.1	76.1	14.8	2.9	0.3	3.2	2.7
22.5	81.9	10.5	3.3	0.2	1.8	2.3
26.3	84.8	8.4	3.3	0.2	1.4	2.2
37.6	83.8	8.9	3.7	0.2	1.2	2.2
46.5	83.8	9.1	3.6	0.4	0.9	2.1
53.2	89.1	5.7	2.4	0.4	0.7	1.7
61.1	86.8	5.8	2.7	0.4	0.4	3.9
64.7	84.4	6.7	2.4	0.3	0.6	5.5
68.1	88.2	6.0	1.6	0.5	—	3.8
72.4	87.9	6.5	1.4	0.4	—	3.9
76.9	80.3	10.7	1.4	0.8	—	6.8
79.7	67.8	22.1	1.7	3.6	—	4.8
80.9	57.4	30.9	1.6	6.1	—	3.9

Note. All percentages are based on weight. Abbreviations: Di, dimethyldichlorosilane; Tri, methyltricholosilane; Mono, trimethylchlorosilane; MH, methyldicholosilane; TMS, tetramethylsilane; Res, residue, compounds with boiling point >85°C.

such that the C 1*s* peak occurred at 284.60 eV. All the elements found on the surface were quantitated using peak areas and calculated sensitivity factors derived as the product of the Scofield ionization cross sections and an electron mean free path term proportional to $(KE)^{0.7}$. The instrument transmission was initially assumed constant but, for the main elements of interest (Cu, Cl, Zn, Si), standards were used to verify quantification results.

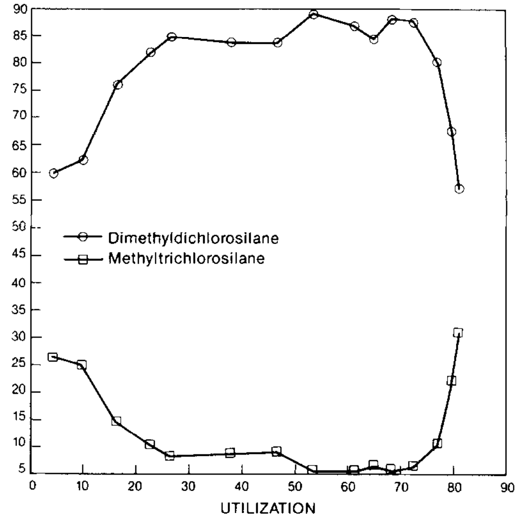


FIG. 2. Plot of dimethyldichlorosilane and methyltrichlorosilane concentrations (wt%) verses silicon utilization from which samples were taken for surface analysis.

RESULTS

Table 1 summarizes the product distribution for a run conducted as described above. The data for dimethyldichlorosilane and methyltrichlorosilane are presented graphically in Fig. 2. XPS analysis was performed on the following:

(i) the Si starting material (Fig. 3A)

(ii) the Si, CuCl, Sn mixture after mixing and hexane removal (Figs. 3B and 4A)

(iii) the Si, Cu, Sn, and Zn mixture following activation (heating to 380 in Ar) just prior to reaction with CH_3Cl (Figs. 3C and 4B)

(iv) reacted Si fluidized bed sample taken at 25% Si utilization (Figs. 3D and 4C)

(v) reacted Si fluidized bed sample taken at 60% Si utilization (Figs. 3E and 4D)

(vi) reacted Si fluidized bed sample taken at 81% Si utilization (Figs. 3F and 4E).

Table 2 is a summary of the surface concentrations for these various samples. In examining Table 2, it should be noted that the 600-μm area analyzed by the XPS data represents a concentration averaged over the entire surface of many particles. The values in Table 2 are valuable for comparison be-

TABLE 2

Atomic Surface Concentrations for a Typical Lab Batch Run Determined by XPS

	Si	Cu	Zn	Cl	O	C
Si starting material	41	—	—	—	38	21
Si + CuCl and Sn	31	3.5	—	3.5	28	34
Si + CuCl, Sn, and Zn (heated)	24	1	3	3	37	32
Reacted with CH_3Cl (25% Si utilization)	24	1	4	6	35	28
Reacted with CH_3Cl (60% Si utilization)	30	0.5	0.6	5	38	26
Reacted with CH_3Cl (81% Si utilization)	25	1	1	3	29	40

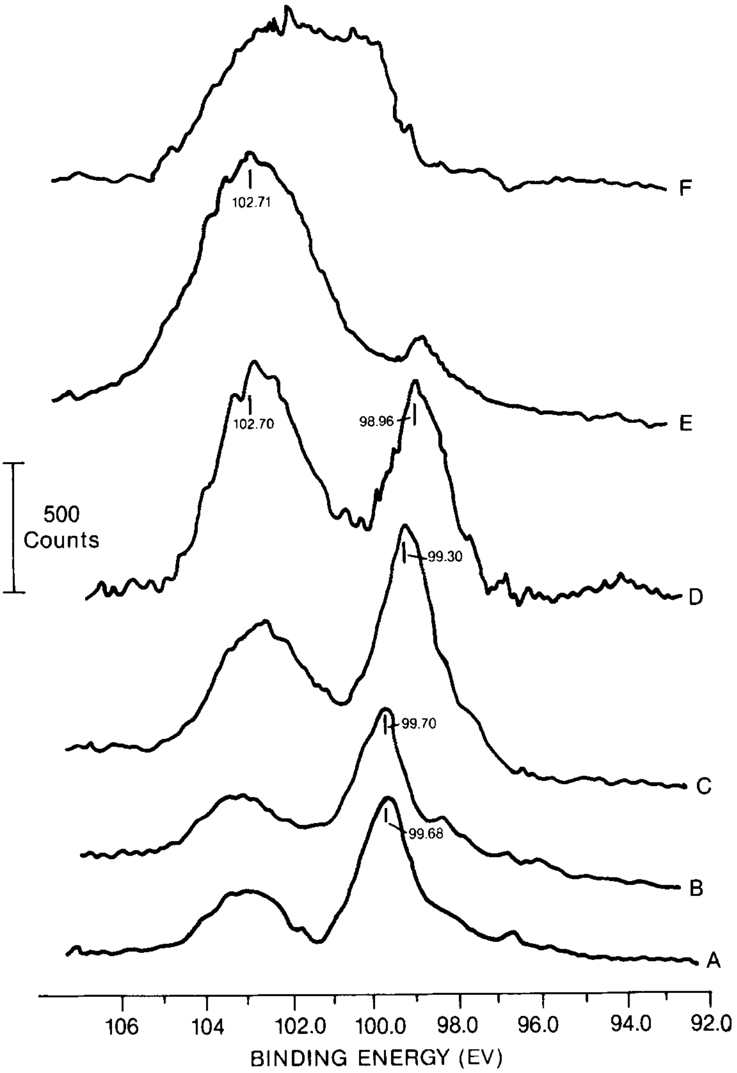


FIG. 3. XPS detailed spectra of Si 2*p* peak taken at various points in a batch reaction of Si with CH_3Cl in a lab-scale fluidized bed shown in Fig. 2: (A) spectrum obtained from metallurgical grade Si powder (no catalysts), (B) spectrum obtained from Si powder + CuCl and Sn (7.5 wt% Cu metal, and 87 ppm Sn), (C) "activated contact mass" = mixture described in (A) after 2 h at 380°C in Ar and addition of 0.75 wt% Zn, (D) samples taken from fluidized bed at 25% Si utilization, (E) sample taken from fluidized bed at 60% Si utilization, (F) sample taken from fluidized bed at 81% utilization. All samples from the fluidized bed were taken using the inert transfer procedure described in the text.

tween samples, but the absolute concentrations do not account for the heterogeneities present. Figures 3 and 4 are high-resolution XPS spectra of the Si 2*p* and Cu $2P_{3/2}$, peaks for the various samples.

The starting material shows only Si, O, and C, as is expected. Even though there is about 3000 ppm Fe in the starting silicon, the surface concentration was below the XPS detection limits, indicating no surface segregation. The surface composition and Si 2*p* detail are typical of Si possessing a native oxide. The high-resolution Si 2*p* spectrum (Fig. 3A) exhibits a Si metal and SiO_2 component with an area ratio of 2-to-1, indicating a thin native oxide (*12*).

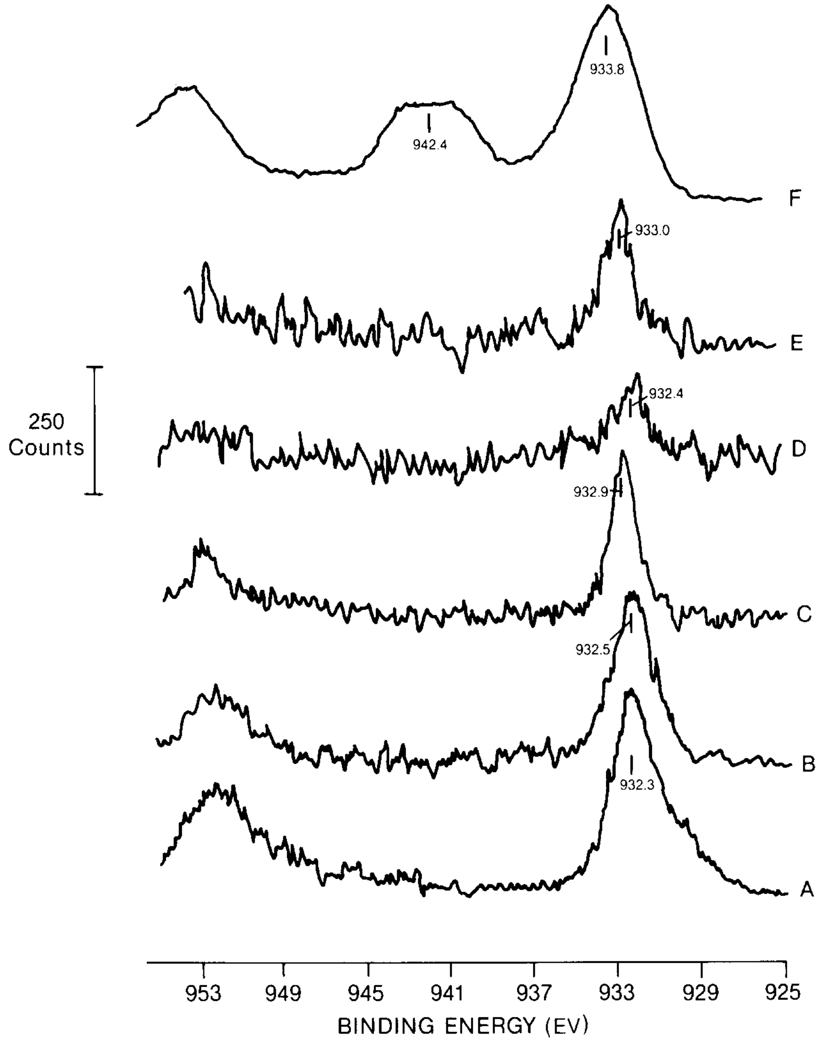
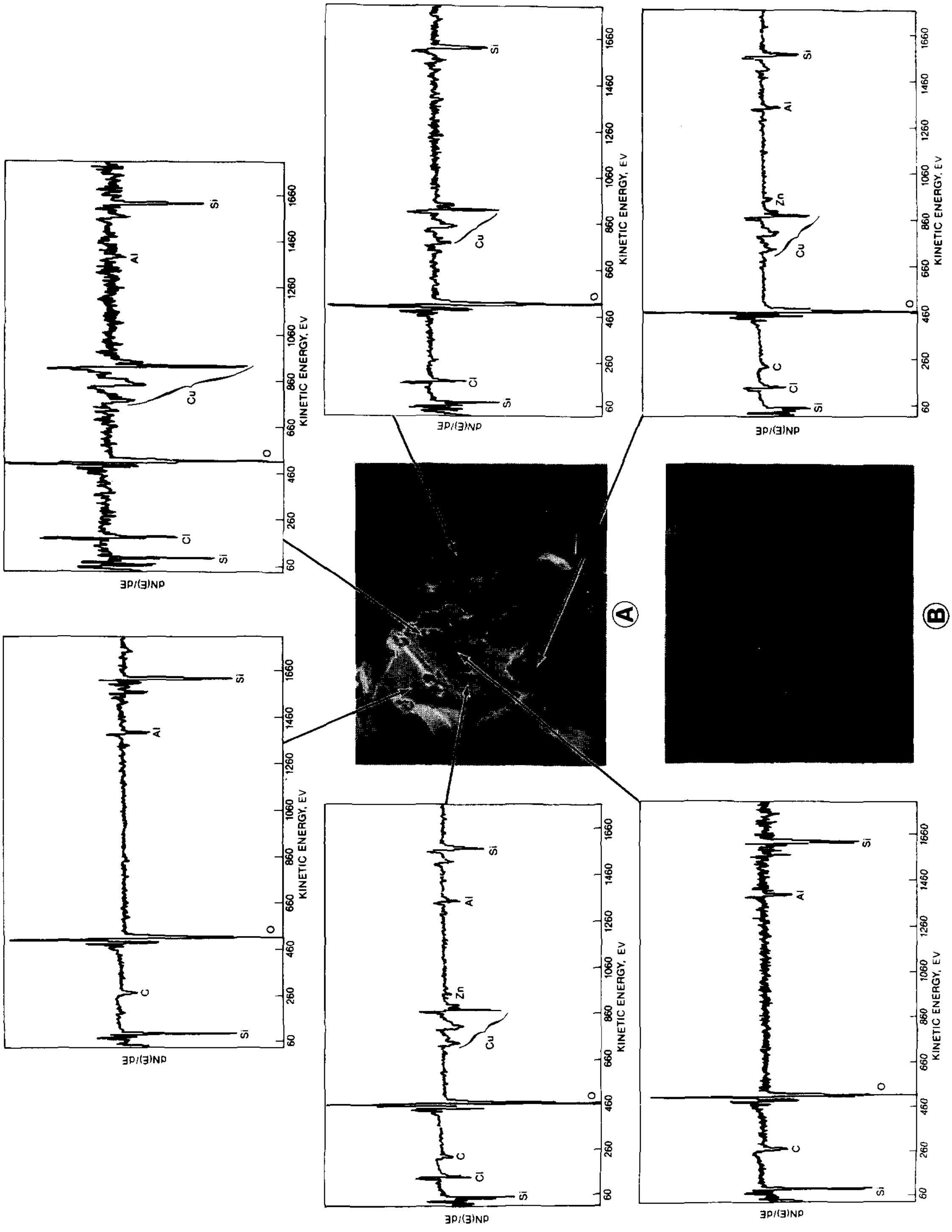


FIG. 4. XPS detailed spectra of Cu $2p_{3/2}$ peak taken at various points in a batch reaction of Si with CH_3Cl in a lab-scale fluidized bed: (A) spectrum obtained from Si powder + CuCl and Sn (7.5 wt% Cu metal, and 87 ppm Sn), (B) "activated contact mass" = mixture described in (A) after 2 h at 380°C in Ar and addition of 0.75 wt% Zn, (C) sample taken from fluidized bed at 25% Si utilization, (D) sample taken from fluidized bed at 60% Si utilization, (E) sample taken from fluidized bed at 81% utilization, (F) spectra of CuO for reference showing satellite characteristic of Cu^{2+}. All samples from the fluidized bed were taken using the inert transfer procedure described in the text.

The sample taken after the CuCl/Sn addition but prior to heating in Ar shows the presence of Cu (3 at.%) and Cl (3 at.%), in addition to the Si, O, and C. Although Sn was also added during the CuCl addition, its concentration was below the detection levels of the XPS.

Following heating (activation) of the Si/CuCl/Sn mixture, the Cu concentration decreased from 3 to 1 at.%, and the Cu $2p_{3/2}$ detailed spectra displayed a single peak centered at 932.3 eV with no indication of a satellite peak (see Fig. 4B). The Cl level remained constant. Adding 0.75 wt% Zn produced a surface concentration of 4 at.%. There was little change in the Si $2p$ spectra (Fig. 3C) following heating of the Si/CuCl/Sn mixture.


dN(E)/dE
KINETIC ENERGY, EV
60
260
460
660
860
1060
1260
1460
1660
Si
Cl
C
O
Cu
Zn
Al
A
B

After 25% of the Si had reacted with CH_3Cl, the Cu and Zn surface concentrations remained nearly the same as at the start of the reaction, but the Cl level increased to 6 at%. There was little change in either the Si $2p$ (Fig. 3D) or the Cu $2p_{3/2}$ (Fig. 4C) detailed spectra.

At 60% Si utilization, both the Cu and the Zn surface concentrations decreased (Cu 1 to 0.5 and Zn 3 to 1%), while there was a slight decrease in the Cl from 6 to 5%. The Cu $2p_{3/2}$ (Fig. 4D) detailed spectra did not indicate much change in the Cu environment, but the Si $2p$ detail spectra (Fig. 3E) indicated that the component at 102.7 eV had increased. The decrease in the Cu level probably reflects completion of Cu diffusion in to the Si particles.

At 81% Si utilization, there was an increase in the Cu, Zn, and C concentrations, while the Cl, O, and Si levels decreased from their values at 60% utilization. Little change was noted in the Cu $2p_{3/2}$ detailed spectra between 60 and 82% (Figs. 4D and 4E, respectively), but the Si component present near 99 eV at lower Si utilizations was absent from the spectrum taken at 81% (Fig. 3F).

To determine the spatial variation of the elements, a sample taken at 25% Si utilization was examined by scanning Auger analysis. Figure 5 displays several Auger spectra taken at different points on the particle shown in the SEM photo marked (A). These pits observed in the particle were the reacting areas producing methylchlorosilanes (*6*). Figure 5B is a Cu Auger map obtained over the same area displayed in Fig. 5A. The Auger spectra and Cu map clearly show that Cu and Zn are concentrated in the areas reacting with CH_3Cl.

The Cu concentration was found to increase away from the surface (into the particle). Figure 6B is a Cu map obtained from the area shown in Fig. 6A. Also included is a spectrum taken from one of the Cu-rich areas (Fig. 6D). The particle was sputtered for 20 min to remove about 140 nm, and the Cu map and Auger spectra were repeated (Figs. 6C and 6D, respectively). Following sputtering, the concentration of Cu in the reacting areas was even more obvious, and the Cu signal was increased by a factor of nearly 4.

In all experiments, Sn was difficult to detect on the surface. Sn has been shown to have a dramatic effect on the direct process even when present at extremely low levels, e.g., 80 ppm (*11*). To explain this, it was hypothesized that Sn, like Cu and Zn, was concentrated only in the reacted area. To test this supposition, a typical reaction was begun. At 25% Si utilization, $SnCl_4$ was injected into the CH_3Cl feed stock such that, if all the Sn was retained in the Si bed, the Sn bulk concentration would be 7500 ppm. The reaction was stopped and a sample examined by scanning Auger analysis. Figure 7 presents spectra taken at several points on a particle removed from the bed. The spectra show that Sn was only in the reacted areas along with Cu and Zn. Sputtering for only a few (45) seconds totally removed the Sn signal.

DISCUSSION

The direct process proceeds only when Cu is present. Other elements can act as promoters, but Cu is the only truly effective catalyst. The scanning Auger data clearly indicate that there is Cu in the reacted areas and not in the unreacted regions. In all experiments the Cu was never found by XPS on the surface at concentrations exceeding 3 at.%. It has been suggested that the active Cu–Si form in the direct process is Cu_3Si (η phase) (*2*). X-ray diffraction data have indicated that the η phase is present in reacting Si masses (*2*), and more recent results with only Cu_3Si present demonstrated the pro-

FIG. 5. Scanning Auger data obtained from a particle removed from the fluidized bed after 25% of the Si had reacted with CH_3Cl: (A) SEM photo indicating regions from which Auger data were acquired; (B) Cu Auger map over area displayed in (A).

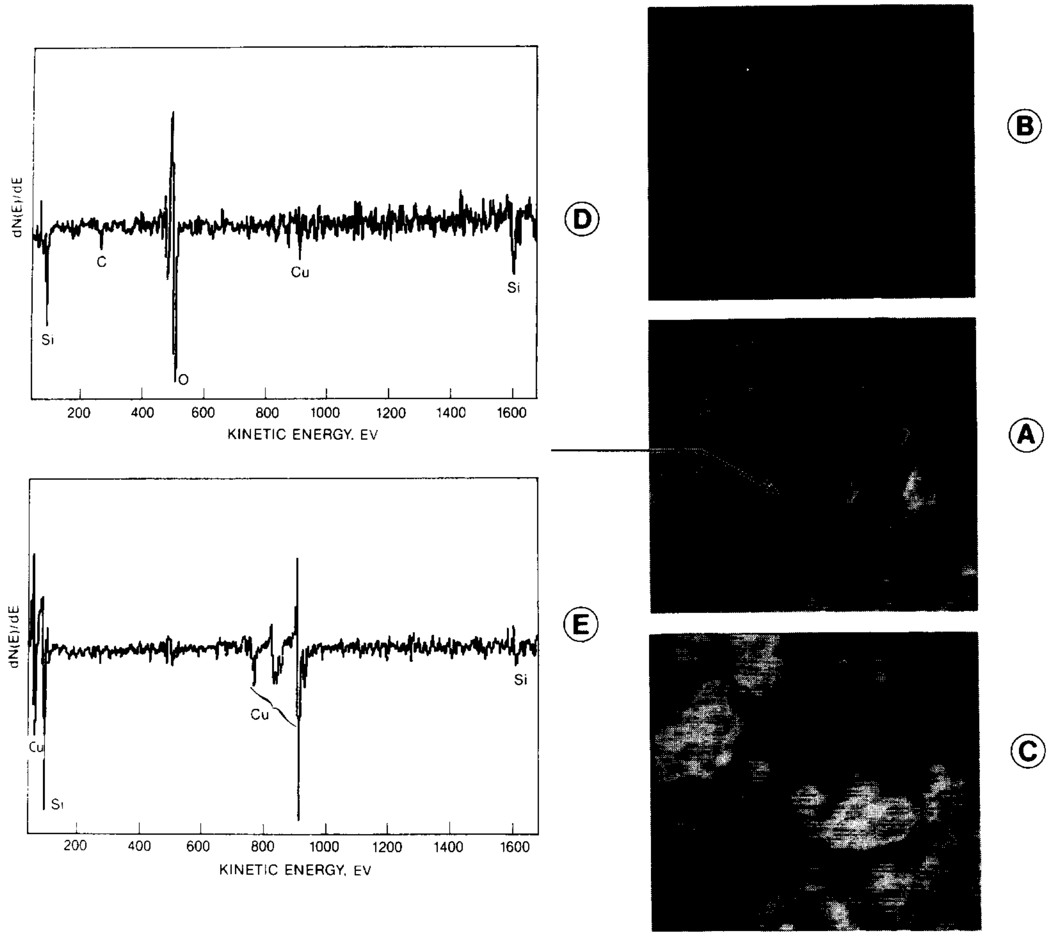


FIG. 6. Scanning Auger data acquired from a particle removed from the fluidized bed after 25% of the Si had reacted with CH_3Cl: (A) SEM photo of indicating point Auger spectra collected from, (B) Cu Auger map over area displayed in (A), (C) Cu Auger map of area displayed in (A) after removing ca. 140 nm by sputtering, (D) Auger spectrum acquired from point indicated in (A), (E) Auger spectrum acquired from point indicated in (A) after removing about 140 nm by sputtering.

duction of methylchlorosilanes (*4*, *5*). If Cu_3Si is present on the surface and is the active catalyst species, one would expect the Cu-to-Si ratio on the surface to be near 3. In this study (including a great deal of data not displayed), the ratio determined from XPS data never exceeded 0.1. The scanning Auger data indicate that the surface of the reacting particles is very nonuniform and that, in averaging over the entire surface of many particles, the XPS data erroneously underestimate the surface concentration in the reactive regions.

Rough estimates of the Cu/Si ratio in the reactive regions can be obtained from the peak-to-peak ratios determined from the Auger derivative spectra. Using sensitivity factors determined from measurements on Cu_3Si, the Cu/Si ratio in the active regions varies from <0.5 to 2, with the majority of the values near 1. While ratios determined this way are only accurate to within 20–50%, it was determined that even in the regions of high Cu levels, the surface Cu/Si ratio was less than 3. Thus, one may question the hypothesis that Cu_3Si is the active species in the direct process.

Frank and Falconer (*3*) and Lewis *et al.*

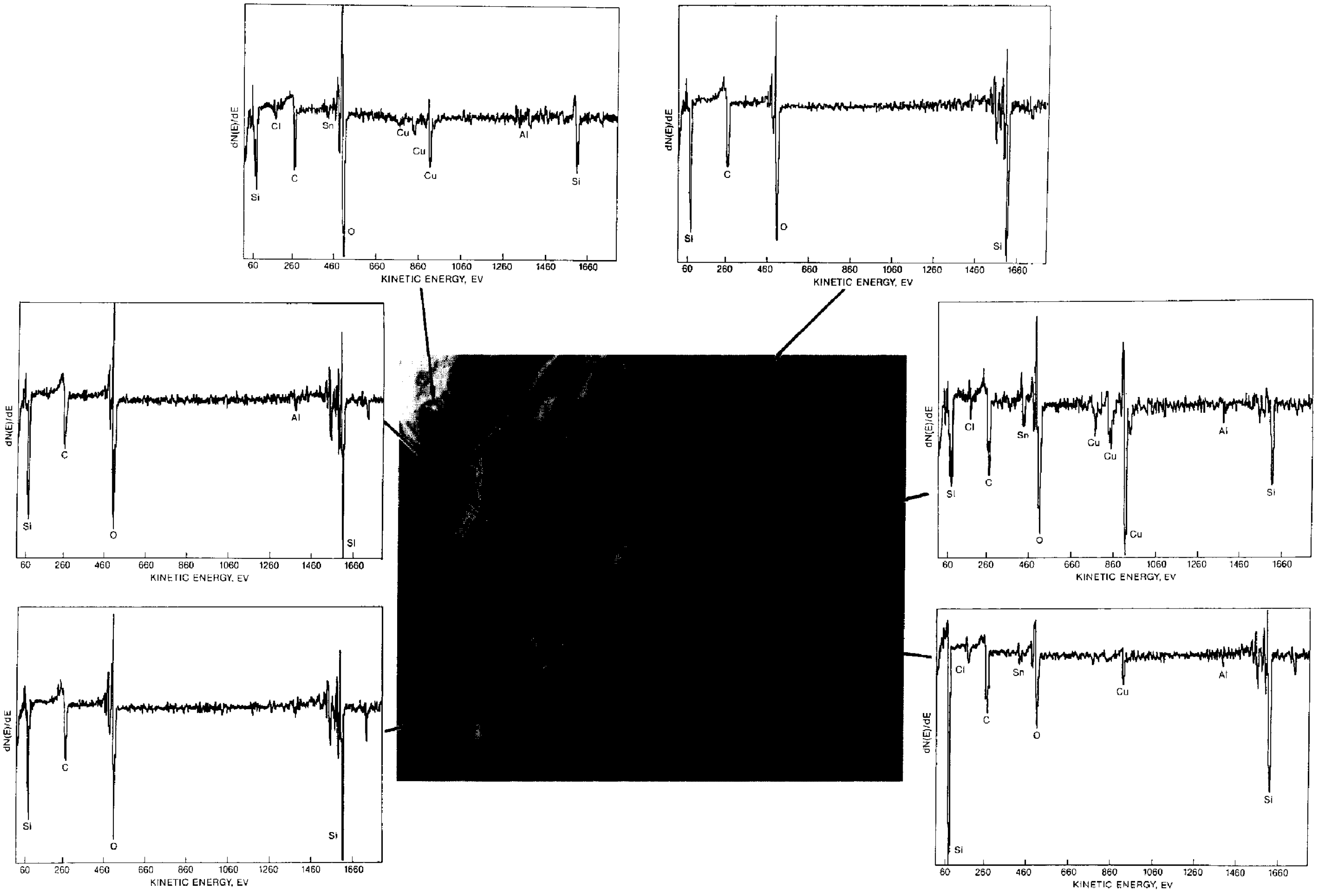


FIG. 7. Scanning Auger data obtained from a fluidized bed at 25% Si utilization following injection of $SnCl_4$. See text for details.

(*9*) have recently discussed the segregation of Si in Cu_3Si. Lewis *et al.* postulate that the active phase in the direct process (that reacting with methyl chloride to produce products) is really a Si-enriched surface with a Cu-to-Si ratio near 1. The Cu-to-Si ratio of 1 determined in this study is remarkably close to the predicted value of Lewis *et al.*, thus supporting their hypothesis. Removing the surface by sputtering increased the Cu-to-Si ratio of a value of 3. This suggests that the bulk of the Cu may be present as η phase, but the *surface* of the reacting areas is enriched in Si.

A second factor that must be kept in mind is that, although care was taken to assure inert sampling of the system, total exclusion of O_2 or H_2O from the samples is impossible. The samples were exposed for approximately 15 min to 760 Torr of dried N_2 during the transfer into the spectrometers. If the N_2 contained 0.1 ppm of O_2, this would result in an O_2 exposure of 1140 Langmuirs. Exposure of 2000 Langmuirs of O_2 to Cu_3Si has been shown to decrease the Cu/Si ratio (*7*). Thus, the low Cu levels may be partly due to the unavoidable O_2 exposure. The authors feel that this is a minor consideration and note that the surface segregation of Si in η phase observed in the work of Frank and Falconer (*3*) was carried out with no O_2 exposure. Further, the oxygen peak in all of the spectra increased dramatically when the sample was exposed to air.

The absence of any satellite from the Cu $2p_{3/2}$ XPS detailed spectra, combined with the peak position of 932.5, indicates that Cu is not present in a 2+ oxidation state, as reported by Sharma and Gupta (*8*). This is in agreement with Gentle and Owen, who indicated that Cu was present as Cu^0 (*10*). The oxidation state of Cu in η phase is zero and the XPS spectra are very similar to that of pure Cu^4. The increased Cu oxidation state observed by Sharma *et al.* may have resulted from different reaction conditions during the direct process or, as suggested by Gentle and Owen, oxidation during sample preparation.

The Zn level was initially present at one-tenth the concentration of Cu, yet it was present on the surface in concentrations greater than or equal to that of Cu. While removal of the surface by sputtering increased the Cu signal, the Zn signal disappeared. The implication of this is that Zn does not alloy with the Si as Cu, but remains on the surface. The confinement of Zn to the surface allows it to act as a promoter with a higher effective concentration than would be expected from the bulk levels.

Sn is also confined to the surface of a *reacting* area. The data in Fig. 7 indicated that Sn went only to active areas and was not found on the unreacted Si surface. Furthermore, it was also found only on the surface. This point helps explain why low levels of Sn (75 ppm) can have such a dramatic effect on the selectivity. Because this is a heterogeneous reaction, only the Si atoms on the surface are reacting with CH_3Cl to form methylchlorosilanes. The concentration of Sn on the surface of only the reacting sites makes it effective when present at very low bulk levels.

From analysis of reaction bed, it has been determined that Zn and Sn are lost from a Si bed as a batch reaction proceeds. This loss presumably occurs as the volatile metal chlorides form and leave the reactor. The formation of a volatile species will transport the promoters throughout the Si bed. This will help transport the promoters throughout the Si bed. This will help distribute them, providing a uniform concentration within the reacting Si bed, even though large particles of metal are initially used. The chlorides will impinge on the entire surface of particles. With such a transport mechanism, it might be expected that the Zn and Sn would be deposited on the entire surface of the particles. The scanning Auger results demonstrated that Zn and Sn were primarily in the reacting regions.

There must be a chemical potential that concentrates the promoters in the active areas. Because the Si was exposed to air, it undoubtedly was covered by a native SiO_2

layer. It has been suggested that active sites form at defects in this SiO_2 layer (*6*). If this is the case, then the surface of nonreactive regions must be mainly SiO_2. At 300°C, there is probably little physisorption of the metal chlorides. Thermodynamically, Zn and Sn chlorides should react with Si to form $SiCl_4$, but they will not react with SiO_2. Thus the metallic Si present in the active site may not only react with the methyl chloride forming methylchlorosilanes but also be responsible for concentrating the promoters in active regions.

The decrease in the Si component (99.7 eV) in the Si 2*p* XPS peak is expected for a batch reaction. As the Si bed reacts, it is constantly losing Si, as evidenced by the pits. Thus, the surface of the particles continually loses metallic Si, which must be replaced by diffusion. Cu readily diffuses in Si (*13*); thus, reaction continues as Cu diffuses into the Si forming an alloy (η phase). As this process proceeds, the metallic Si/Cu interface moves further and further from the surface and is eventually exhausted, and the reaction stops. The initial decrease in the metallic Si peak results as the Cu/Si surface moves deeper into the particle, reducing the surface sampled by the instrument. At the end of the run (81% Si utilization), there is no metallic Si seen on the surface (Fig. 3F). The broad peak shape observed in Fig. 3F is, in part, due to charging. At the end of a run, the bed powder is very fine, making it very difficult to avoid some charging.

The increase in the carbon surface concentration at the end of the run coincides with a decrease in selectivity. A carbon mass balance calculated using carbon feed to the reactor as CH_3Cl and that exiting the reactor in the product distribution indicates that there is a buildup of C in the bed near the end of a run. It has been found generally true that, as selectivity degrades, there is an increase in the C content of the bed. Near the end of a run the bed becomes Cu rich. This is evident by quantitative analysis, as well as visual examination of a bed. Near the end of a run, the bed increasingly appears Cu colored. The η-phase is a silver color; thus, the red color suggests that some free copper may be present. Also note that the Cu surface concentration increases from 0.5 to 1 at.% in going from 60 to 81% Si utilization. As the Si is depleted, some of the Cu might be expected to present in an unalloyed state. The presence of free Cu may cause cracking of the CH_3Cl, which could cause coking. The decrease in concentration of methyl groups caused by cracking would also explain why the product distribution near the end of the run contains a higher Cl content than that in the middle. While this hypothesis explains the results, it is impossible to tell whether it is the buildup of free Cu and C that degrades the selectivity or whether the decrease in selectivity is a result of a buildup of C in the bed.

CONCLUSIONS

Based on the results discussed above, the following conclusions can be drawn.

—Cu is present on the surface at levels lower than expected if it was in the form of Cu_3Si. It is present only in the Si regions that show reaction and is there as Cu^0. The Cu concentration increases with depth below the surface.

—Zn is present at about the same surface concentrations as Cu, even though the bulk Zn level is 10% that of Cu. It is found only on the surface of *reacting* areas and does not extend into the bulk.

—Sn, when present at the optimum bulk levels for selectivity (as reported by Ward *et al.* (*11*)), is difficult to be detected on the surface. Sn, like Zn, concentrates only on the surface of *reacting* Si areas.

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