# Direct Formation of (CH$_3$)$_2$HSiCl from Silicon and CH$_3$Cl

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A Cu-catalyzed reaction procedure was found for the selective formation of dimethylchlorosilane [(CH$_3$)$_2$HSiCl] from the direct reaction of CH$_3$Cl with solid Si. The new procedure is a two-step process. A Cu/Si sample is prepared by evaporating Cu onto clean polycrystalline Si under ultrahigh vacuum, and the Cu/Si surface is first activated by exposure to 10% HSiCl$_3$/CH$_3$Cl at 598 K. After the HSiCl$_3$/CH$_3$Cl mixture is evacuated from the reactor, the activated Cu/Si surface is reacted in fresh CH$_3$Cl. For low surface concentrations of Cu, the partially hydrogenated silane, (CH$_3$)$_2$HSiCl, is selectively produced. Trichlorosilane was also found to activate polycrystalline Si (in the absence of Cu) for production of highly chlorinated methylchlorosilanes at a much higher rate than on the Cu/Si surface but with poor selectivity to (CH$_3$)$_2$HSiCl. All reactions are carried out at atmospheric pressure in a reactor that is attached to an ultrahigh-vacuum chamber. This allows surface analysis by Auger electron spectroscopy, which detected SiCl$_x$ on reacted surfaces. These SiCl$_x$ sites, which appear necessary for methylchlorosilane formation, are apparently formed during activation by HSiCl$_3$.

## Introduction

In the presence of a Cu catalyst, solid Si reacts with gaseous CH$_3$Cl to selectively produce dimethyldichlorosilane (DMD), which is required for the industrial production of long-chain silicone polymers.[1] Other methylchlorosilanes (MCS) are also produced during this industrial reaction (known as the direct-synthesis reaction), which uses powdered Si and CuCl as the starting solids in a fluidized bed. We attempted to model this process with a planar sample, so that its surface composition could be measured, by evaporating Cu onto a polycrystalline Si surface. Surfaces prepared this way did not react with CH$_3$Cl. However, we found that a Cu/Si surface could be activated to selectively form dimethylchlorosilane [(CH$_3$)$_2$HSiCl].

Dimethylchlorosilane contains a reactive Si–H bond, which facilitates formation of complex silicones. Dimethylchlorosilane is used industrially to produce a cross-linked, high molecular weight silicone polymer for dental implants and as a starting material for potting compounds, which are used to separate components on printed circuit boards.[2] Previously, the best process for (CH$_3$)$_2$HSiCl production required H$_2$,[3] and the selectivity was only 40%. Dimethylchlorosilane is produced in less than 2% yield during the industrial production of DMD.[4-6]

This paper presents a new process that forms this partially hydrogenated methylchlorosilane. Copper/silicon surfaces are activated by exposure to a HSiCl$_3$/CH$_3$Cl mixture at 598 K. Both HSiCl$_3$ and CH$_3$Cl react, but they also modify the surface so that it subsequently can react with CH$_3$Cl alone; the activated surface was 90% selective for the formation of (CH$_3$)$_2$HSiCl during reaction with CH$_3$Cl.

The HSiCl$_3$/CH$_3$Cl mixture also activates Si surfaces (without Cu), and highly chlorinated methylchlorosilanes (HSiCl$_3$, CH$_3$-HSiCl$_2$, CH$_3$SiCl$_3$) form on these activated Si surfaces at 598 K. Silicon is consumed at a much higher rate from activated Si surfaces than from activated Cu/Si surfaces. Unactivated silicon does not react with CH$_3$Cl except after long exposure at higher temperatures, and different MCS products form.[7]

Reactions on the Si and Cu/Si surfaces were studied in an atmospheric pressure, differential reactor, which was attached to an ultrahigh-vacuum system that contained an Auger spectrometer. Auger electron spectroscopy (AES) provides elemental surface composition and some chemical bonding information for Si because the Si(LVV) Auger transition is sensitive to the valence state of Si. All reactions were carried out at 598 K because this corresponds to the highest temperature used in previous studies on Cu$_3$Si bulk alloys[8] and it is in the upper temperature range

of the industrial direct-synthesis process. Surfaces were analyzed after reaction by both AES and SEM.

## Experimental Methods

Reaction was carried out at atmospheric pressure on 1-cm$^2$ samples of Si and Cu/Si in a differential batch reactor. A transfer mechanism moved a sample between the atmospheric pressure reactor and an attached ultrahigh-vacuum system (UHV) without intermediate air exposure. Samples were prepared and characterized by AES in the UHV chamber and then moved to the reaction chamber. Reaction was carried out in CH$_3$Cl or in a 10% HSiCl$_3$/90% CH$_3$Cl mixture at 1 atm and 598 K.

A metal bellows pump recirculated reaction gases over the sample, and a Valco GC sampling valve was used to inject samples into an HP 5712 GC equipped with a thermal conductivity detector.[7] The samples were separated at 323 K on a column containing 70% OV-210 and 30% OV-1 (20% wt loading on 80/100-mesh Chromasorb PAW-DMCS). Calibrations were done with mixtures of methylchlorosilanes in CH$_3$Cl. Reaction rates were determined from slopes of product concentration versus time. Distributions among MCS products were calculated from rate measurements at a given time. The non-silicon-containing products (non-silanes) were not separated from each other, and they were not considered in calculating product distributions.

For reaction in pure CH$_3$Cl, the reactor was evacuated and then filled with CH$_3$Cl (Matheson; 99.5%) that was purified over a sieve trap at 275 K. For the HSiCl$_3$/CH$_3$Cl reaction mixture, the reactor was pressurized with CH$_3$Cl to 0.9 atm and the vapor above liquid HSiCl$_3$ (Petrarch System, Inc.) was admitted to the reactor until the pressure was 1 atm. The liquid HSiCl$_3$ was degassed first in several freeze–pump–thaw cycles. Complete mixing, as determined by GC, was obtained after 15 min. Subsequent to reaction in the mixture, the system was evacuated and refilled with pure CH$_3$Cl for further reaction studies.

*Silicon Samples.* Polycrystalline Si (Dow Chemical) was etched for 2–5 min in an aqueous, hot solution of a 1:1 mixture of 30% HF and 5 M K$_2$Cr$_2$O$_7$ to remove native oxide[4] before being

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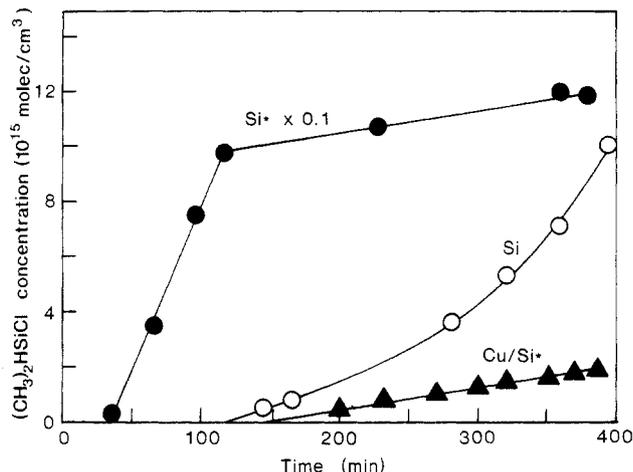(8) Frank, T. C.; Kester, K. B.; Falconer, J. L. *J. Catal.* **1985**, *91*, 44.

**Figure 1.** Gas-phase $(CH_3)_2HSiCl$ concentration versus time. The polycrystalline Si (open circles) reacted with a 10% $HSiCl_3/CH_3Cl$ mixture. The Si* and Cu/Si* surfaces reacted with $CH_3Cl$ after activation by reaction in $HSiCl_3/CH_3Cl$.

mounted on a stainless steel holder. Samples were heated by conduction from a resistively heated Mo bar clamped to the backside of the Si. A chromel–alumel thermocouple was spot-welded to the back of the Mo bar to measure sample temperature. Silicon samples were cleaned by cycles of $Ar^+$ bombardment and annealing (625 K, 15 min), and cleanliness was verified by AES. Even after extended cleaning cycles, small concentrations of C, Cl, and O remained because of residual $CH_3Cl$ in the system.

For studies on Cu/Si surfaces, Cu was evaporated from a heated $Al_2O_3$ crucible. Copper coverages up to 4 nm were deposited on clean Si at 300 K, and samples were analyzed by AES before transfer into the reaction chamber. Copper thickness, which was reproducible to ±5%, was estimated from the Cu/Si Auger peak intensity ratio and calibrations obtained by Rossi et al.[9] Depth profiling and profilometry verified the thickness for Cu evaporated onto a quartz substrate. Copper deposition increased C and Cl surface compositions, but these species are deposited after a short exposure to $CH_3Cl$ and thus no effort was made to further reduce their concentrations.

*Surface Analysis.* Samples were characterized before and after reaction by AES. A 3-keV, 30-$\mu$A electron beam was used. Surface compositions were *estimated* from the AES peak-to-peak amplitudes of Si (1619 eV), Cu (917 eV), Cl (180 eV), C (273 eV), and O (510 eV) transitions and published sensitivity factors.[10] The high-energy Si transition was used because the low-energy Si peak, though more surface sensitive, changes line shape and amplitude with chemical environment. The high-energy Cu peak was used so that the escape depths of Si and Cu Auger electrons were similar. After reaction, samples were removed from the reactor system and examined by SEM.

## Results

*1. Uncatalyzed Reactions. 1a. Si + $CH_3Cl$.* A cleaned Si sample did not react with $CH_3Cl$ to form methylchlorosilanes, even after 8 h at 598 K. After 10 min of $CH_3Cl$ exposure, however, low-boiling, non-silane products formed at a rate of 5 × $10^{13}$ molecules/cm²·s. These products apparently formed from $CH_3Cl$ decomposition on Si since Auger analysis showed significant amounts of surface C (12%) though not much Cl (1%). Similar results have been reported on Si(100), which did not react with $CH_3Cl$ to form MCS even after 31 h at 670 K.[7] Thus, the Si surface does not readily react with $CH_3Cl$.

*1b. Si + $HSiCl_3/CH_3Cl$.* In contrast, a $HSiCl_3/CH_3Cl$ mixture reacted with clean Si to form $CH_3HSiCl_2$, $(CH_3)_2HSiCl$,

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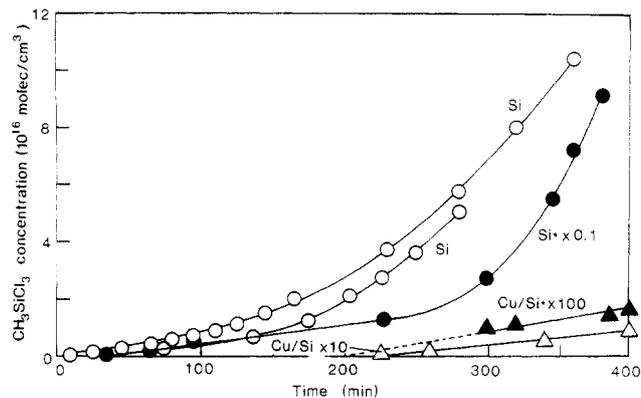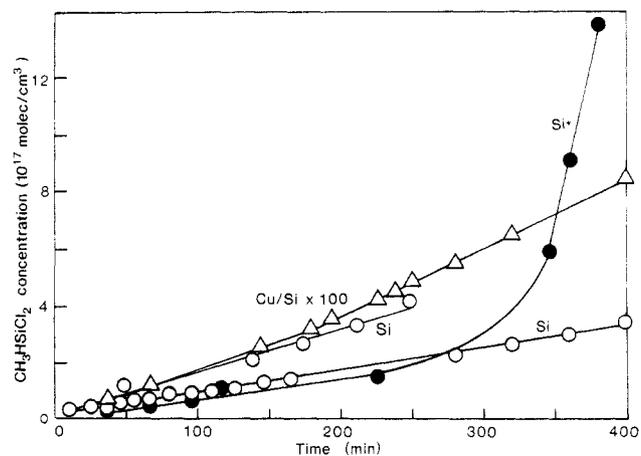


**Figure 2.** Gas-phase $CH_3SiCl_3$ concentration versus time for the reaction of polycrystalline Si and Cu/poly-Si surfaces (open symbols) with a 10% $HSiCl_3/CH_3Cl$ mixture. The Si* and Cu/Si* surfaces reacted with $CH_3Cl$ after activation in $HSiCl_3/CH_3Cl$.



**Figure 3.** Gas-phase $CH_3HSiCl_2$ concentration versus time for the reaction of polycrystalline Si and Cu/poly-Si surfaces (open symbols) with a 10% $HSiCl_3/CH_3Cl$ mixture. The Si* surface reacted with $CH_3Cl$ alone after activation in $HSiCl_3/CH_3Cl$.

**TABLE I: Methylchlorosilane Induction Times**

| products | induction time, min | | | |
|---|---|---|---|---|
|  | $Si^a$ | $Cu/Si^a$ | $Si^{*b}$ | $Cu/Si^{*b}$ |
| non-silanes | 0 | 0 | 0 | 0 |
| $HSiCl_3$ | c | c | 25 | – |
| $(CH_3)_2HSiCl$ | 125 | 420 | 20 | 150 |
| $CH_3HSiCl_2$ | 0 | 5 | 10 | – |
| $CH_3SiCl_3$ | 10 | 225 | 30 | 250 |

$^a$ Surface reacted in 10% $HSiCl_3/CH_3Cl$. $^b$ Asterisk indicates surface reacted in $CH_3Cl$ after evacuation of 10% $HSiCl_3/CH_3Cl$. $^c HSiCl_3$ is a reactant.

**TABLE II: Methylchlorosilane Formation Rates after 360 min of Reaction**

| products | areal rate, $10^{14}$ molecules/cm²·s | | | |
|---|---|---|---|---|
|  | $Si^a$ | $Cu/Si^a$ | $Si^{*b}$ | $Cu/Si^{*b}$ |
| non-silane | 105 | 3 | 1100 | 0.5 |
| $HSiCl_3$ | –112 | –34 | 210 | – |
| $(CH_3)_2HSiCl$ | 3 | – | 35 | 0.6 |
| $CH_3HSiCl_2$ | 68 | 3 | 200 | – |
| $CH_3SiCl_3$ | 26 | 0.5 | 175 | 0.05 |

$^a$ Surfaces reacted in 10% $HSiCl_3/CH_3Cl$. $^b$ Asterisk indicates samples reacted in $CH_3Cl$ after evacuation of 10% $HSiCl_3/CH_3Cl$.

and $CH_3SiCl_3$. Over a 7-h reaction period, the rates of formation of $(CH_3)_2HSiCl$ (Figure 1) and $CH_3SiCl_3$ (Figure 2) increased while the rate of $CH_3HSiCl_2$ formation was constant (Figure 3). The $HSiCl_3$ concentration decreased (Figure 4), and its rate of consumption was equal to the total rate of MCS formation.
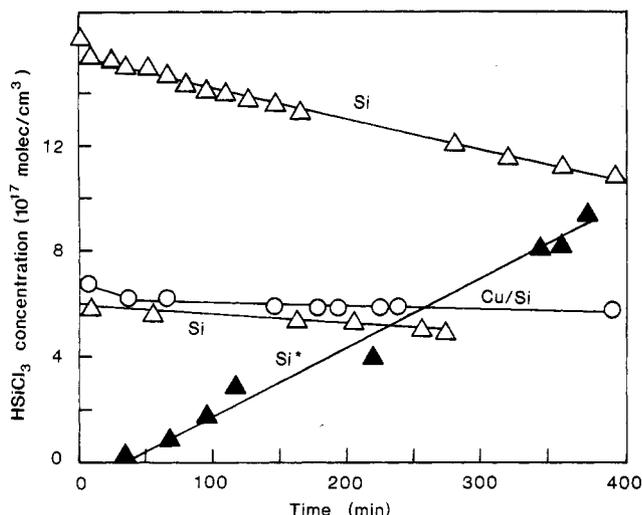
**Figure 4.** Gas-phase $HSiCl_3$ concentration versus time for the reaction of Si and Cu/poly-Si surfaces (open symbols) with a 10% $HSiCl_3$/$CH_3Cl$ mixture. The Si* surface reacted with $CH_3Cl$ after activation on $HSiCl_3$/$CH_3Cl$.

**TABLE III: Product Distributions after 360 min of Reaction**

| products | product distribution, % | | | |
|---|---|---|---|---|
| | Si[a] | Cu/Si[a] | Si*[b] | Cu/Si*[b] |
| $HSiCl_3$ | c | c | 34 | – |
| $(CH_3)_2HSiCl$ | 2 | – | 6 | 90 |
| $CH_3HSiCl_2$ | 70 | 86 | 32 | – |
| $CH_3SiCl_3$ | 28 | 14 | 28 | 10 |

[a] Surfaces reacted in 10% $HSiCl_3$/$CH_3Cl$. [b] Asterisk indicates surfaces were further reacted in MeCl after evacuation of 10% $HSiCl_3$/$CH_3Cl$. [c] $HSiCl_3$ was a reactant, and this was not considered in determining the product distribution.

**TABLE IV: Estimated Surface Compositions after Reaction**

| surface | concn, atom % | | | | | | reactn time, min |
|---|---|---|---|---|---|---|---|
| | Si | Cu | Cl | C | O | S | |
| Si[a] | 70 | 0 | 1 | 12 | 17 | 0 | 480 |
| Cu/Si[a] | 27 | 32 | 9 | 25 | 5 | 2 | 600 |
| Si*[b] | 50 | 0 | 9 | 26 | 15 | 0 | 400 |
| Cu/Si*[b] | 39 | 1 | 25 | 19 | 14 | 2 | 775 |
| Si**[c] | 29 | 0 | 17 | 53 | 1 | 0 | 380 |
| Cu/Si**[c] | 40 | 1 | 19 | 39 | 2 | 0 | 1250 |

[a] Surface reacted with $CH_3Cl$. [b] Asterisk indicates surface reacted with 10% $HSiCl_3$/$CH_3Cl$. [c] Double asterisk indicates further reaction in $CH_3Cl$ after evacuation of $HSiCl_3$/$CH_3Cl$.

Essentially, no induction time was seen before $CH_3HSiCl_2$ and $CH_3SiCl_3$ formed, but $(CH_3)_2HSiCl$ had an induction time of 125 min (Table I). After 6 h of reaction, the products were 70% $CH_3HSiCl_2$. The areal rates for these products are presented in Table II, and product distributions are in Table III. Rates determined from experiments on two samples were similar, as shown in Figures 2 and 3.

*1c. Activated Si + CH₃Cl.* After reaction in the $HSiCl_3$/$CH_3Cl$ mixture, the sample was analyzed by AES and then further reacted in pure $CH_3Cl$. The AES analysis (Table IV) showed that the $HSiCl_3$/$CH_3Cl$ mixture had chlorinated the surface, and an Auger peak was observed at 84 eV (Figure 5a) that corresponds to Si–Cl bonding.[7] Since we have observed Cl on Si surfaces without the 84-eV peak being present, we associate the 84-eV peak with multiple chlorine atoms bound to Si and will refer to this as a $SiCl_x$ species.

This chlorinated surface reacted with pure $CH_3Cl$ after a short induction time (Table I) to form $CH_3HSiCl_2$, $CH_3SiCl_3$, and $HSiCl_3$ (Figure 2–4) in approximately equal amounts. Less than 10% of the MCS products was $(CH_3)_2HSiCl$ (Figure 1). The rates of formation of $CH_3HSiCl_2$ and $CH_3SiCl_3$ were constant until 250 min and then increased, while $HSiCl_3$ formed at a constant
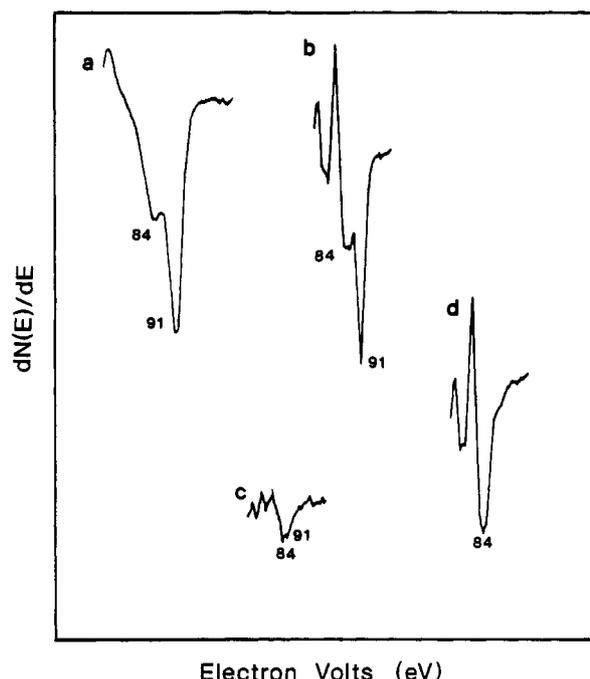


Electron Volts (eV)

**Figure 5.** Si(LVV) Auger transitions for (a) a polycrystalline Si surface after reaction in 10% $HSiCl_3$/$CH_3Cl$ at 598 K, (b) a Cu/Si sample after reaction with 10% $HSiCl_3$/$CH_3Cl$ at 598 K, (c) activated polycrystalline Si after futher reaction in pure $CH_3Cl$ at 598 K, and (d) activated Cu/Si after further reaction in pure $CH_3Cl$ at 598 K.

rate over the entire reaction period. The rate of $(CH_3)_2HSiCl$ formation decreased after 120 min. The rates of MCS formation are 3–15 times larger than the corresponding rates for reaction of the $HSiCl_3$/$CH_3Cl$ mixture with Si. Non-silanes formed on this activated Si surface at a rate that was larger than the sum total of the MCS rates (Table II). On one sample, reaction continued until the Si was almost completely consumed. After a long reaction time, large amounts of C and Cl were present on the surfaces (Table IV), and the 84-eV peak due to $SiCl_x$ was still present (Figure 5c).

*2. Copper-Catalyzed Reactions. 2a. Cu/Si + CH₃Cl.* A Si surface with 4 nm of evaporated Cu had an Auger spectrum that showed surface Si and Cu and a split Si peak, which is indicative of Cu–Si bonding.[11–14] This Cu/Si surface did not behave in the same manner as the Si and CuCl powders in the industrial direct-synthesis reaction. Methylchlorosilanes were not produced even after 30 h in $CH_3Cl$ at 598 K. In the same reactor, bulk $Cu_3Si$ alloys readily formed dimethyldichlorosilane with high selectivity.[8] Though not active for MCS formation, the Cu/Si surface decomposed $CH_3Cl$ to non-silanes at a rate of $10^{13}$ molecules/cm²·s. This rate is 1–2 orders of magnitude lower than that on the surfaces of alloys of $Cu_3Si$ bulk composition.

The Auger spectrum of the clean Cu/Si surface (Figure 6a) was similar to but not identical with that of $Cu_3Si$ (Figure 6b). For both surfaces, the compositions were similar (70% Cu), and the Si(LVV) peak was split into two peaks at 90 and 94 eV. The Cu/Si surface was slightly contaminated by C (3%), Cl (2%), and O (1%). The other significant difference is that the 90-eV peak was smaller than the 94-eV peak on $Cu_3Si$ but equal to the 94-eV peak on the Cu/Si surface. These results were quite reproducible and may indicate a subtle difference in bonding between Cu and Si on the two surfaces.

After 30 h in $CH_3Cl$, a Cu/Si surface contained Cu, Si, C, Cl, O, and S (Table IV). In repeat experiments, sulfur was not seen but the reactivity was the same. The Si present gave a single

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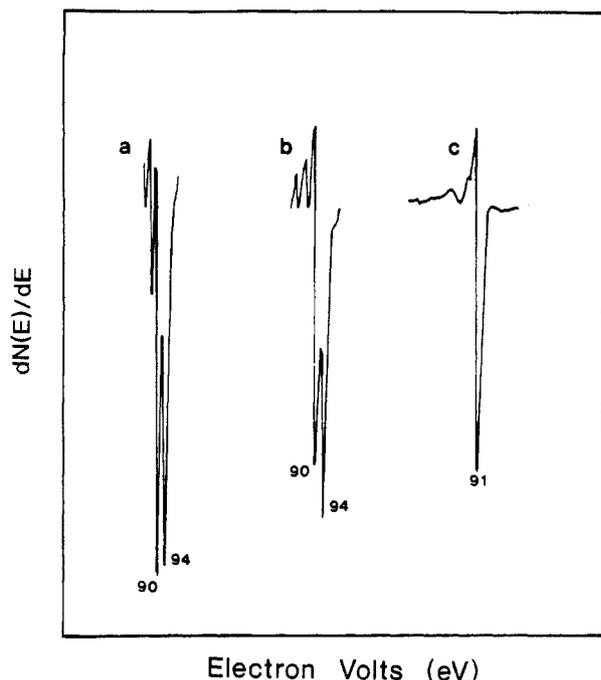
**Figure 6.** Si(LVV) Auger transitions for (a) polycrystalline Si with 4 nm of evaporated Cu, (b) clean $Cu_3Si$, and (c) clean polycrystalline Si.



**Figure 7.** Gas-phase concentrations of reaction products for the reaction of a Cu/poly-Si surface with 10% $HSiCl_3/CH_3Cl$ mixture.

Auger peak at 91 eV after $CH_3Cl$ exposure. This indicates that a majority of the Si was in its elemental state and was not bonded to Cu.

*2b. $Cu/Si + HSiCl_3/CH_3Cl$.* Though Cu/Si surfaces were unreactive in $CH_3Cl$, they reacted with a $HSiCl_3/CH_3Cl$ mixture. Methyldichlorosilane [$CH_3HSiCl_2$] formed after a short induction time (Figure 3), $CH_3SiCl_3$ formed after 225 min (Figure 2), and $(CH_3)_2HSiCl$ started forming after 420 min. As these MCS products formed, $HSiCl_3$ was consumed at 10 times the rate of MCS formation. Rates of formation of all products were constant for 13 h, when reaction was stopped (Figure 7). The $HSiCl_3/CH_3Cl$ mixture reacted on the Cu/Si surface; no MCS products formed when the mixture was exposed to a Ta surface for 6 h at 598 K.

*2c. Activated $Cu/Si + CH_3Cl$.* After reaction with the $HSiCl_3/CH_3Cl$ mixture, the Cu/Si sample was analyzed by AES and then further reacted in pure $CH_3Cl$. The surface contained more Si than before reaction and a large amount of surface Cl (Table IV). As indicated by the 84-eV shoulder on the Si(LVV) peak (Figure 5b), some Cl was bound to Si. Methyl chloride reacted with this surface, after significant induction periods (Table I), to form $(CH_3)_2HSiCl$ and $CH_3SiCl_3$ (Figures 1 and 2). Of the MCS products, 90% was $(CH_3)_2HSiCl$, and the MCS formation rates were constant for 22 h, when reaction was stopped. The rates were much smaller than the rates of MCS formation from the $HSiCl_3/CH_3Cl$ mixture (Table II). After reaction, carbon covered 39% of the surface (Table IV), and most of the surface Si was in the $SiCl_x$ form (Figure 5d).

**Discussion**

Neither Si nor Cu/Si surfaces form methylchlorosilanes from $CH_3Cl$ alone at 598 K, though both surfaces decompose $CH_3Cl$ (as indicated by both non-silane formation and C and Cl deposits on the surface). Though both types of surfaces contained Cl after $CH_3Cl$ exposure, the Cl was not bonded to Si as the $SiCl_x$ species that was seen on $Cu_3Si$ surfaces.[8] Analysis by SEM showed no change in surface structures for the Si surfaces, even after 33 h in $CH_3Cl$. The Cu/Si surface had deposits of CuCl (identified by EDX) that apparently formed as $CH_3Cl$ decomposed to form Cl.

An $HSiCl_3/CH_3Cl$ mixture activated both Si and Cu/Si surfaces for $CH_3HSiCl_2$ and $CH_3SiCl_3$ formation, and the $SiCl_x$ species was present on both reacted surfaces. Thus, it appears that $SiCl_x$ surface species are necessary for methylchlorosilane
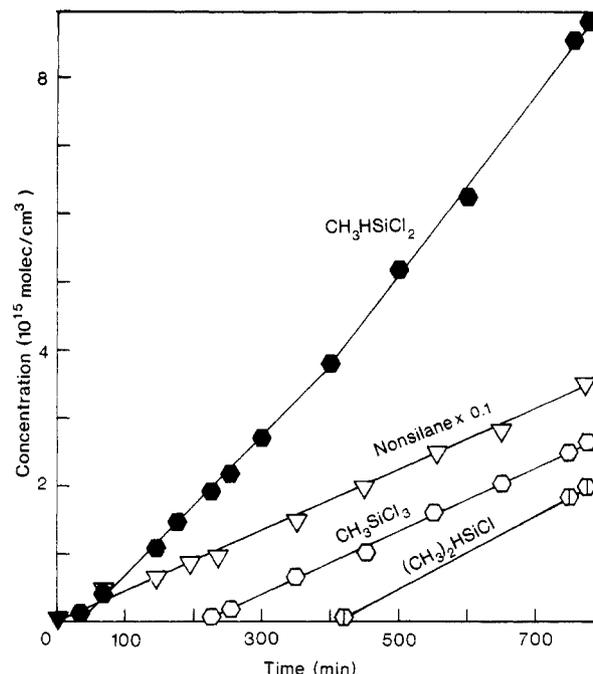
formation from Si. Rates were 1–2 orders of magnitude lower, and induction times were 1 order of magnitude longer on the Cu/Si surfaces than on Si alone, however. Selectivity for $CH_3HSiCl_2$ was also higher on the Cu/Si surfaces. Further reaction of these activated surfaces (activated by the $HSiCl_3/CH_3Cl$ mixture) with pure $CH_3Cl$ produced different product distributions, and the Cu/Si surfaces were highly selective for $(CH_3)_2HSiCl$ production. Analysis by SEM after reaction with $CH_3Cl$ indicated large increases in surface areas of both Si and Cu/Si samples. We will first discuss the uncatalyzed reaction process and then the process in the presence of a Cu catalyst.

*1. Uncatalyzed Reactions.* Without activation, the Si surface did not form MCS at 598 K. Frank and Falconer[7] found that Si(100) reacted wtih $CH_3Cl$ after 9 h at 695 K (after an initial 31-h exposure to $CH_3Cl$ at 670 K) to form MCS, but in agreement with the present studies, they saw no reaction for 31 h at 670 K. Their active surface contained a $SiCl_x$ species (84-eV Si Auger peak). This species may be necessary for reaction since Cl was also on the polycrystalline surface in the present study, but it was not in the $SiCl_x$ form and the surface was not reactive.
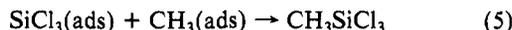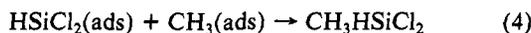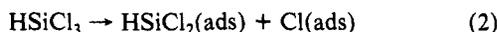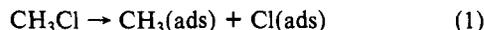
*1a. Reaction with $HSiCl_3/CH_3Cl$.* Though unreactive with $CH_3Cl$ alone, clean Si readily reacts with a $HSiCl_3/CH_3Cl$ mixture. The 5-min induction period at 598 K is significantly shorter than the 40-h induction at 670–695 K for $CH_3Cl$ alone on Si(100).[7] Auger analysis after exposure to $HSiCl_3/CH_3Cl$ shows that this mixture effectively chlorinated the surface and formed $SiCl_x$ species (84-eV Si peak). Apparently, these sites are required for MCS formation. These sites form only at elevated temperatures; exposure of clean Si at 300 K for 1 h to a $HSiCl_3/CH_3Cl$ mixture deposited some Cl, but no $SiCl_x$ species were detected. Moreover, after exposure, this surface did not react with $CH_3Cl$ alone to form MCS at 598 K.

A mass balance indicates that the Si in the MCS products may be from $HSiCl_3$. Since the MCS products are 70% $CH_3HSiCl_2$ and 28% $CH_3SiCl_3$, one possible mechanism is $HSiCl_3$ dissociation by statistical removal of either an H or a Cl atom; the bond dissociation energies in $HSiCl_3$ are 92 kcal/mol for the Si–H bond[15,16] and 104.8 for the Si–Cl bond.[16] Thus, the Si–H bond appears more likley to break, but this may be affected by how $HSiCl_3$ adsorbs. If the Si–H and Si–Cl bonds have similar

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probabilities of dissociating on the surface, then the concentration of HSiCl$_2$(ads) species would be 3 times that of SiCl$_3$(ads) species. If these species are all methylated by CH$_3$Cl, a product distribution of 75% CH$_3$HSiCl$_2$ and 25% CH$_3$SiCl$_3$ is expected. This is close to the measured distribution; the small amount of (CH$_3$)$_2$HSiCl (2%) may form by secondary reactions. This scheme requires CH$_3$Cl dissociation, and the CH$_3$ species must react with the SiCl$_3$(ads) and HSiCl$_2$(ads) fragments much more rapidly than the Cl and H atoms on the surface react with these fragments. A proposed reaction sequence is as follows:

$$CH_3Cl \rightarrow CH_3(ads) + Cl(ads) \tag{1}$$

$$HSiCl_3 \rightarrow HSiCl_2(ads) + Cl(ads) \tag{2}$$

$$HSiCl_3 \rightarrow SiCl_3(ads) + H(ads) \tag{3}$$

$$HSiCl_2(ads) + CH_3(ads) \rightarrow CH_3HSiCl_2 \tag{4}$$

$$SiCl_3(ads) + CH_3(ads) \rightarrow CH_3SiCl_3 \tag{5}$$

The Cl and H atoms can recombine to form Cl$_2$, HCl, and H$_2$. According to this scheme, all the Si in the product is from HSiCl$_3$, and this is consistent with the mass balance. Since all of the Si-containing products contain CH$_3$ groups (i.e., SiCl$_4$ or SiH$_4$ were not observed), both HSiCl$_3$ and CH$_3$Cl are necessary for the observed reactions.

Another possible mechanism for CH$_3$HSiCl$_2$ formation is that HSiCl$_3$ forms HCl, which can react with CH$_3$Cl. The reaction of HCl and CH$_3$Cl has been reported to form methyldichlorosilane with high selectivity, and CH$_3$SiCl$_3$ as a secondary product.[17]

*1b. CH$_3$Cl Reactions with Activated Surfaces.* On the activated surface, reaction of CH$_3$Cl alone formed MCS at a rate 3–12 times faster than reaction of the HSiCl$_3$/CH$_3$Cl mixture, and the products (HSiCl$_3$, CH$_3$HSiCl$_2$, CH$_3$SiCl$_3$) were more highly chlorinated. Only a short induction period was seen. All the Si could be reacted to MCS, but when reaction was stopped with Si remaining, the surface was highly porous (as determined by SEM) and contained SiCl$_x$ sites, as well as high carbon concentrations.

The HSiCl$_3$/CH$_3$Cl reaction activated the surface for reaction with CH$_3$Cl. On Si(100) activated by long exposures to CH$_3$Cl at high temperatures,[7] the products formed were similar, except that SiCl$_4$ was also a major product and (CH$_3$)$_2$HSiCl was not seen. Thus, similar processes may occur in both cases.

*2. Copper-Catalyzed Reactions.* Though Si was bonded to Cu, as indicated by the split Si(LVV) Auger peaks, the Cu/Si surface was unlike bulk alloys such as Cu$_3$Si, which readily react with CH$_3$Cl to selectively form dimethyldichlorosilane.[8] As mentioned, the Si(LVV) Auger spectra of the Cu/Si surfaces are different from those of Cu$_3$Si surfaces. Thus, a Cu/Si surface with the 90-eV peak of amplitude similar to the 94-eV peak does not react with CH$_3$Cl. Moreover, even after activation, the Cu/Si surfaces have different product distributions from bulk alloys. Thus, there appears to be a strong correlation between the surface interactions of the Cu/Si and the reactivity with CH$_3$Cl.

*2a. Reaction with HSiCl$_3$/CH$_3$Cl.* The addition of Cu to Si reduced the reaction rates (Table II) of HSiCl$_3$/CH$_3$Cl mixtures and increased the CH$_3$SiCl$_3$ induction times; the primary product, CH$_3$HSiCl$_2$, formed after 5 min at 598 K. The product distribution changed somewhat (Table III), and selectivity to CH$_3$HSiCl$_2$ increased. A mass balance on Si indicates that 10 times more HSiCl$_3$ reacted than MCS products formed, and thus, the solid Si may not be in the reaction products. The reacted surface also contained more Si than the fresh surface (Table IV), and this may also be an indication of Si deposition. That is, Cu may increase the rate of HSiCl$_3$ decomposition.

The Cu/Si surfaces, after reaction with HSiCl$_3$/CH$_3$Cl mixtures, contained more Cl than the Si surfaces did after similar treatment (Table IV). Analysis of reacted surfaces by EDX, however, showed that CuCl crystals formed, and thus, only some

**TABLE V: Product Distribution after 270 min of Reaction**

| methylchlorosilane | product distribution, % | | | |
| --- | --- | --- | --- | --- |
| | Cu$_3$Si[a] | Cu$_3$Si[b] | Cu$_3$Si[c] | Cu/Si[d] |
| (CH$_3$)$_2$SiCl$_2$ | 75 | – | 20 | 51 |
| CH$_3$SiCl$_3$ | 22 | 56 | 55 | 21 |
| CH$_3$HSiCl$_2$ | – | 25 | 22 | 19 |
| (CH$_3$)$_2$HSiCl | 1 | 19 | 1 | – |
| HSiCl$_3$ | – | – | 1 | – |
| (CH$_3$)$_3$SiCl | 3 | – | – | – |

[a] Reacted with CH$_3$Cl only at 598 K. [b] Sample in (a) reacted with 10% HSiCl$_3$/CH$_3$Cl. The HSiCl$_3$ was added at 300 K. [c] Sample in (b) further reacted in pure CH$_3$Cl only. [d] Sample of powdered Cu$_4$Si that was reacted with HSiCl$_3$/CH$_3$Cl at 640 K.[5]

of the Cl was present as SiCl$_x$ (as shown by the 84-eV shoulder on the Si(LVV) Auger peak). Studies of Cl$_2$ adsorption on Cu films[18] also showed that CuCl$_x$ ($x$ = 0–2) forms on Cu surfaces.

*2b. Reactions with Activated Cu/Si Surfaces.* One of the most interesting aspects of this work is the high selectivity to form (CH$_3$)$_2$HSiCl on the activated Cu/Si surface. This selective process can be carried out at a constant rate for long times. The 90% selectivity is much higher than that obtained either during the direct synthesis reaction on Cu$_3$Si (only 2%) or in a process that required H$_2$ in the feed (40%).[3]

The activated Si surfaces without Cu showed poor selectivity for (CH$_3$)$_2$HSiCl, but their overall rate of formation of methylchlorosilanes was almost 500 times higher. The rate of (CH$_3$)$_2$HSiCl formation was over 50 times higher on the activated Si surface without Cu than on the activated Cu/Si surface. Thus, the Cu dramatically reduces reaction rates but acts as a selective inhibitor. On bulk Cu–Si alloys, reaction rates to MCS are also slower than on the activated Si surface.

After reaction, the C surface coverage was much higher than that seen after HSiCl$_3$/CH$_3$Cl activation. This carbon is a by-product of CH$_3$Cl decomposition, which creates the H atoms that bond to Si in (CH$_3$)$_2$HSiCl. Apparently, when CH$_3$Cl decomposes, it does so completely because no chlorinated methyl groups (CH$_2$Cl, CHCl$_2$) appear in the MCS products.

*2c. Reactions on Cu$_3$Si Surfaces.* Because the activated Cu/Si surfaces did not produce DMD, the desired product for linear silicones production, a Cu$_3$Si sample was reacted with a HSiCl$_3$/CH$_3$Cl mixture. The Cu$_3$Si surface is active by itself for selective formation of DMD.[8] Exposure of a clean Cu$_3$Si surface to a HSiCl$_3$/CH$_3$Cl mixture did not result in the formation of DMD, however, and the products (Table V) were also different from those observed on Cu/Si (Table III). This is a futher indication that Cu deposited on Si does not form a Cu$_3$Si alloy at 600 K. Lobusevich and Endovin[5] injected HSiCl$_3$ into a reacting bed of Cu and Si at 640 K and observed DMD, but they also saw a significant amount of CH$_3$HSiCl$_2$ (Table V). The differences from Cu$_3$Si may have been due to the 40 K higher temperature they used or the different form of Cu and Si. Also, introducing HSiCl$_3$ after the reaction had started may have made a difference.

Futher exposure of the "activated" Cu$_3$Si surface to CH$_3$Cl shifted the product distributions (Table V); the (CH$_3$)$_2$HSiCl product that formed from the HSiCl$_3$/CH$_3$Cl mixture was replaced by DMD. That is, H appears to displace Cl from DMD during reaction with HSiCl$_3$.

## Conclusions

Clean polycrystalline Si and Si with evaporated Cu layers are shown to be unreactive for methylchlorosilane formation from CH$_3$Cl, but these surfaces slowly decompose CH$_3$Cl. A mixture of HSiCl$_3$ and CH$_3$Cl is reactive with these surfaces, however, and this reactivity appears related to the formation of SiCl$_x$ active sites on the surface. Though CH$_3$Cl alone does not form these sites, the HSiCl$_3$/CH$_3$Cl mixture does. Most interestingly, once activated by HSiCl$_3$/CH$_3$Cl, these surfaces react with CH$_3$Cl to

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form methylchlorosilanes. Though none of these surfaces formed dimethyldichlorsilane, which is formed in the industrial direct-synthesis reaction, a highly selective reaction to $(CH_3)_2HSiCl$ was discovered for Cu/Si surfaces. Over 90% of the methylchlorosilanes formed on Cu/Si was $(CH_3)_2HSiCl$. Though Cu changes selectivity, it also decreases reaction rates. Thus, the activated Si surface (activated by $HSiCl_3/CH_3Cl$) formed $HSiCl_3$, $CH_3HSiCl_2$, and $CH_3SiCl_3$ in equal amounts and at rates 2 orders of magnitude higher than methylchlorosilane formation rates on the Cu/Si surfaces. The activating reaction on Si appears to proceed by methylation (by $CH_3$(ads) from $CH_3Cl$) of fragments from $HSiCl_3$; the probability of breaking H–Si and Si–Cl bonds in

$HSiCl_3$ appears to be about the same, and thus, $CH_3HSiCl_2$ and $CH_3SiCl_3$ form in a 3:1 ratio.

# Molecular Sieving by Electropolymerized Porphyrin Films Only a Few Monolayers Thick

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Polymeric films can be formed on smooth Pt electrodes by oxidative polymerization of cobalt tetrakis(*o*-aminophenyl)porphyrin, [Co(*o*-NH$_2$)TPP]. Although the films are extremely thin, as few as two monomolecular layers of porphyrin sites, they exhibit permeabilities to molecular monomers that fall in a regular order of permeant molecular volume. The molecular sieving property is taken as evidence that membrane transport, rather than pinhole transport, is the predominant transport mechanism in these films. The permeability data are supported by film thickness measurements by electrochemical reactivity, surface profilometry, transmission spectrophotometry, ellipsometry, and X-ray photoelectron spectroscopy.

Rates and molecular specificity of mass transport through molecular films and membranes have both fundamental and technological significance.[1] For example, biological cell membrane transport has great fundamental interest, whereas membranes employed for gas separations are technologically important. In either domain, the relative dimensions of membrane permeant and membrane structural characteristics determine whether the membrane permeability is permeant size sensitive, i.e., whether or not molecular sieving is observed. Membranes containing pores that are physically much larger than permeant dimensions and through which permeants can freely diffuse from one side of the membrane to the other will in the absence of charge effects show little, if any, molecular selectivity. Films and membranes lacking such mechanically large transport channels are likely to exhibit some molecular sieving. These phenomena are well-known in the context of gel permeation chromatography.[2] Transport through defect-free membranes can be regarded, in the simplest case, as a membrane phase into which the permeant first partitions and then diffuses. Both the partition coefficient and membrane diffusion coefficient can be sensitive to the molecular size and nature of the permeant.

This paper describes the permeation properties of ultrathin, 15–4600-Å, polymeric porphyrin films supported on Pt electrodes. These films are prepared by electrooxidative polymerization[3] of cobalt tetrakis(*o*-aminophenyl)porphyrin [Co(*o*-NH$_2$)TPP] onto Pt disk electrodes. The thicknesses of the porphyrin films, generally determined from their own electroactivity, were confirmed with surface profilometry, vis–UV transmission spectrophotometry, ellipsometry, and X-ray photoelectron spectroscopy. Permeation is measured as a transport impedance offered to electroactive monomer solutes that react at the Pt electrode at potentials at which the porphyrin film itself does not efficiently mediate electron transfer. We find that the permeation rates change regularly with

the molecular volume of the electroactive substance, evidence for primarily partition/diffusion permeation as opposed to permeation through film defects.

A particularly remarkable aspect of the permeation results was that polymer films containing as few as two monomolecular layers of porphyrin sites could exhibit permeabilities (scaled for thickness) identical with those of much thicker polymerized films. It was unexpected that such thin polymer films could be prepared without leaving substantial amounts of naked electrode exposed (pores). The dimensions of the thinnest polymer films approach those of self-assembled hydrophobic monolayers. The self-assembled monolayers exhibit[4] apparently lower permeabilities than those of the electropolymerized porphyrins, but the former measurements have been made exclusively in aqueous solvents while the polymerized porphyrins are used in the organic solvent acetonitrile.

## Experimental Section

*Chemicals, Electrodes, and Instrumentation.* The cobalt tetrakis(*o*-aminophenyl)porphyrin was prepared and purified as described previously.[3] Acetonitrile (Burdick & Jackson Spectroquality, stored over 4-Å molecular sieves) and tetraethylammonium tetrafluoroborate (prepared by literature procedures,[5] recrystallized three times from methanol and petroleum ether) were used throughout as electrochemical solvent and supporting electrolyte, respectively. Electrodes were Teflon-shrouded Pt disks polished with 1-μm diamond paste and rinsed thoroughly with acetone and water. Potentials are reported vs a NaCl-saturated calomel electrode (SSCE). Conventional three-electrode cells and electrochemical instruments were employed. Rotated-disk experiments were done with a Pine Instruments Model MSR rotator

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