

Catalytic Formation of Silanes on Copper–Silicon Alloys

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Areal rates of silane formation from CH_3Cl and silicon were measured in a differential batch reactor at atmospheric pressure and 520–620 K, on three clean, nonporous, silicon-containing surfaces. These surfaces were characterized with Auger spectroscopy by transferring them directly between UHV and atmospheric pressure, without exposure to air. On pure silicon, a long induction time was seen before steady-state reaction; the main products at steady-state were HSiCl_3 and $\text{CH}_3\text{HSiCl}_2$. On Cu_3Si and Cu_3Si containing 0.4 atm% Zn, the overall silane formation rates were an order of magnitude lower than on pure silicon. Copper catalyst, however, dramatically increased selectivity to 85% $(\text{CH}_3)_2\text{SiCl}_2$, the desired product for silicone production. Copper also decreased the induction time by increasing the rate of active-site formation. Zinc promoter in Cu_3Si further increased $(\text{CH}_3)_2\text{SiCl}_2$ selectivity to 95% without significantly changing activity. No induction time was seen with the Zn promoter. Silicon diffusion in Cu_3Si limited silane formation, and a mathematical model is presented. Reaction on Cu_3Si containing Zn was not limited by diffusion. These are the first measurements of silane direct-synthesis kinetics on Cu_3Si of known surface area, and they show directly that Cu_3Si provides an active surface for selective formation of $(\text{CH}_3)_2\text{SiCl}_2$. Rates and selectivities on the alloys were similar to those measured for higher-surface-area solids. © 1985 Academic Press, Inc.

INTRODUCTION

One of the main steps in the production of silicones is the formation of methylchlorosilanes by the direct-synthesis reaction. In this solid-catalyzed, gas–solid reaction, gaseous methyl chloride reacts with solid silicon. Copper catalyzes the selective formation of the desired product, dimethyldichlorosilane $((\text{CH}_3)_2\text{SiCl}_2)$; the effect of copper has been attributed to the formation of an active Cu_3Si alloy (1, 2). Most kinetic studies of the direct-synthesis reaction have used physical mixtures of powdered silicon and copper to mimic industrial conditions (1, 2). Thus, reaction rates per unit surface area (areal rates) have not been measured, nor have studies directly shown that Cu_3Si is the active catalytic component. The induction period usually observed with physical mixtures has been at-

tributed to the time required to form Cu_3Si (1, 2).

To understand the role of Cu_3Si in the direct-synthesis reaction, we measured reaction rates on a Cu_3Si alloy and thus eliminated any induction due to Cu_3Si formation. Reaction rates were also measured on Cu_3Si containing 0.4 atm% zinc, since zinc is a selective promoter for $(\text{CH}_3)_2\text{SiCl}_2$ formation (1). The uncatalyzed reaction was studied using a silicon single crystal.

Rates were measured on nonporous, low-surface-area samples ($\approx 1 \text{ cm}^2$) in an atmospheric-pressure chamber which was connected to an ultrahigh vacuum (UHV) system by a sample transfer mechanism. The surfaces were cleaned in UHV, the surface compositions measured with Auger electron spectroscopy (AES), and the samples then transferred directly into the differential batch reactor. Because Cu_3Si alloys are very sensitive to oxygen (3), this direct transfer without intermediate exposure to air was necessary. After reaction at atmospheric pressure, the samples were trans-

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ferred back to the UHV chamber for surface analysis.

Reaction was carried out at temperatures and pressures (520–620 K, 1 atm) that are similar to those used by previous investigators (1, 2), so that the results can be directly compared to those on high-surface-area mixtures. Industrial conditions are 4–6 atm and 550 K (1).

This is the first study of the direct-synthesis reaction for a surface of known composition and surface area. The activities, selectivities, and induction periods will be reported as a function of temperature for Cu_3Si , $\text{Cu}_3\text{Si-Zn}$, and Si surfaces. Studies of the effect of reaction on the surface composition will be reported in a future paper (4). Large differences in selectivities, induction periods, surface compositions, and rates of silicon diffusion to the surface were observed for the three surfaces. These studies demonstrate the utility of surface-analysis techniques for studying a solid-catalyzed, gas–solid reaction.

EXPERIMENTAL

Atmospheric-pressure reaction was carried out in a differential batch reactor which was isolated from an ion-pumped UHV chamber by a straight-through valve. Samples were mounted on a metal bellows transfer mechanism so that the samples could be moved between the reactor and the UHV chamber without exposure to air (3). This system allowed AES analysis with a PHI model 10-155 CMA before and after reaction.

Surfaces were cleaned with an ion bombardment gun (Varian) using procedures previously described (3). The cleaned Cu_3Si surface contained mostly copper and silicon; no oxygen was present and the carbon and chlorine concentrations were below 1%. After reaction, carbon, chlorine, and a small amount of oxygen were present (4). The Cu_3Si samples (approx. $1 \times 5 \times 13$ mm) were mounted in stainless-steel clamps and resistively heated. A chromel-

alumel thermocouple was spotwelded to the edge of the alloy. The silicon sample was heated by conduction from a resistively heated stainless-steel bar which was clamped to its backside. A chromel-alumel thermocouple was clamped to the silicon surface with a 0.25-mm-o.d. tungsten wire clamp.

Kinetics were measured in the batch reactor system (335 cm^3 total volume), which contained a Metal Bellows (model MB-158) recirculation pump. Methyl chloride conversion was kept below 5 mol% for all runs, and a Valco GC valve with 0.5 cm^3 sampling volume was used to sample the recirculating gas. The valve was immersed in a dry N_2 atmosphere to minimize oxygen leakage into the system. An HP Model 5712 gas chromatograph with thermal conductivity detector analyzed reaction products. A 1.8-m column containing 70% OV-210 and 30% OV-1 (20% weight loading) on Chromasorb PAW-DMCS (80/100 mesh) separated the silanes in six minutes at 323 K (5). Pure silanes were used for calibration. Injections of SiCl_4 did not produce an HCl peak, verifying the absence of H_2O in the He carrier gas (1).

Procedure. The sample was cleaned by ion bombardment, annealed at 570 K for 15 min, analyzed by AES, and then transferred into the reaction chamber. The reactor was pressurized to 81 kPa (635 Torr) with CH_3Cl , the recirculation pump switched on, and the sample heated to reaction temperature (520–620 K). For reaction on the alloys, gas samples were taken and analyzed with the GC every 10 to 60 min, depending on reaction temperature, and runs lasted from 0.5 to 23 hr. After reaction at each temperature, the alloy was cooled to 310 K, the reactor evacuated, and the straight-through valve opened. Auger studies of clean Cu–Si alloys indicated no surface composition changes on cooling from 770 to 300 K (3). The sample was moved into the UHV chamber for AES analysis within 5 min after evacuation. The alloys were recleaned before each isothermal run.

For reaction on Si, rates were measured at several temperatures in succession without recleaning the sample or interrupting the reaction.

The AES spectra were recorded with a 2 keV, 5 μ A beam to minimize beam-induced damage. For higher sensitivity, the sample was later characterized with a 3 keV, 30 μ A beam. A 1 V p-p modulation was used for all peaks except for Si (1620 eV), for which 6 V p-p was used.

Materials. The Cu_3Si alloy contained 23.1 atm% Si and 77% Cu, since silicon precipitates formed at higher concentrations (6). The promoted alloy (Materials Research Laboratory, Orangeburgh, N.Y.) contained 22.1 atm% Si, 77.5% Cu, and 0.4% Zn (7). The Cu_3Si phase was verified for both alloys using polarized light microscopy (3) and X-ray diffraction (3, 7). The Cu_3Si sample was also extensively characterized by AES (3). Alloys were sliced with a diamond saw and polished with Linde B abrasive (0.5 μm Al_2O_3). The Si sample was an n-type (100) single crystal (Monsanto) which contained 0.1 ppm P.

The sample surfaces were cleaned before each reaction run with argon ion bombard-

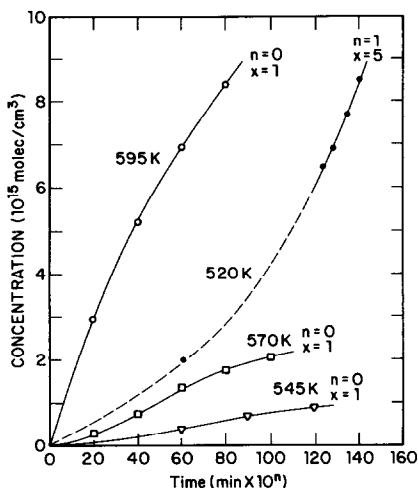


FIG. 1. $(\text{CH}_3)_2\text{SiCl}_2$ formation on Cu_3Si ; gas-phase concentration versus reaction time. For each curve, the time scale is multiplied by 10^n and the concentration scale by $1/x$.

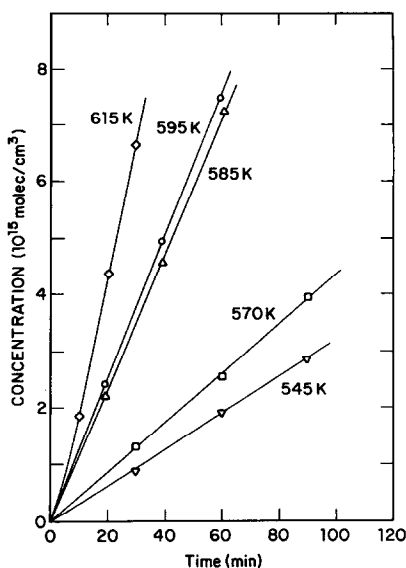


FIG. 2. $(\text{CH}_3)_2\text{SiCl}_2$ formation on Cu_3Si (0.4 atm% Zn); gas-phase concentration versus time.

ment and annealing at 570 K. The argon was 99.9995% pure (Scientific Gas Products, research grade). Methyl chloride gas (Matheson, 99.5% pure) was further purified by passing it through a 5A molecular sieve at 273 K to remove methanol impurities. Gas purity was checked by AES analysis of the Cu_3Si surface after exposure to CH_3Cl , since oxygen-containing contaminants readily adsorb onto the Cu_3Si surface. No oxygen was present in the Auger spectra after exposure to purified CH_3Cl at 635 Torr and 300 K for 5 min.

RESULTS

Reaction rates and selectivities were measured on the 3 surfaces at 84 kPa (635 Torr) at temperatures from 520 to 620 K. Plots of $(\text{CH}_3)_2\text{SiCl}_2$ concentration versus time for the alloys are shown in Figs. 1 and 2. Dimethyldichlorosilane is the main product formed on the two alloys, but its yield is insignificant on pure silicon. Little scatter is seen in the data, indicating that precise rates could be obtained. Similar plots were obtained for CH_3SiCl_3 , the next largest product on the alloys. On pure silicon, concentration versus time plots were obtained

for the four main products: HSiCl_3 , $\text{CH}_3\text{HSiCl}_2$, SiCl_4 , and CH_3SiCl_3 (8). Areal reaction rates were obtained from slopes of the concentration versus time plots, the reactor volume, and the geometric surface area of the sample. Reaction was carried out for the minimum time necessary to obtain rate measurements in order to minimize the buildup of surface oxygen and to minimize the number of silicon layers reacted.

Rate Measurements

In Fig. 1, three reaction regimes are evident on Cu_3Si :

(a) An induction period, which is most noticeable for the shorter times at 520 K. On pure silicon the induction period was quite long (8).

(b) A region of constant slope, indicating a steady-state reaction rate.

(c) A region in which the rate decreases, apparently because bulk diffusion of silicon affects the rate. This is most noticeable at high temperatures and longer times.

On $\text{Cu}_3\text{Si-Zn}$, essentially one regime is seen (Fig. 2); the induction period is very short, and there are no indications of diffusion limitations at long times. Table 1 shows that the areal rates (Si atoms react-

TABLE 1
Areal Reaction Rates

Surface	Temperature (K)	Rate		Total Si reacted (10^2 monolayers)
		Silane formation		
		Exp.	Model	
Cu_3Si	520	0.19	0.19	4.4
	545	0.56	0.59	4.6
	570	1.5	2.4	5.3
	595	7.7	11	2.2
$\text{Cu}_3\text{Si-Zn}$	545	1.2		6.1
	570	1.6		8.3
	595	4.8		16
	615	8.9		14
Si(100)	545	16		1920
	570	28		1830
	595	57		1680
	620	77		1380

TABLE 2
Induction Times

Surface	Temperature (K)	Induction time (min)
Cu_3Si	520	1000
	540	60
	570	40
	595	<5
$\text{Cu}_3\text{Si-Zn}$	545-615	<5
Si(100)	670,695 ^a	>2000

^a For reaction on Si, after the induction at 670 and 695 K, rates were measured at several temperatures in succession without evacuating the reactor.

ing per sample area per second) on the alloys are an order of magnitude smaller than those for the uncatalyzed reaction. For Cu_3Si , the initial rates of $(\text{CH}_3)_2\text{SiCl}_2$ formation, after induction, were determined both from the maximum slopes in Fig. 1, and by modeling silicon diffusion in the alloy. The diffusion model (to be discussed) provides a better measure of the initial rates; the continuously decreasing rates at the higher temperatures in Fig. 1 make accurate measurements of the initial rates difficult. The rate of CH_3Cl consumption was larger than that indicated by the silane mass balance, apparently due to CH_3Cl decomposition on the surface.

The concentrations of CH_3SiCl_3 were low for short reaction times so that the initial rates of CH_3SiCl_3 formation were difficult to measure. Thus, selectivities were determined from rate data at longer reaction times, and initial CH_3SiCl_3 rates were estimated from $(\text{CH}_3)_2\text{SiCl}_2$ rates by assuming that selectivities did not change with conversion. This should yield reasonable estimates since selectivity did not change with time (conversion) at 595 K, where direct measurements were possible at short reaction times.

For the alloys, rates were measured at each temperature on a clean, annealed (570 K) surface, which is enriched in silicon (3). For pure silicon, a very long induction period was seen, and rates were measured af-

TABLE 3
Apparent Activation Energies (kcal/mol)^a

Product	Cu ₃ Si		Cu ₃ Si-Zn	Si(100)
	Exp.	Model		
Overall	28 ± 3	33 ± 2	20 ± 3	16 ± 2
(CH ₃) ₂ SiCl ₂	31 ± 3	35 ± 2	20 ± 3	—
CH ₃ SiCl ₃	21 ± 3	24 ± 2	32 ± 2	24 ± 2
HSiCl ₃	—	—	—	11 ± 1
CH ₃ HSiCl ₂	—	—	—	27 ± 2
SiCl ₄	—	—	—	21 ± 4

^a Energies were obtained by linear least-squares regression (98% uncertainty interval).

ter 31 hr at 670 K and 9 hr at 695 K by changing the temperature without recleaning the sample. Table 2 lists the induction periods for the three samples. Table 3 lists the apparent activation energies for the various products; Arrhenius plots for Cu₃Si-Zn are shown in Fig. 3.

Selectivity

Product distributions for the silanes formed during the uncatalyzed reaction, after induction, are given in Table 4. The main product at low temperatures was HSiCl₃, but at 595 and 620 K, HSiCl₃ and CH₃HSiCl₂ were formed in comparable amounts. Selectivity for (CH₃)₂SiCl₂ formation on Si(100) was always less than 1%.

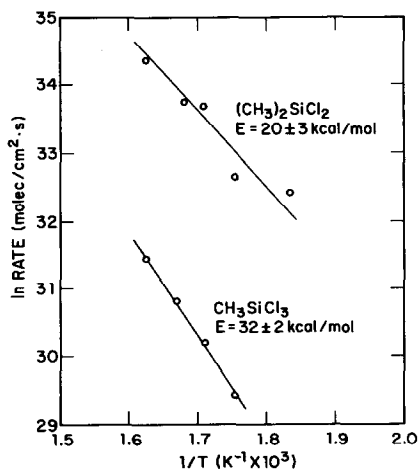


FIG. 3. Arrhenius plots for (CH₃)₂SiCl₂ and CH₃SiCl₃ formation on Cu₃Si (0.4 atm% Zn).

TABLE 4
Production Distributions on Si(100)

Temperature (K)	Products (mole%) ^a				
	HSiCl ₃	MeHSiCl ₂	SiCl ₄	MeSiCl ₃	Me ₂ SiCl ₂
545	74	18	6.3	1.2	0.5
570	70	23	3.5	2.6	0.9
595	57	34	5.4	3.2	0.4
620	51	36	8.5	4.2	0.3

^a Me = CH₃.

The copper catalyst dramatically changed selectivity while reducing overall activity an order of magnitude. For example, at 545 K, the product compositions for Cu₃Si and Cu₃Si-Zn were 85 and 100% (CH₃)₂SiCl₂, respectively (Table 5). The Zn promoter, though present in small concentrations at the surface (≈2 atm%) (4), significantly increased the selectivity. On Cu₃Si-Zn, the selectivity decreased slightly with increased temperature, but on Cu₃Si selectivity increased with temperature. The secondary product on both alloy surfaces was CH₃SiCl₃. The only other silane product, detected in low concentrations, was (CH₃)₃SiCl.

DISCUSSION

Role of Catalyst and Promoter

The effect of copper catalyst on the reaction of silicon and methyl chloride is dramatic; selectivity to (CH₃)₂SiCl₂ increases

TABLE 5
Product Distributions on Alloys

Surface	Temperature (K)	Products (mole%) ^a		
		Me ₂ SiCl ₂	MeSiCl ₃	Me ₃ SiCl
Cu ₃ Si	520	74	26	—
	545	85	15	—
	595	88	8	4
Cu ₃ Si-Zn	545	100	—	—
	595	95	5	—
	615	94	5	1
Cu, Si, Al, Zn (ref. 9)	554	78.5	10.0	4.0
	600	84.5	8.3	3.2
	620	86.2	7.5	2.4

^a Me = CH₃.

from less than 1% to approximately 85%, and induction time decreases two orders of magnitude. Zinc promoter further increases selectivity to nearly 100% and almost eliminates induction. Rates of $(\text{CH}_3)_2\text{SiCl}_2$ formation on the alloys are an order of magnitude faster than on pure silicon. Thus, copper catalyst increases selectivity by both increasing the rate of $(\text{CH}_3)_2\text{SiCl}_2$ formation and suppressing formation of other silanes. Zinc promoter increases selectivity by further suppressing the formation of CH_3SiCl_3 .

Selectivity for $(\text{CH}_3)_2\text{SiCl}_2$ on Cu_3Si increases with temperature; the activation energy is greater for $(\text{CH}_3)_2\text{SiCl}_2$ formation than for CH_3SiCl_3 (Table 3). On $\text{Cu}_3\text{Si-Zn}$, the activation energy is lower for $(\text{CH}_3)_2\text{SiCl}_2$ than for CH_3SiCl_3 , so selectivity decreases with increasing temperature. The differences in selectivities and apparent activation energies on Cu_3Si and $\text{Cu}_3\text{Si-Zn}$ may indicate different mechanisms are operating. The overall apparent activation energies (Table 3) are within the range of previously reported values (2).

Activity and selectivity on our Cu_3Si surface are similar to those obtained in a fluidized bed for physical mixtures of Cu and Si (9). The fluidized solids used by Voorhoeve *et al.* (9) were 10 wt% Cu, 89.9% Si, 0.1% Zn, and 0.05% Al; most of the Cu was alloyed as Cu_3Si . Selectivities on these particles were 75–85%; these are similar to our selectivities on Cu_3Si but lower than those on $\text{Cu}_3\text{Si-Zn}$. The higher conversions in the studies by Voorhoeve *et al.* (9) may allow secondary reactions to influence the product distribution; our experiments were run under differential conditions.

Voorhoeve *et al.* (9) modeled their non-porous Si particles (50–150 μm) as spheres with 1 μm Cu_3Si spheres embedded in them, and estimated the Cu_3Si surface area to be 560 cm^2/cm^3 Si. This model yields an areal rate for the Cu_3Si surface of 5×10^{14} Si atoms/ $\text{cm}^2 \cdot \text{s}$ at 580 K, essentially the same as our value of 3×10^{14} Si atoms/ $\text{cm}^2 \cdot \text{s}$ (Table 1). That is, our study shows di-

rectly that Cu_3Si provides an active surface for selective formation of dimethyldichlorosilane. The composition of the active surface, however, differs from that of the clean surface or the bulk (4).

Uncatalyzed Reaction

The uncatalyzed reaction has not been studied in detail. Rochow (10) reported, in a study with poor reproducibility, high selectivity for SiCl_4 and CH_3SiCl_3 at 555 K. He also reported that the activity was lower than for the copper-catalyzed reaction. Golubstov *et al.* (11) reported for a pulse chromatography study that mainly CH_3SiCl_3 and SiCl_4 formed on silicon pretreated with chlorine. Dimethyldichlorosilane formed in smaller amounts (0–15%). The percentage of SiCl_4 increased from 10% at 620 K to 50% at 820 K, while that for CH_3SiCl_3 decreased from 80 to 50%. Our steady-state results for a clean Si(100) surface at low conversions, where secondary reactions are less likely to occur, are somewhat different. A long induction period was seen and steady-state silane formation was faster than for the copper catalyzed reaction. The main products at 545–645 K were HSiCl_3 and $\text{CH}_3\text{HSiCl}_2$; however, at 695 K, CH_3SiCl_3 and SiCl_4 were produced in nearly equal amounts and comprised 70% of the products.

The uncatalyzed reaction followed an Arrhenius temperature dependence up to 620 K (Table 3); above 620 K the temperature dependence of individual products was complex due to competing side reactions. The details will be presented in a future paper (8).

Induction Period

The number of monolayers reacting during induction was significantly different on the three surfaces. For an assumed site density of $10^{15}/\text{cm}^2$, approximately 9000 monolayers reacted during induction at 695 K on Si(100), but less than 30 monolayers reacted on $\text{Cu}_3\text{Si-Zn}$ between 545 and 615 K. On Cu_3Si , approximately 150 ± 50

monolayers reacted at 545 and 570 K. At 595 K, reaction was fast so measurement was difficult, but less than 200 monolayers reacted. Thus, the number of monolayers that reacted during induction was approximately independent of temperature on Cu_3Si .

The number of silane molecules produced per site during induction is much larger than one on Cu_3Si and on $\text{Si}(100)$, suggesting that active-site formation is slow. Initial active sites produce many silane molecules before the maximum active-site density is reached. A simple model for the overall rate, R , assumes that the turnover number, N_t , is the same for all active sites at a given temperature on a given surface, and the site density, $S(t)$, increases with time:

$$R = S(t) \cdot N_t. \quad (1)$$

The induction time, t_i , is determined by the rate of active-site formation, dS/dt , and the maximum active-site density, S_{\max} . The total number of monolayers reacted during induction is then,

$$M = \frac{1}{\rho_s} \int_0^{t_i} S(t) \cdot N_t dt \quad (2)$$

where ρ_s is the density of silicon atoms at the surface (atoms/cm²). If dS/dt and N_t are given by Arrhenius expressions, then

$$\frac{dS}{dt} = a_s e^{-E_s/RT} \left(1 - \frac{S}{S_{\max}}\right)^n \quad (3)$$

and, for zero or first-order formation ($n = 0$ or 1),

$$M = \text{Const} \cdot \exp\left(\frac{E_s - E_N}{RT}\right). \quad (4)$$

The number of monolayers reacted during induction, M , is then only independent of temperature if the activation energy for site formation, E_s , is the same as the activation energy for reaction, E_N (33 kcal/mol for Cu_3Si). Another estimate of E_s can be obtained since the active-site formation rate is inversely proportional to induction time. A

plot of $\ln(1/t_i)$ versus $1/T$ gives $E_s = 37 \pm 7$ kcal/mol; this indicates the above model is reasonable. The similar values for E_s and E_N may indicate the rate-controlling steps are similar for both active-site formation and silane product formation on Cu_3Si . This suggests that elementary steps unique to product formation, such as desorption, are not rate limiting. These results indicate that copper and zinc reduce induction times dramatically by increasing the rate of active-site formation.

Induction times for solid-catalyzed, gaseous reactions appear to be much shorter (12–14) than for the direct-synthesis reaction. Apparently the maximum active-site density is obtained for these gaseous reactions before appreciable product formation occurs.

Voorhoeve *et al.* (9) saw that induction was complete for selective formation of $(\text{CH}_3)_2\text{SiCl}_2$ in a fluidized bed after 10% silicon conversion, regardless of temperature. Their induction time also decreased with increased temperature. They (9) attributed induction to formation of additional Cu_3Si . Since we started with Cu_3Si , our induction is not due to alloy formation, but may be due to the time required for accumulation of carbon or chlorine on the surface to form active sites; Auger spectroscopy indicates that a fraction of the surface silicon is bound to chlorine after reaction (4). The induction observed by Voorhoeve *et al.* (9) may be due to both effects.

Diffusion Model

After induction, reaction rates on Cu_3Si decreased with time; this was not due to equilibrium limitations ($K_{eq} > 10^{26}$ for $(\text{CH}_3)_2\text{SiCl}_2$ formation by direct synthesis at 500 K). Rather, the rate was probably affected by Si diffusion in the alloy. To test this and to determine the individual rates of reaction and diffusion, the silicon mass balance was modeled:

$$\frac{\partial X_{\text{Si}}}{\partial t} = D \frac{\partial^2 X_{\text{Si}}}{\partial Z^2}. \quad (5)$$

X_{Si} is the Si atomic fraction, Z is distance into the bulk ($Z = 0$ at the surface), and t is time. Atomic density, C , and silicon diffusivity, D , are assumed to be independent of position or time. Boundary conditions are

$$X_{\text{Si}} = 0.25 \text{ at } t = 0, \text{ for all } Z, \\ \text{and as } Z \rightarrow \infty, \text{ for all } t \quad (6)$$

$$kX_{\text{Si}}|_{Z=0} = CD \left. \frac{\partial X_{\text{Si}}}{\partial Z} \right|_{Z=0}. \quad (7)$$

The surface mass balance (Eq. (7)) is assumed to be first order in silicon concentration; i.e., after induction a constant fraction of the surface silicon is active sites. Silicon accumulation at the surface is neglected in Eq. (7), since nearly all the silicon that reacts at the surface is supplied from the bulk. The initial surface concentration may differ from the assumed value (Eq. (6)); however, the model requires only that the surface reaction rate is *proportional* to X_{Si} at $Z = 0$ (Eq. (7)). The rate constant accounts for any differences between the initial surface concentration and the bulk value, since surface concentration is likely to be proportional to bulk concentration (3).

Equations (5)–(7) are analogous to those for convective heat transfer from a semi-infinite slab (15). The Si atomic fraction at the surface is then given by (15):

$$X_{\text{Si}}|_{Z=0} = 0.25 \exp\left(\frac{k^2 t}{C^2 D}\right) \left[1 - \operatorname{erf}\left(\frac{kt^{1/2}}{CD^{1/2}}\right)\right]. \quad (8)$$

The gas-phase product concentration, C_g , is given by,

$$C_g = \frac{A}{V_r} \int_0^t kX_{\text{Si}}|_{Z=0} dt \quad (9)$$

where A , V_r , and t are the reacting Cu_3Si surface area, reactor volume, and reaction time. Integration yields

$$C_g = \frac{0.25 AC^2 D}{V_r k} \left\{ \exp\left(\frac{k^2 t}{C^2 D}\right) \left[1 - \operatorname{erf}\left(\frac{kt^{1/2}}{CD^{1/2}}\right)\right] + \frac{2kt^{1/2}}{CD^{1/2}\sqrt{\pi}} - 1 \right\}. \quad (10)$$

The parameters k and D were adjusted to match experimental data after the induction time (Fig. 1). Figure 4 shows that the model fit the data quite well at the three temperatures. Diffusivities obtained from the model are 5.5×10^{-12} , 2.0×10^{-13} , 6.0×10^{-14} cm^2/s , at 595, 570, and 545 K, respectively. These values yield an activation energy for silicon diffusion of 60 ± 10 kcal/mol, and they are within the range of typical solid diffusivities of 10^{-8} to 10^{-18} cm^2/s (16). The activation energy differs from that for initial reaction rates (Table 3) because *initial* rates are not controlled by diffusion. The model is sensitive to changes in diffusivity, and allows precise determination of D ($\pm 5\%$). The best-fit k values yield initial rates, given by $kX_{\text{Si}}|_{Z=0}$ at $t = 0$, which are close to experimental rates (Table 1).

Kolster et al. (17) compared silane formation on pure Cu_3Si particles with silane formation on particles containing Cu_3Si plus excess silicon. Reaction rates for the pure alloy particles decreased with time, while rate and selectivity were constant for particles containing excess silicon. The authors attributed the rate decrease to slow silicon diffusion in Cu_3Si . Our results show directly that diffusion does limit silane formation on Cu_3Si in the absence of excess silicon.

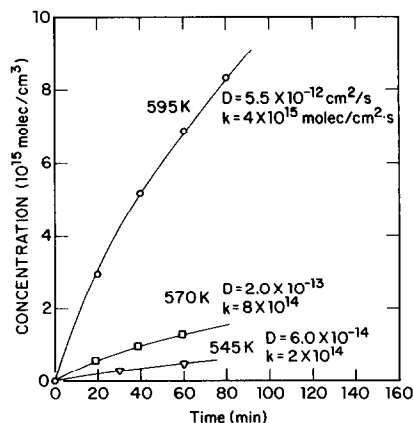


FIG. 4. $(\text{CH}_3)_2\text{SiCl}_2$ formation on Cu_3Si ; gas-phase concentration versus time for the diffusion model (curved lines) and from experiment (data points). Values of diffusivity, D , and rate constant, k , are listed.

Silane formation depletes the Cu_3Si surface of silicon. The thickness of the depletion layer (diffusion length) increases with time, causing the diffusion rate to decrease. Thus, diffusion limits silane formation on Cu_3Si so that $C_g \propto t^{1/2}$ (Eq. (10)) and $dC_g/dt \propto t^{-1/2}$, for sufficiently long reaction times.

Pure copper rapidly diffuses through Cu_3Si to react with pure silicon to form Cu_3Si ; a diffusivity of 7×10^{-8} cm^2/s was measured at 595 K and the activation energy was 23.3 kcal/mol (18). Our results indicate that silicon diffusion in reacting Cu_3Si is much slower in the absence of excess silicon. Thus, the driving forces and resistances for diffusion are quite different in the two situations.

Reaction on $\text{Cu}_3\text{Si-Zn}$ was not limited by silicon diffusion; reaction rates did not change with time (Fig. 2). This indicates a diffusivity greater than 10^{-10} cm^2/s at 595 K, approximately two orders of magnitude larger than for pure Cu_3Si . This result also shows that the decreases in rates for Cu_3Si were not due to experimental artifacts. Since zinc is enriched at the surface (4), it may affect diffusion by also concentrating at grain boundaries (19); diffusion along grain boundaries dominates in metals at low temperatures (e.g., below 900 K for polycrystalline Ag (20)). The model diffusivities must be regarded as effective values, since the orientation and size of crystallites present in the polycrystalline Cu_3Si are unknown. The absence of diffusion limitations for $\text{Cu}_3\text{Si-Zn}$ is not due to the presence of excess silicon, since Auger spectra of the clean, annealed (570 K) alloy indicated no elemental silicon was present (4).

CONCLUSIONS

Areal rates of silane formation from methyl chloride and silicon were measured under well-defined surface conditions at industrial temperatures and atmospheric pressure. Studies on three clean, nonporous surfaces, Si(100), Cu_3Si , and Cu_3Si (0.4 atm% Zn) show:

a) Cu_3Si provides an active surface for selective formation of $(\text{CH}_3)_2\text{SiCl}_2$.

b) Copper markedly increases selectivity for $(\text{CH}_3)_2\text{SiCl}_2$ by increasing the $(\text{CH}_3)_2\text{SiCl}_2$ formation rate and suppressing formation of other silanes. Total silane formation is an order of magnitude higher on Si(100), but selectivity for $(\text{CH}_3)_2\text{SiCl}_2$ is less than 1%; the main products are HSiCl_3 and $\text{CH}_3\text{HSiCl}_2$.

c) Zinc promoter further increases selectivity for $(\text{CH}_3)_2\text{SiCl}_2$ by suppressing CH_3SiCl_3 formation.

d) Copper and zinc significantly reduce induction times by increasing the rate of active-site formation. The apparent activation energies for formation of active sites and formation of silane products are similar on Cu_3Si , suggesting that both processes involve the same rate-controlling step.

e) The rate of silane formation on the alloys is fast ($\sim 2 \times 10^{14}$ atoms/ $\text{cm}^2 \cdot \text{s}$ at 570 K) but limited by silicon diffusion on Cu_3Si . The addition of zinc increases the diffusion rate so that reaction is not diffusion limited.

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