Role of Metallic Promoters in the Direct Synthesis of Methylchlorosilanes

L. D. GASPER-GALVIN,*,1 D. M. SEVENICH,† H. B. FRIEDRICH,†
AND D. G. RETHWISCH*,2

*Department of Chemical and Biochemical Engineering and †Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Overall reaction rates and selectivities for dimethyldichlorosilane were determined for the direct reaction of silicon with methyl chloride to produce methylchlorosilanes. Copper was used as the catalyst, and zinc, tin, and aluminum were investigated as promoters. To unambiguously determine effects of the promoters, high-purity reagents were used for contact mass sample preparation. Others have reported that tin significantly increases both reaction rate and selectivity for samples prepared using technical grade silicon. However, promotion of high purity samples with tin alone (i.e., SiCuSn) significantly decreased both the reaction rate and selectivity. These conflicting results are explained in terms of the aluminum impurities present in technical grade silicon. Tin is suggested to promote this reaction synergistically with zinc and aluminum by lowering the melting points and surface tensions of the catalyst/promoter alloys which form on the surface. © 1991 Academic Press, Inc.

INTRODUCTION

The direct reaction of methyl chloride and silicon in the presence of a copper catalyst was first discovered by Rochow in 1939 (*1*):

$$2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2.$$
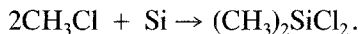
The direct reaction is now the most widely used industrial method for the production of methylchlorosilanes (*2*). Dimethyldichlorosilane (DMDCS) is the major product, typically constituting 90% or more of the industrial product. Other products include silanes with the general structure $(CH_3)_xH_ySiCl_z$ (where $x + y + z = 4$), and trace amounts of hydrocarbons and disilanes. DMDCS is the preferred product, since it has the greatest number of large-volume commercial applications. DMDCS is used as the starting material to produce linear polysiloxane fluids, polymers for the production of heat-cured rubber elastomers, and silicone rub-

ber elastomers which are vulcanizable at room temperature (*3*).

The direct reaction has been investigated by many researchers with varying results. Although it is well established in the literature that copper is the best catalyst for selective formation of DMDCS, there has been controversy concerning the effects of various promoters and impurities. In this work, a promoter is defined as a substance which is deliberately added in amounts of 1 wt% or less to the copper–silicon contact mass. Promoters and poisons in concentrations as low as several parts per million have been shown to have a significant effect on the reaction kinetics (*2*). For most studies of the direct reaction, low-purity starting materials were employed. Therefore, it has been difficult to unambiguously determine the effects of these elements.

Recently, several investigators have reported studies in which the composition of the reaction mass was carefully determined (*4–15*). In one such study, Ward *et al.* (*4*) reported that for technical grade silicon, zinc and tin are both promoters at concen-

trations of 0.5 wt% and 0.005 wt%, respectively; furthermore, they found that when zinc and tin are present together, a strong synergism is observed.

In this paper, we report the results of the investigation of the direct reaction over contact masses prepared from high purity reagents. The effects of tin, zinc, and aluminum in combination with pure silicon and copper(I) chloride were determined. The synergism of the binary promoter systems zinc–tin and aluminum–tin were also studied. The results for promotion of high-purity contact masses with tin are significantly different than those reported for samples prepared from technical grade silicon.

METHODS

High-purity silicon flakes (Union Carbide, 99.99% pure) were pretreated before use in contact mass synthesis. The silicon flakes were ball milled and sieved to 80 × 100 mesh (149–177 μm). The silicon was then cleaned by room temperature treatments of 90 min each in concentrated HNO_3 and concentrated HCl. After each treatment the silicon was rinsed to neutrality with distilled water. The silicon was then boiled in distilled water to remove traces of acid. Finally, the silicon was treated in 1 wt% HF for 3 min, rinsed with distilled water, fil-

TABLE 1

Concentrations of Impurities in Samples

Element	Concentration (ppm)			
	Pure silicon		SiCu (4.2 wt% copper)	
	As received	Acid-etched	As prepared	Post reaction
Phosphorus	12	6.3	21	25
Aluminum	130	77	<25	<25
Antimony	<10	<20	<50	<75
Arsenic	<0.5	<0.5	<25	<25
Bismuth	<25	<25	<50	<75
Iron	330	21	13	33
Lead	<5	<5	<10	<25
Indium	<25	<25	<50	<75
Tin	—	—	—	<10
Zinc	12	8	150	170

TABLE 2

Composition of Reaction Masses[a]

Sample	Silicon	Copper	Zinc	Aluminum	Tin
Cu	95	5	0	0	0
CuZn	94.5	5	0.5	0	0
CuAl	94.5	5	0	0.5	0
CuSn	94.99	5	0	0	0.01
CuZnSn	94.49	5	0.5	0	0.01
CuAlSn	94.49	5	0	0.5	0.01

[a] Approximate initial concentrations in wt%.

tered, and dried under flowing nitrogen (Air Products, 99.99% pure) at greater than 373 K. These treatments reduced the level of metallic impurities (see Table 1). The HF treatment removes the thick oxide layer which passivates the silicon surface. Removal of the SiO_2 layer increases the measured reaction rates and reduces the induction periods (5). The nitrogen BET surface area of the resulting purified silicon was 0.14 m^2/g.

The contact masses were prepared as described by Ward et al. (4, 5). Copper(I) chloride and promoters (where used) were ball milled in a hexane slurry for ca. 4 h for copper chloride alone or 24 h when promoters were added. This slurry was poured over the cleaned silicon, and the hexane was removed by heating the sample to 373 K in a vacuum oven (ca. 10^{-2} Torr) for 1 h. The sample was then treated in flowing nitrogen for 2 h at 653–673 K and stored in a desiccator until use. The reagents used for contact mass preparation included Cu(I)Cl (Aesar, 99.999% pure), zinc powder (Aesar, 99.9999% pure), tin powder (Aesar, 99.9999% pure), and aluminum powder (Aesar, 99.99% pure). Contact mass names were derived from the catalyst and promoters used. For example, SiCuZnSn contains ca. 94.49% silicon, 5 wt% copper, 0.5 wt% zinc, and 0.01 wt% tin. The chemical compositions of the contact masses are summarized in Table 2. Levels of impurities for a typical sample, both as prepared and after reaction, are shown in Table 1. The low level

of impurities indicates that the preparation and reaction techniques did not introduce impurities into the contact mass samples. Tin concentrations were determined by Galbraith Laboratories (using graphite furnace atomic absorption), while all other metals were determined by the Iowa State Hygienic Laboratory (using inductively coupled plasma emission spectroscopy (ICP)).

Reaction kinetics were carried out using a 316 stainless-steel, continuous flow, fixed-bed reactor system. For previous studies of the direct reaction, both fixed-bed and fluidized-bed reactors have been used, with the majority of studies using fluidized beds. The fixed-bed reactor was selected for these studies because smaller sample amounts could be used and the reactor was easier to operate. To ensure rapid heat transfer, a 0.25-in o.d., 0.18-in i.d., (0.64-cm o.d., 0.46-cm i.d.) reactor was used. Approximately 2 g of sample was loaded into the reactor, pretreated in flowing helium (Air Products, 99.998% pure) at reaction temperature for ca. 12 h, and then the flow of CH_3Cl (Matheson, 99.5% pure) was initiated. The flow rate was controlled to maintain CH_3Cl conversion below 40% (more typically less than 25%) and the reactor was modeled as differential. Comparison to an integral model at high conversion indicated that the differential model was in error by less than 5%. Overall silicon conversion was maintained below 40% for all samples, except for reaction of SiCuZnSn at 673 K, for which overall silicon conversion was 54%. All reaction masses were aged at least 2 months before conducting kinetic studies, except for SiCuAlSn and fresh SiCu, which were aged for only 4–8 days and 1–10 days, respectively.

Product composition was determined using a gas chromatograph (GC) and a gas sampling valve. The GC contained a $\frac{1}{8}$-in (3.2 mm) o.d., 10-ft (3.05 m) stainless-steel analytical column packed with 70% FS1265 and 30% OV-101, 20% on 80/100 mesh Chromosorb P-AW. Operating parameters for the GC included (1) a temperature program

of 16 min at 313 K, followed by ramping at 25 K/min, and 14 min at 473 K; (2) injector and thermal conductivity detector temperatures of 523 K; and (3) helium carrier gas flow of 24 cc/min. Disilanes were observed in the GC trace of the products; however, the amount of disilane could not be reproducibly quantified though it was less than ca. 2 mol% for all samples. For some studies, a gas-phase IR cell was placed downstream of the reactor and the product composition was determined using an FT–IR spectrometer. Both detection techniques gave essentially the same results; however, while the GC took approximately 1 h per data point, the FT–IR could collect a data point in as little as 15 s (*14*).

The first data point for each sample was collected 30 min after CH_3Cl flow was initiated, and data points were collected hourly thereafter. An induction period of 90 min was observed for the aged SiCu (see results for a description of the "aged SiCu" samples) and SiCuSn samples; these samples reached relatively steady activity and selectivity by the second data point. The other samples did not show an induction period with respect to reactivity, indicating that if an induction period were present, it was less than 30 min. Many of the other contact masses, however, did show 90-min induction periods with respect to product distribution.

RESULTS

The results of the reaction kinetics for the direct reaction are summarized in Table 3. The reaction rates and selectivities were averaged over the entire 8.5-h run, except for the first injection at 0.5 h, due to the induction period. In the case of the experiments conducted at 623 K, reaction rates and selectivities were averaged for two or three runs. The units of the reaction rate are moles of the CH_3Cl consumed per second per gram of initial reaction mass. The overall reaction rate for the direct reaction decreased in the order SiCuZnSn > aged SiCu > SiCuAlSn

TABLE 3

Reactivities and Selectivities of Direct Reaction Contact Masses[a]

Reaction mass	T (K)	Rate[b] (*10^7) mol/g-s	Selectivities (mol%)[c]						
			$(CH_3)_2SiCl_2$ D	CH_3SiCl_3 T	T/D	CH_4	CH_3HSiCl_2	$(CH_3)_3SiCl$	$(CH_3)_2HSiCl$
Aged SiCu	623	5.3 (1.4)	30	19	0.63	33	10	2	6
	613	3.8 (0.6)	40	16	0.40	26	6	3	10
	603	3.0 (0.7)	46	15	0.33	25	4	4	6
Fresh SiCu	623	1.5 (0.5)	13	19	1.46	44	19	1	5
SiCuZn	623	4.3 (0.7)	32	11	0.34	33	20	2	1
	598	2.5 (0.3)	58	7	0.12	25	7	2	1
	573	1.3 (0.2)	55	7	0.13	30	7	2	1
SiCuAl	623	2.1 (0.5)	21	18	0.86	38	17	1	6
	598	0.87 (0.07)	20	16	0.80	43	13	1	6
SiCuSn	623	1.2 (0.3)	24	14	0.58	46	14	0	3
SiCuAlSn	623	4.3 (0.7)	51	14	0.27	18	8	4	6
SiCuZnSn	623[d]	12 (2)	75	6	0.08	13	2	4	1
	598	7.3 (0.4)	78	5	0.06	13	2	3	1
	573	4.4 (0.3)	80	4	0.05	13	1	3	0

[a] Values averaged over entire run except for the first analysis at 0.5 h (due to induction time).

[b] Reaction rate in moles CH_3Cl consumed per second per gram of initial reaction mass; values in parentheses are standard deviations.

[c] Selectivity defined as ratio of moles of given product to total moles of analyzed product times 100; error in selectivity in typically <5 mol%.

[d] Values averaged over first 6 h only.

$\cong$ SiCuZn > SiCuAl > fresh SiCu $\cong$ SiCuSn. The selectivity for DMDCS decreased in the order SiCuZnSn > SiCuAlSn > SiCuZn $\cong$ aged SiCu > SiCuSn $\cong$ SiCuAl > fresh SiCu.

For SiCu samples, the effect of aging the contact mass was investigated. For these studies, "fresh SiCu" refers to contact masses which were aged for 10 days or less before being used for reaction kinetics studies. "Aged SiCu" refers to contact masses which were stored for 4 months before measurement of reaction kinetics. The aged SiCu showed a 3.5-fold greater reaction rate and more than double the selectivity for DMDCS than observed for fresh SiCu.

The reaction rates and selectivities of most of the samples were relatively constant with time (reaction rates typically decreased gradually by ca. 25% over 8.5 h). However, SiCuSn, SiCuAl, and aged SiCu displayed induction periods. Initially, the primary product for SiCuSn, SiCuAl, and aged SiCu was methane; after 0.5 h on-stream, SuCuAl produced the greatest amount of methane (i.e. 90 mol%). By the time the second data point was taken (ca. 90 min) the reaction rate and/or selectivities reached relatively stable values and they changed only slowly over the remainder of the experiment. The initial high production rates of methane for these samples suggests the deposition of carbon and chlorine on the surface. This is consistent with reports that the deposition of surface carbon and chlorine is necessary to activate an inactive surface (9).
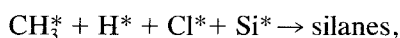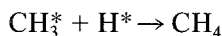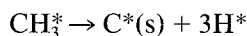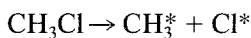
The reaction rate and selectivity of SiCuZnSn at 623 K were relatively constant for the first 4.5 h but then they both decreased rapidly over the remaining 4 h. The decrease in rate and selectivity roughly coincides with the point at which 40% of the silicon has been consumed; above 40% silicon consumption the reaction rate in the

TABLE 4

Average Stoichiometry of Methylchlorosilanes
$(CH_3)_x H_y SiCl_z$ for Each Reaction Mass

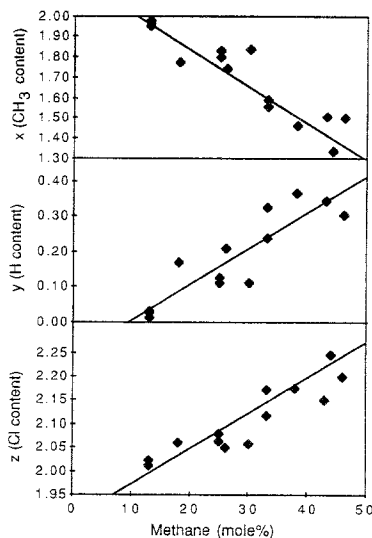| Reaction mass	T (K)	Methyl x	Hydrogen y	Chlorine z
Aged SiCu	623	1.59	0.24	2.17
	613	1.74	0.21	2.05
	603	1.80	0.12	2.08
Fresh SiCu	623	1.33	0.42	2.24
SiCuZn	623	1.56	0.32	2.12
	598	1.83	0.11	2.06
	573	1.83	0.11	2.06
SiCuAl	623	1.46	0.37	2.17
	598	1.51	0.34	2.15
SiCuSn	623	1.50	0.30	2.20
SiCuAlSn	623	1.77	0.17	2.06
SiCuZnSn	623	1.95	0.03	2.02
	598	1.96	0.03	2.01
	573	1.98	0.01	2.01

FIG. 1. Average number of methyl, hydrogen, and chlorine groups per silane produced in the direct reaction plotted versus methane production. The methane fraction is taken from Table 3 and the average silane compositions are taken from Table 4. Note; $(CH_3)_x H_y SiCl_z$.

direct reaction is commonly observed to decrease (2), though no decrease was observed at 40% in a more recent study (4).

The average number of methyl groups, chlorine atoms, and hydrogen atoms per silane produced for each reaction mass are indicated in Table 4. In Fig. 1, the average number of methyl groups, chlorine groups, and hydrogen atoms per silane (from Table 4) is plotted versus the selectivity of that sample for methane (from Table 3). The lines are included only to guide the eye. A positive correlation is observed between chlorine and hydrogen content of the silanes and methane production, while a negative correlation is observed between methyl content and methane production. This result is explained by the simplified reaction sequence for carbon deposition,

$$CH_3Cl \rightarrow CH_3^* + Cl^*$$

$$CH_3^* \rightarrow C^*(s) + 3H^*$$

$$CH_3^* + H^* \rightarrow CH_4$$

$$CH_3^* + H^* + Cl^* + Si^* \rightarrow silanes,$$

where starred species indicate surface species. Production of methane is indicative of carbon deposition on the samples. Hydrogen-containing silanes and methane are the result of hydrogen produced during carbon deposition.

For the reaction masses in which the promoters had a positive effect on the selectivity for $(CH_3)_2SiCl_2$ (i.e., SiCuZnSn, SiCu AlSn, and SiCuZn), there was an increase in the average methyl content of the product silanes. This increase was accompanied by a decrease in the selectivities for CH_3SiCl_3, $(CH_3)_2HSiCl$, and CH_4. This suggests that these promoters either inhibit carbon deposition (eliminating the hydrogen source), or increase the rate of production of the methylated silanes relative to the hydrogen-containing products. The latter argument is consistent with the proposed methylating power for the promoters. Hurd previously demonstrated the methylating power of zinc and aluminum in experiments in which he passed vapors of a chlorosilane together with an alkyl halide over finely divided aluminum or zinc at 300–500°C (16); this resulted in the replacement of part or all of the chlorine of the chlorosilane by alkyl groups. Furthermore, Gilliam showed that in amounts greater than 1 wt%, aluminum or

zinc substantially increase the selectivity for trimethylchlorosilane, while decreasing $(CH_3)_2SiCl_2$ (17). This argument is further strengthened by post-reaction Auger spectroscopy analysis which indicated that the SiCuZnSn sample (which had the lowest production of hydrogen-containing silanes and CH_4) had significant carbon deposition. Frank and co-workers (8, 18) also reported that zinc promotes carbon deposition, and the conversion of carbide to graphitic carbon.

Scanning electron micrographs of aged SiCu and SiCuZnSn are shown in Fig. 2. On unreacted SiCu (micrograph a), the copper tended to agglomerate on the surface (X-ray microprobe analysis showed that the lighter portions of the particle contain the greatest amount of copper). After reaction, the copper showed increased dispersion from the unreacted state (micrograph b). In every case, prior to reaction, the promoted samples appeared to have better metal dispersion than the SiCu samples. A typical example of a promoted sample, unreacted SiCuZnSn, is shown in micrograph c. Post reaction micrographs of the most reactive samples, such as SiCuZnSn (micrograph d), showed a significant amount of spalling or flaking of metal-containing silicon particles from the surface.

X-ray microprobe point analysis showed that the contact mass surfaces were quite heterogeneous. However, definite trends in chlorine content were observed. Analysis of unreacted contact masses indicated that masses which contained aluminum or zinc retained 15 to 60% more chlorine (from preparation with Cu(I)Cl) than those which contained only copper or copper and tin. Post reaction analysis of SiCuZnSn, Si CuAl, and SiCuSn, using energy dispersive spectroscopy (EDS) scans and point analysis, also indicated that SiCuZnSn and Si CuAl contained significantly more chlorine than SiCuSn (15).

Post-reaction elemental analysis of the samples indicated that the concentrations of copper, aluminum, tin, and other metals generally increased near the top of the bed, as expected, due to consumption of silicon. However, the concentration of zinc in Si CuZnSn decreased during reaction and zinc was transported down the reaction bed. For example, the initial concentration of zinc in the unreacted SiCuZnSn mass was 4200 ppm. Following 8.5 h of reaction in methyl chloride at 623 K, the concentration of zinc at the top of the sample bed was 1300 ppm while at the bottom of the bed it was 3900 ppm (15). Zinc may have been transported through the bed by several mechanisms, including spalling and blowing of zinc particles, and formation of various volatile zinc compounds (such as $Zn(CH_3)_2$) which contain chlorine and/or methyl groups. Under similar conditions $Zn(CH_3)_2$ has been observed by infrared spectroscopy (15).

Increasing the temperature generally increased the reaction rate, but decreased the selectivity for DMDCS while increasing the selectivity for the chlorinated products (CH_3HSiCl_2 (MDCS) and MTCS. Frank et al. (9) have reported that the selectivity for DMDCS increases with increasing temperature in the range from 520 to 595 K. The decrease in selectivity for DMDCS and increase in other chlorine-containing products observed in this study may be caused by the rapid increase in the rate of carbon deposition near 623 K (2). Indeed, a carbon balance on the product stream and post-reaction analysis indicated that carbon was being deposited in the reaction bed at these temperatures. The apparent activation energies for SiCuZn and SiCuZnSn were determined to be 16.8 and 13.5 kcal/g mol, respectively (insufficient data were available to make calculations of the activation energies for the other contact masses). These activation energies are somewhat lower than literature values which range from 20 to 30 kcal/g mol (4, 9, 19–21) for various copper–silicon alloys, with or without significant amounts of impurities and promoters. The activation energies in this study may have been lower by the HF pretreatment. Golubtsov et al. (22) showed that pretreat-
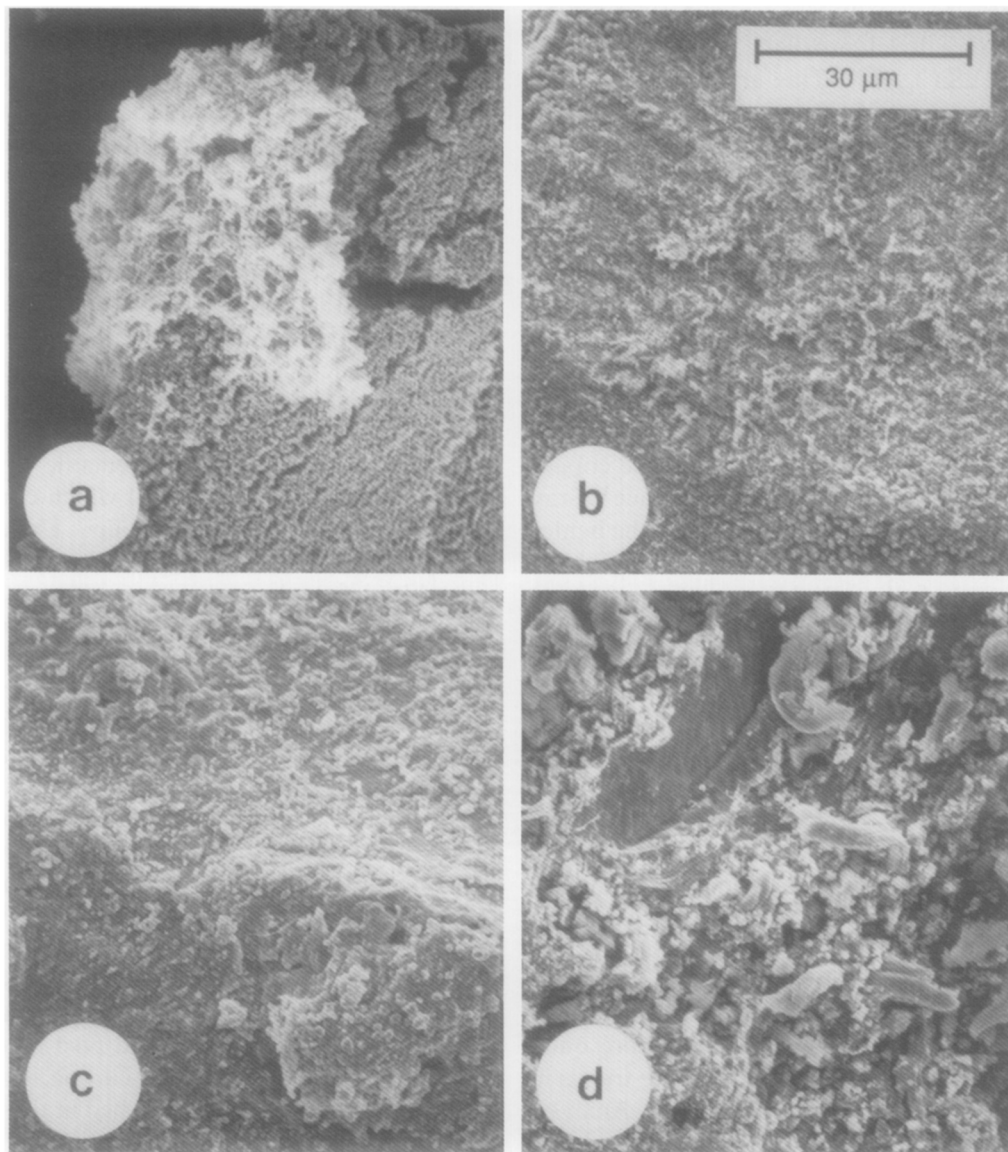
FIG. 2. Scanning electron micrographs of SiCu and SiCuZnSn reaction masses (magnification 1000 ×).
(a) Unreacted SiCu; (b) reacted SiCu; (c) unreacted SiCuZnSn; (d) reacted SiCuZnSn.

ment of a copper–silicon alloy with HF resulted in a lowering of the temperature at which the formation of halomethylsilanes was observed to begin.

DISCUSSION

Although there is an extensive body of literature on the effects of promoters on the direct reaction, many of the reported results are contradictory. These contradictions are often due to differences in contact mass purity. The results of this study resolve several of these apparently contradictory reports.

Effect of zinc. There is general agreement in the literature that promotion of the direct reaction with 0.1–1.5 wt% zinc increases the selectivity for DMDCS and slightly increases the reaction rate (2, 4, 9). Copromo-

tion with zinc and tin produces a synergistic relationship which greatly increases the reaction rate, and yields selectivities for DMDCS of as high as 95% (4, 5, 7). In this study, the SiCuZn mass showed an increase in reaction rate with respect to fresh SiCu, and an increase in selectivity compared to both fresh and aged SiCu.

Zinc appears to be a strong methylating agent, as evidenced by the low T/D (MTCS to DMDCS) ratio (Table 3). This effect is enhanced by the synergism between zinc and tin, which yields a T/D ratio that is nearly an order of magnitude lower than that for several of the other contact masses.

Effect of aluminum. Since aluminum is a common impurity in technical grade silicon, its effect on the direct reaction is difficult to evaluate. At high concentration (ca. 5 wt%) it was claimed that aluminum increased the selectivity for TMCS (23), while another study indicated that 0.2 to 0.3 wt% aluminum decreased the selectivity for DMDCS (24).

In the current study, the promotion of high-purity samples with 0.5 wt% aluminum (i.e., SiCuAl) decreased the reaction rate by a factor of two and decreased the selectivity for DMDCS relative to aged SiCu. Copromotion with 0.5 wt% aluminum and 0.01 wt% tin (SiCuAlSn) had little effect on the reaction rate, but increased the selectivity for DMDCS relative to aged SiCu, and decreased the induction period to less than 0.5 h. Thus, aluminum alone does not appear to act as a promoter for high-purity samples; however, the addition of only 0.01 wt% (100 ppm) tin to an aluminum-promoted system leads to a strong synergism which significantly increases both the reactivity and selectivity with respect to the Si CuAl sample.

Effect of tin. The literature indicates that the effect of tin on the direct reaction is uncertain. One study reported that it has no effect on the direct reaction (25) while others indicated that it acts as an inhibitor (2, 26). This confusion may have been caused in part by the high concentrations which were used. Also, in many studies cemented copper was used; however, cemented copper contains 400–3000 ppm of tin. More recently, promotion with tin at low levels (ca. 100 ppm) has been reported to increase both the reaction rate and the selectivity for DMDCS (4).

In the current study, the promotion of high-purity contact masses with 0.01% tin (i.e., SiCuSn) decreased the reaction rate by a factor of four and decreased the selectivity for DMDCS by 20% compared to aged SiCu. However, in the presence of either zinc or aluminum, 0.01 wt% tin causes a strong synergism. This synergism results in improved selectivity for DMDCS, and, in the case of SiCuZnSn, doubles the reaction rate over that for aged SiCu.

The apparent contradictions reported for promotion with tin are explained by the impurities in the technical grade silicon. Ward et al. (4) reported that addition of 0.01 wt% tin to a reaction mass prepared using technical grade silicon increased both the reaction rate and the selectivity for DMDCS. The technical grade silicon contained significant traces of aluminum (ca. 0.3 wt%) and iron (ca. 0.6 wt%). We observed that while Si CuAl and SiCuSn showed no promotion over aged SiCu (see Table 3), the SiCuAlSn samples in our study increased the reaction rate with respect to fresh SiCu, and increased the selectivity relative to both fresh and aged SiCu. We propose that the previously reported promotional ability of tin alone for technical grade silicon is caused by a synergistic interaction between tin and impurities (particularly aluminum) in the silicon.

As discussed above, tin displays a synergistic effect in promoting the direct reaction in the presence of zinc or aluminum. There are several potential explanations for these results. Tin may produce this synergism by acting as a methyl transfer agent or by decreasing the melting point and surface tension of the mixture of metals on the contact mass surface (resulting in increased disper-

sion of catalyst/promoters on the surface and increased diffusion rates in the surface phase). These explanations will be considered briefly below.

The addition of zinc to a reaction mass increased the selectivity for methyl-containing species, suggesting that zinc is a methylating agent. This is consistent with the observation in our lab that flowing $Zn(CH_3)_2$ and CH_3Cl over silicon at temperatures as low as 493 K produces large amounts of $Si(CH_3)_4$ and $(CH_3)_3SiCl$. Similarly, methyltin compounds are reported in the organometallic literature to be methylating agents, and tin is known to readily change coordination number of accommodate additional ligands (27,28). Thus, though both zinc and tin may act as methylating agents, the ability of tin to accommodate extra ligands may provide a more kinetically favored pathway to transfer methyl groups to silicon. The CH_3–metal bond strength increases in the order $Zn–CH_3$ < $Sn–CH_3$ < $Si–CH_3$ (29). This suggests that zinc surface species may methylate surface tin species, which would in turn transfer the methyl group to a surface silicon. The primary silane biproducts of the reaction contain only one methyl group (MTCS and MDCS); therefore, increased methylation would also increase the selectivity for DMDCS. For the observed enhancement in selectivity and reaction rate of SiCuZnSn relative to SiCuZn, each tin atom would transfer one methyl group per second (i.e., a turnover frequency of $1 \ s^{-1}$). While this number is large, it is not unrealistic.

As discussed above, tin may also produce the synergism by modifying the alloy properties of the copper, zinc, aluminum, and silicon. The effects could include decreasing the melting point and surface tension of the mixture of metals on the contact mass surface (resulting in increased dispersion of catalyst/promoters on the surface), and increasing the mobility of the metals in this surface alloy. The increase in dispersion would increase the number of active surface sites.

Binary phase diagrams of Sn–Zn and Sn–Al show that small amounts of tin can cause the melting points of zinc and aluminum to decrease. Mixed solid and liquid phases exist above 471 K for Sn–Zn mixtures of greater than 1.7 wt% Zn, and above 502 K for Al–Sn mixtures of greater than 0.01 wt% Sn (30). There are few ternary phase diagrams available for the Cu–Zn–Sn and Cu–Al–Sn systems. But the high-temperature phase diagram shown by Butts for Cu–Sn–Zn generally indicates that greater amounts of tin cause greater decreases in melting point (31). Segregation of tin at the surface, which has been observed by Goumiri and Joud using Auger spectroscopy, suggests that the concentration of tin at the surface may be quite high (32). Furthermore, Goumiri and Joud reported that when aluminum is alloyed with elements of the fourth and fifth group of Mendeleev's system (Sn, Pb, Sb, and Bi) in amounts of a few thousandths or hundredths of a percent, the surface tension is strongly reduced. Lower surface tension results in a greater degree of wetting and spreading of the metals on a substrate surface (33). Decreased surface tension would also increase the ability of the liquid-phase metals to penetrate into small crevices in the silicon, thus creating more active sites of contact between the copper catalyst, the promoters, and pure silicon.

The increased reaction rate with contact mass aging has been largely ignored in the literature. The amount of time which has elapsed between synthesis of a contact mass and the measurement of reaction kinetics is rarely reported. However, both the present study and studies by DeCooker indicate the effect of aging the reaction mass on the reaction kinetics of the direct reaction (34). In both studies, it was seen that the activity of the contact mass increased with age. More specifically, DeCooker showed an increase in average reaction rate of a mass for which kinetics were measured from 1 to 23 days after preparation; the average reaction rate was approximately 25% higher after 23 days of aging as compared with one day of aging.

Further investigations will be required to determine the cause of the increased activity with contact mass aging.

CONCLUSIONS

The overall reaction rate for the direct reaction at 623 K decreased in the order SiCuZnSn > aged SiCu > SiCuAlSn ≅ SiCuZn > SiCuAl > fresh SiCu ≅ SiCuSn. The selectivity for DMDCS (the desired product) at 623 K decreased in the order SiCuZnSn > SiCuAlSn > SiCuZn ≅ aged SiCu > SiCuSn ≅ SiCuAl > fresh SiCu. The selectivities further indicate that promoters increase the selectivity for methylated products. Promotion of samples with tin or aluminum alone decreased or had no effect on the reaction rates and selectivities. Zinc is proposed to promote the direct reaction by acting as a methylating agent. Tin is suggested to promote this reaction synergistically with zinc and aluminum by reducing the melting points and surface tensions of metal alloys on the contact mass surface. This causes increased wetting and spreading of the copper/promoter mixture on the surface, resulting in increased reactive surface area.

ACKNOWLEDGMENTS

REFERENCES

1. Rochow, E. G., *J. Amer. Chem. Soc.* **67**, 963 (1945).
2. Voorhoeve, R. J. H., "Organohalosilanes: Precursors to Silicones." Elsevier, Amsterdam, 1967.
3. Shade, R. W., U.S. Patent 4,281,149 (July 28, 1981).
4. Ward, W. J., Ritzer, A. L., Carrol, K. M., and Flock, J. W., *J. Catal.* **100**, 240 (1986).
5. Banholzer, W. F., Lewis, N., and Ward, W. J., *J. Catal.* **101**, 405 (1986).
6. Banholzer, W. F., and Burrell, M. C., *Surf. Sci.* **176**, 125 (1986).
7. Banholzer, W. F., and Burrell, M. C., *J. Catal.* **114**, 259 (1988).
8. Frank, T. C., and Falconer, J. L., *Appl. Surf. Sci.* **14**, 359 (1982/1983).
9. Frank, T. C., Kester, K. B., and Falconer, J. L., *J. Catal.* **91**, 44 (1985).
10. Agarwala, J. P., and Falconer, J. L., *Int. J. Chem. Kinet.* **19**, 519 (1987).
11. Sharma, A. K., and Gupta, S. H., *J. Catal.* **93**, 68 (1985).
12. Lewis, K. M., McLeod, D., and Kanner, B., in "Proceedings, 10th North American Meeting of the Catalysis Society, May 1987, San Diego, CA."
13. Gentle, T. M., and Owen, M. J., *J. Catal.* **103**, 232 (1987).
14. Friedrich, H. B., Sevenich, D. M., Gasper-Galvin, L. D., and Rethwisch, D. G., *Anal. Chim. Acta* **222**, 221 (1989).
15. Gasper-Galvin, L. D., PhD dissertation, University of Iowa, Iowa City, 1989.
16. Hurd, D. T., *J. Amer. Chem. Soc.* **67**, 1545 (1945).
17. Gilliam, W. F., U.S. Patent 2,464,033 (March 8, 1949).
18. Frank, T. C., Kester, K. B., and Falconer, J. L., *J. Catal.* **95**, 396 (1985).
19. Voorhoeve, R. J. H., Geertsema, B. J. H., and Vlugter, J. C., *J. Catal.* **4**, 43 (1965).
20. Voorhoeve, R. J. H., Lips, J. A., and Vlugter, J. C., *J. Catal.* **3**, 414 (1964).
21. Belyi, A. P., Gorbunov, A. I., Fel'dshtein, N. S., and Golubtsov, S. A., *Russian J. Phys. Chem.* **46**(2), 303 (1972).
22. Golubtsov, S. A., Andrianov, K. A., Ivanova, N. T., Turetskaya, R. A., Fel'dshtein, N. S., Chernyshev, E. A., and Dzvonar, V. G., *Zh. Obshch. Khim.* **45**(4), 808 (1975).
23. Brit. Pat. 609172, 609173; Ch. A. **44**, 6426 (1950).
24. Trofimova, I. V., Lobusevich, N. P., Golubtsov, S. A., and Andrianov, K. A., *Zh. Obshch. Khim.* **32**, 841 (1962).
25. Lobusevich, N. P., Trofimova, I. V., Andrianov, K. A., Golubtsov, S. A., and Belyi, A. P., *Khim. Prakt. Primen. Kremneorg. Soedin. Tr. Konf. 2nd 1958*, 6, 28 (1961); *Chem. Abstr.* **56**, 10971 (1962).
26. Lainer, D. I., Malysheva, L. A., and Sotnikova, L. I., *Tr. Gos. Nauchno. Issled. Proektn. Inst. Obrab. Tsvetn. Met.* 20, 17 (1961); *Chem. Abstr.* **57**, 6669 (1962).
27. Poller, P. C. "The Chemistry of Organotin Compounds." Academic Press, New York, 1970.
28. Davies, A. G., and Smith, P. J. in "Comprehensive Organometallic Chemistry, Volume 2" (G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds.). Pergamon Press, Oxford, 1982.
29. Skinner, H. A. in "Advances in Organometallic Chemistry, Volume 2" (F. G. A. Stone and R. West, Eds.). Academic Press, New York, 1964.
30. Lyman, T., (Ed.) "Metals Handbook: Metallography, Structure and Phase Diagrams," Vol. 8, 8th ed. American Society for Metals, Metals Park, OH, 1973.

31. Butts, A., "Copper: The Science and Technology of the Metal, Its Alloys and Compounds," ACS Monograph Series. Reinhold, New York, 1954.

32. Goumiri, L., and Joud, J. C. *Acta Metall.* **30,** 1397 (1982).

33. Stevenson, S. A., Dumesic, J. A., Baker, R. T. K., and Ruckenstein, E., Eds., "Metal-Support Interactions in Catalysis, Sintering, and Redispersion." Van Nostrand–Reinhold, New York, 1987.

34. De Cooker, M. G. R. T., PhD dissertation, Delft, 1976.