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Catalysis of the Rochow Direct Process

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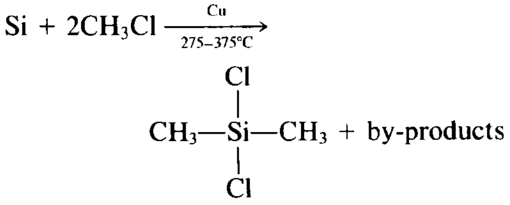
The synthesis of dimethyldichlorosilane by the "Direct Process' is at the heart of the silicone industry. The Direct Process has been the object of intensive research and development over the past 40 years, yet there are aspects of the reaction that remain in an elementary state of understanding. The goal of this work was the discovery of previously unknown variables, including trace elements, which affect product distribution and rate. Fluidized and stirred bed reactors were used. Trace quantities of tin were found to affect the Direct Process profoundly, and the effects of tin and zinc were synergistic. A catalyst system consisting of copper, zinc, and tin was discovered which yielded 90% dimethyldichlorosilane with nearly complete silicon utilization. This is a major improvement over the best previously reported performance. © 1986 Academic Press, Inc.

INTRODUCTION

In 1939 Eugene Rochow (*1*) discovered what is now known as the Direct Process, the most important example of which is the synthesis of methylchlorosilanes from silicon and methyl chloride. The Direct Process provides an economic route to organohalosilanes, particularly dimethyldichlorosilane, and it is this synthesis which is at the heart of the silicone industry. Based on Rochow's discovery the silicone industry was launched after World War II, and the Direct Process is still the only economical route to methylchlorosilanes.

The Direct Process, which is the subject of this paper, is



$$\mathrm{Si} + 2\mathrm{CH_3Cl} \xrightarrow[275\text{–}375^\circ\mathrm{C}]{\mathrm{Cu}} \mathrm{CH_3{-}}\overset{\displaystyle \mathrm{Cl}}{\underset{\displaystyle \mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}CH_3} + \text{by-products}$$

Rochow's great discovery was copper catalysis. The reactants are essentially inert without it. In the presence of copper, the reaction proceeds and the main product is dimethyldichlorosilane (di).

Because of the enormous industrial significance of the Direct Process, it has been the subject of a great deal of research, and there are thousands of papers in the literature dealing with it. The best single source of information is the book by Voorhoeve (*2*) which covers his own extensive work, and includes an exhaustive survey of the literature. The object of much of the work reported in the literature has been to identify variables which affect the product distribution and rate of the Direct Process, and ultimately to understand the mechanism of the reactions involved. For those concerned with economic significance, the goal has been to maximize the yield of dimethyldichlorosilane. An enormous number of factors control the Direct Process, some of which undoubtedly are not yet known. Complicating the situation is that it is notoriously difficult to carry out the Direct Process reproducibly, and much of the literature is of questionable value.

The goal of the present work has also been discovery of variables, including trace elements, that affect product distribution and rate, specifically to find that combination of variables which maximizes the yield of di. To that end, labortory-scale reactor

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systems were developed in which important reaction parameters were known and carefully controlled. All materials fed to the reactors (silicon, catalysts, and methyl chloride) were highly purified and/or exhaustively analyzed. Because of the critical importance of these factors, much of this paper is devoted to a description of the reactor system, procedures, and chemical analysis. Finally, results are presented, with emphasis on the discovery of a new catalyst system consisting of copper, zinc, and tin which provides a significantly higher yield of dimethyldichlorosilane than has previously been reported.

DIRECT PROCESS PRODUCT DISTRIBUTION AND SELECTIVITY

Many compounds are formed in the Direct Process. The principle monomers (and abbreviations to identify them) are shown in the first part of Table 1 in order of increasing boiling point. Several other monomers usually made in trace quantities are also shown. All products boiling above 80°C, including disilanes, are referred to as residue. The disilanes are shown in Table 1.

Figures of merit for the Direct Process from an economic standpoint are percentage di in the crude, the ratio of tri to di (T/D), percentage MH, and percentage residue. Typically in the literature the crude characterization given is not complete, making comparison with the present work impossible. From the relatively few cases where crude characterization has been complete, it can be concluded that normal good practice of the Direct Process on a laboratory scale yields 80 to 85% di. The best set of results known to the authors are those of Takasa (*3*), and are shown in Table 2.

EXPERIMENTAL

Materials

Silicon. Pulverized silicon with numerous trace elements is used in the Direct Process. Particle size, size distribution, and trace element composition are all critically important. The same batch of silicon powder was used throughout this work. The silicon was "chemical" grade and contained the trace elements listed in Table 3A, as determined by atomic absorption spectroscopy. Silicon pieces centimeters in size

TABLE 1

Major Products of the Direct Process

Chemical Name	Formula	Abbreviation	n. bp (°C)
Principle monomers			
Methyldichlorosilane	$(CH_3)HCl_2Si$	MH	40.7
Trimethylchlorosilane	$(CH_3)_3SiCl$	M or Mono	57.9
Methyltrichlorosilane	CH_3SiCl_3	T or tri	66.4
Dimethyldichlorosilane	$(CH_3)_2SiCl_2$	D or di	70.3
Trace monomers			
Tetramethylsilane	$(CH_3)_4Si$	S	26.6
Trichlorosilane	$HSiCl_3$	TCS	31.5
Dimethylchlorosilane	$(CH_3)_2HSiCl$	M_2H	36.0
Silicon tetrachloride	$SiCl_4$	Q	57.6
Residue (disilanes)			
Hexamethyldisilane	$(CH_3)_6Si_2$		~113
Pentamethylchlorodisilane	$(CH_3)_5Si_2Cl$		~130
Sym-tetramethyldichlorodisilane	$(CH_3)_4Si_2Cl_2$		~150
Trichlorotrimethyldisilane	$(CH_3)_3Si_2Cl_3$		~156
Sym-tetrachlorodimethyldisilane	$(CH_3)_2Si_2Cl_4$		~158

TABLE 2

Direct Process Product Distribution of Takasa *et al.* (1981)

	Weight percentage
di	85
T/D	0.085
Mono	4.7
MH	1.3
Residue	1.9

were ball-milled, aerodynamically separated into various size fractions using an Alpine American 100 MZR particle classifier, and then blended to obtain a mixture having a surface area of 0.5 m^2/g. The size distribution of this mixture is listed in Table 3B, and was determined with a Coulter Counter TA-II using Isoton II/30% glycerol electrolyte.

Copper. The amount used, and its initial chemical and physical form are important variables. Cuprous chloride has often been used and was used in the present work. Several sources were used, including Alpha Ventron (99.999%), all of which behaved identically. All CuCl lots used were analyzed by atomic absorption spectroscopy and/or spark source mass spectroscopy. Typically a few parts per million each of silver, nickel, calcium, zinc, and silicon were detected. No other trace elements above 1 or 2 ppm were detected. Based on analytical results and because different sources of CuCl behaved identically, it was concluded that none of them contained trace elements that affected the Direct Process.

Zinc. The zinc used contained lead and cadmium at concentrations of 1700 and 170 ppm, respectively. Iron and aluminum were present at 70 ppm each, a level not sufficient to affect the Direct Process. No other elements were present above approximately 10 ppm. Lead and cadmium have been reported to affect the Direct Process when present in sufficient concentration. To see if their presence was relevant in this work, several runs identical to those reported here were repeated using Alpha Ventron zinc (99.999%). The results were identical to those with the less pure zinc.

Tin. Several tin sources were used, essentially indistinguishable in performance. Tin was added as metal powder (ALFA Products, minus 325 mesh, 99.5%), tin IV oxide powder (99.999% from Aldrich), tin tetrachloride (99.999% from Aldrich), and tetramethyl tin (99.999% from Aldrich). In the latter two cases, addition to the reactor was made by injecting vapor into the MeCl feed line over a period of a few tens of seconds. Vapor injection was convenient because at 23°C approximately 7 ml of the vapor in equilibrium with liquid $SnCl_4$ contains 1 mg of tin, which was a typical size tin addition. In the case of $(CH_3)_4Sn$, 2 ml of vapor was used.

Because all tin sources behaved identically, and all were reagent grade, it was concluded that they, like the CuCl, were "pure."

Methyl chloride. High-purity (99.5%) methyl chloride from Air Products and

TABLE 3

A. Trace Elements in Silicon

Element	Amount (ppm)
Iron	5600
Aluminum	2700
Titanium	850
Manganese	200
Calcium	160
Nickel	120

B. Silicon Size Distribution

Weight %	Particle size (μm)		
	Maximum	Minimum	Midsize
25	25.4	1.3	9.8
19	81	12.7	39
37	64	16	43
11	203	32	92
8	256	521	124

Union Carbide was used. Gas from both sources behaved identically.

Equipment

Because reactor type has been reported (*2*) to affect the Direct Process, both fluidized bed and stirred bed reactors were used in this work. Voorhoeve (*2*) has reviewed many considerations important in reactor design and operation. The emphasis in this work was to assure uniform temperature throughout the mass of reacting silicon powder, and continuous movement of the silicon.

Fluidized bed reactor. The reactor is shown in Fig. 1. It was a 3.8-cm-i.d. glass tube with a glass frit at the center to support the silicon bed. The reactor was heated by the second concentric 5.1-cm-i.d. glass tube. The outside of this tube was coated with a thin, transparent layer of tin oxide. Two pairs of electrodes were fixed to the tin oxide to create two heated sections. One section was for the bottom of the reactor tube below the glass frit, and was used to preheat the MeCl feed. The other section was for the reactor itself, that is, the volume above the glass frit which contained the silicon powder. Separate temperature controllers were used for each heated section. The lower half responded to the lower thermocouple which touched the bottom of the glass frit. The upper half responded to the upper thermocouple which was immersed in the fluidized bed of silicon. The resulting temperature throughout the reacting silicon was uniform to within 0.5°C, and could be maintained as long as the upper thermocouple remained in the silicon bed. The outer 6.4-cm-i.d. glass tube was for thermal insulation and isolation of the reactor. It was very useful to be able to see the bed of silicon during the reaction so that good fluidization could be assured. Above the reactor was a heated dust trap and dust return system to minimize fines loss.

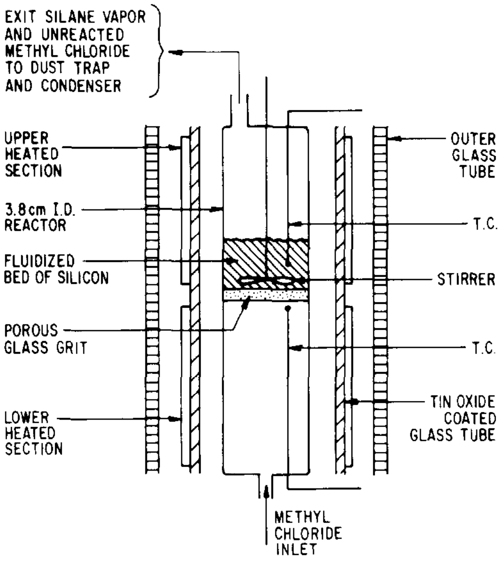

FIG. 1. Fluidized bed reactor.

In order to fluidize the silicon in this small reactor it was necessary both to stir the bed and vibrate the reactor. Vibration was accomplished by attaching one end of a clamp to the reactor, and the other end to the base of a variable intensity test tube shaker. By adjusting the intensity of the vibration and the firmness with which the clamp gripped the reactor, the necessary agitation of the silicon bed was achieved. Stirring speed was approximately 60 rpm. Without stirring and vibration, MeCl merely spouted through the bed at several points, thus bypassing most of the silicon. The depth of the silicon bed when fluidized was approximately 3 cm at the beginning of a run, which was twice the bed height of the powder at rest.

Stirred bed reactor. The reactor is shown in Fig. 2. It was a 2.5-cm-i.d. stainless-steel flanged-end tube, with a helical stirrer inside the tube. The flanged ends were sealed with Allpax gaskets as was the bottom plug which could be adjusted to vary the height of the stirrer bottom cone relative to the bottom flange. This served to keep powder out of the bottom bearing while permitting gas flow upward from the inlet. The upper cap packing ring was secured by a Teflon O-ring and the stirrer was kept vertical by a

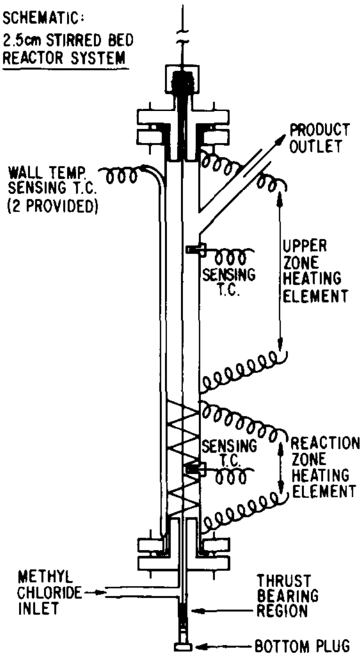

FIG. 2. Stirred bed reactor.

graphite–bronze sleeve bearing. The stirrer traveled on an oilite thrust bearing above the bottom plug.

The reactor was divided into two heated zones. Heating was done with Nichrome wire imbedded in asbestos insulation surrounding the reactor. Temperatures were monitored by thermocouples inserted into ⅛-in.-o.d. stainless tubing that had been welded onto the reactor wall.

Procedures

Prior to using it, CuCl was ground to a particle size of 2 to 5 μm. This was done by preparing of mixture of 3 : 1 hexane/CuCl in a plastic jar containing 1-cm porcelain balls. The jar was sealed and placed on a roller mill for 8–12 h. Shorter (4 h) or longer (24 h) milling did not affect the results. In some cases tin as minus 325 mesh tin dust or as tin (*4*) oxide was added to the slurry to be milled.

Reaction mixtures were prepared by blending silicon powder (20 g for the fluid bed, 50 g for the stirred bed), the CuCl slurry, and additional hexane to make a "soupy" slurry. The slurry was vacuum-dried at 90°C for at least 0.5 h. The dried mixture was placed in a furnace at 280°C or above, through which inert gas (argon) was flowing. In several minutes the exit gas from the furnace became a dense fog when it contacted air. This indicated the evolution of $SiCl_4$ from the silicon mixture. When the fog was no longer visible (1–2 h), the furnace was cooled and the silicon mixture was removed and sealed until use.

Prior to a run the reactor was heated to 300°C, MeCl flow at 12.5 g/h was begun, and the stirrer in the case of the stirred bed, and the stirrer and the vibrator in the case of the fluid bed were turned on. Zinc was added to the silicon mixture which was then dropped into the reactor. Typically in 10 min the first drop of silane was condensed. During the course of a run in the fluid bed reactor occasional adjustments were made in stirrer speed and vibration intensity to keep the bed moving well and properly fluidized while minimizing fines loss.

Silane vapor leaving the reactors was recovered by being passed over a condenser through which methanol at −20°C was circulated. Silane vapor losses past the condenser were negligible at production rates of 2 g or more per hour. At rates below this, a small correction in rate and product composition was made based on available vapor–liquid equilibrium data (Voorhoeve, Ref. (*2*)).

Crude product was analyzed by gas chromatography. Hewlett–Packard and Perkin–Elmer instruments were used, employing thermal conductivity detectors with helium carrier gas. Monomer determinations were carried out utilizing two packed columns in series: 8-ft. × ⅛-in. column 20% SE-30 with 16-ft. × ⅛-in. 20% QF-1 on Chromosorb P (AW-DMCS Alltech Associates) at 80°C. Residue was determined using a 6-ft. × ⅛-in. column 20% SE-30 on Chromosorb W (AW-DMCS) temperature programmed from 35 to 150° at 5°/min following an initial 5 min at 35°C. Response factors were determined by injection of samples of known composition. Major residue components were identified by GC/MS using a similar column and conditions.

Reaction Rate Determination

In order to characterize the rate of reaction in a meaningful way, it was necessary to define a rate constant, based on the observed rate of crude production, which did not vary with the size of the initial silicon charge or with methyl chloride flow rate. A suitable rate constant which will be referred to as K_p (g silane/h, g silicon) is derived in the Appendix.

RESULTS AND DISCUSSION

A complete set of results from a single run is shown in Fig. 3 for the catalyst system consisting of copper, zinc, and tin. This run required 21 h to complete. The rate determination was meaningful out to approximately 55% silicon utilization. Beyond this point the silicon bed dropped below the level of the upper thermocouple, and temperature control was unreliable. As discussed below, rate was strongly affected by temperature, but product distribution was not. To compare results of a large number of runs, a single value of each reaction parameter (i.e., T/D, rate . . .) is given which is characteristic of the entire run. The reproducibility of these reaction parameters for runs carried out under the same conditions was as follows: T/D ± 0.01, residue ± 0.2 (wt%), rate ± 20% of the value, mono ± 0.2 (wt%), MH ± 0.1 (wt%).

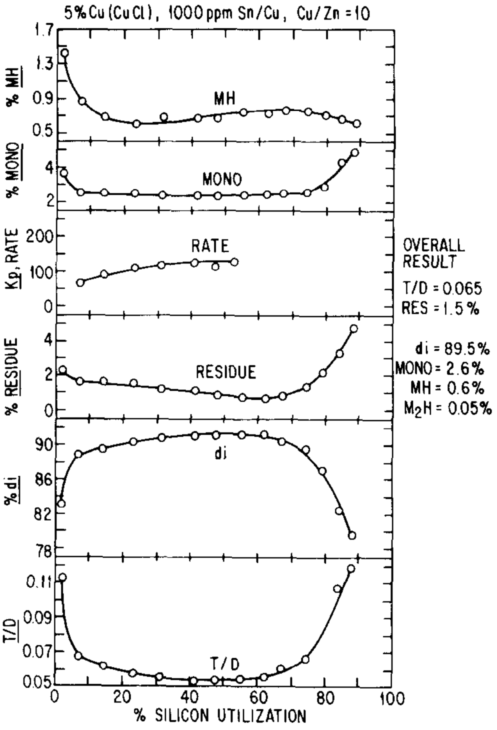

FIG. 3. Rate and product distribution vs silicon utilization for a standard run (5% Cu from CuCl, 0.5% Zn, 1000 ppm Sn/Cu).

First, consider a series of runs performed to evaluate the presence or complete absence of copper, zinc, and tin. Results are summarized in Table 4. As expected, the reaction did not proceed without copper (Run A). Copper alone was sufficient to make the run proceed (Run B), although at low rate and poor selectivity. Adding zinc to copper (Run C) improved selectivity moderately, but had no effect on rate. Adding tin to copper (Run D) improved both rate and selectivity moderately. Finally,

TABLE 4

Effects of Copper, Tin, and Zinc on Rate and Product Distribution[a]

Run	% Cu	% Zn	% Sn	Rate (K_p)	T/D	MH	Mono	Residue
A	0	0.5	0.005	0	—	—	—	—
B	5	0	0	13	0.21	3.7	8.8	1.9
C	5	0.5	0	16	0.09	2.0	3.0	1.9
D	5	0	0.005	46	0.12	1.0	7.2	2.2
E	5	0.5	0.005	84	0.05	0.4	2.4	1.3

[a] Measured at 20% silicon utilization. All runs conducted at 300°C.

adding both zinc and tin to copper (Run E) improved rate and selectivity substantially. The action of tin and zinc are seen to be synergistic.

The performance achieved with copper, zinc, and tin (Run E, Table 4) is significantly superior to any previously reported in the literature (see Table 2) and is highly significant from an economic standpoint.

A series of experiments was done to explore the three component catalyst system. First the tin-to-copper ratio was varied systematically. Results are summarized in Table 5. Tin had a threshold effect on residue, below 2200 ppm Sn/Cu residue was constant, and above this level it was dramatically increased. Tin had a profound effect on rate, but interestingly, it promoted the di and tri rates virtually equally between 420 and 3000 ppm Sn/Cu. Perhaps this indicates that tin promotes an intermediate reaction common to both di and tri.

A series of experiments was done to determine the effect of zinc on rate and selectivity. Results are summarized in Table 6. It is seen that there is an optimum although broad range of the Zn/Cu ratio in order to maximize selectivity. Between Zn/Cu ratios of approximately 0.02 to 0.25 the T/D was at a minimum, and outside this range the T/D was sharply higher. Rate was a weak function of the Zn/Cu ratio. At Zn/Cu values above 0.05 the rate was approximately twice the rate obtained with no zinc.

TABLE 5

Effects of Tin on Rate and Product Distribution

Sn/Cu (ppm)	% Cu	Rate^a (K_p)	Residue^b	T/D^b	MH^b	Mono^b
0	5	16	2.1	0.09	2.8	3.2
420	5	33	1.4	0.06	1.2	2.7
1000	5	84	1.3	0.06	0.6	2.7
1500	5	106	1.6	0.05	0.4	2.2
1500	5	139	1.7	0.06	0.4	2.5
2200	5	132	2.1	0.06	0.3	2.4
3000	5	194	6.4	0.05	0.2	2.5
3000	1.5	239	4.8	0.05	0.3	2.3
1000	1.5	32	1.9	0.06	0.9	3.2

Note. Runs at 300°C, Zn/Cu = 0.10.
[a] Values obtained at 20% silicon utilization.
[b] Cumulative values up to 40% silicon utilization.

TABLE 6

The Effect of Zinc/Copper Ratio on Rate and Product Distribution

Zn/Cu	Rate^a (K_p)	T/D^b	Residue^b	Mono^b	MH^b	M_2H^b
0	46	0.14	2.1	8.4	0.9	1.0
0.02	50	0.06	3.1	3.6	0.6	0.3
0.05	72	0.04	2.3	2.5	0.4	0.2
0.10	84	0.05	1.3	2.6	0.3	0
0.14	61	0.05	0.6	2.6	0.5	0.1
0.20	83	0.06	2.2	3.0	0.3	0.1
0.25	81	0.07	1.6	2.7	0.4	0
0.28	84	0.09	1.4	3.3	0.6	0
0.50	75	0.05	1.3	2.5	0.5	0
0.60	78	0.10	2.0	3.4	0.8	0.1

Note. 1000 ppm Sn/Cu, 5% Cu.
[a] Measured at 20% silicon utilization.
[b] Measured at 40% silicon utilization.

The effect of copper concentrtion on rate and product distribution was determined and results are shown in Table 7. The only effect of varying copper concentration was on rate.

The effect of temperature between 300 and 320°C was investigated. For a pair of runs using 5% Cu, 420 ppm Sn/Cu, and Zn/Cu of 0.1, at 20% silicon utilization the rate at 320°C was 2.6 times larger than the rate at 300°C. For a pair of runs using 1.5% Cu, 1000 ppm Sn/Cu, and Zn/Cu of 0.1, at 20% silicon utilization the rate at 320°C was 2.2 times larger than the rate at 300°C. For an average increase in rate of 2.4 times between 300 and 320°C, the corresponding activation energy is 29.6 kcal/mol. This compares well with a value of 26.6 kcal/mol determined by Voorhoeve (Ref. (*2*), p.

TABLE 7

Effect of Copper Concentration on Rate and Product Distribution

% Cu	Sn/Cu	Rate^a (K_p)	Residue^b	T/D^b	MH^b	Mono^b
1.5	1000	16	2.1	0.05	1.3	2.5
5.0	1000	84	1.3	0.06	0.6	2.7
5.0	420	34	1.5	0.05	1.5	2.3
10.0	420	54	1.5	0.05	1.2	2.1

Note. Runs 300°C, Zn/Cu = 0.1.
[a] Rate at 20% Si utilization.
[b] Cumulative values up to 40%.

166), who did not use tin as a promoter. Temperature had no effect on product distribution in this work, nor did it in the work of Voorhoeve.

CONCLUDING REMARKS

There is general agreement in the literature that copper is required to make the Direct Process proceed at all, and that zinc improves yield. Beyond this there is confusion and contradiction in the literature. Virtually the whole periodic table has been added to Direct Process reactors, but there is little agreement on the results. Dozens of elements in the center of the periodic table undoubtedly affect the Direct Process, but for a variety of reasons these effects have been difficult to determine. The most common fault of work in this area may have been not knowing what trace elements were in fact present, and attributing effects to the wrong causes. In some cases work on trace elements which are now known to be important was not possible even a decade ago because analytical capabilities were lacking.

Perhaps this explains why the profound effect of tin as well as the synergistic effect of tin and zinc was missed in all work prior to this. Voorhoeve (Ref. (*2*), p. 135) reviewed the literature on tin and concluded that its effect was uncertain—either it had no effect or it was a poison. There is only one reference known to the authors, a Serbian language article by Radosavlyevich *et al.* (*4*), which reports a positive effect of tin. At 0.12% tin relative to copper they observed a rate increase of 50%, and there was no comment on product distribution.

The present work represents significant improvements in the practice of the Direct Process. The fluidized bed is unique in that the silicon could be seen as it reacted at 300°C, and the quality of fluidization was apparent at all times. The analytical tools and experimental procedures used in this work were sufficient to achieve excellent reproducibility. This made it possible to delineate quantitatively the roles of copper, zinc, and tin, both individually and in combination, on rate and selectivity. A reaction mixture was discovered which yielded 90% di and nearly complete silicon utilization. This is a major advance over the best previously reported performance (Table 3, 85% di). Nevertheless there is much to learn. Complete empirical knowledge of the highly interdependent actions of copper and the many promoters and poisons, as well as mechanical factors which affect the Direct Process, is not available and is needed for rigid control of the process. Finally, there remains the ultimate goal of understanding the discrete chemical steps involved in the formation of each product of the Direct Process.

APPENDIX: DERIVATION OF A REACTION RATE CONSTANT

Voorhoeve (Ref. (*2*), p. 229) presents a kinetic rate expression which involves the partial pressures of methylchloride and reaction product, which in this case is assumed to be all di. Since these partial pressures vary as methylchloride passes through the reacting bed of silicon, the rate expression must be integrated to obtain a reaction rate constant. In the following, the differential equation describing the reaction and using the kinetic rate expression is set up and integrated.

A plug flow reactor is assumed. That is, gas flows uniformly through the silicon bed with no back mixing and no back diffusion.

Let the moles of MeCl into a differential mass of silicon be

$$F \cdot X$$

where

F = MeCl flow, mol/h
X = fraction MeCl reacted.

The moles of MeCl leaving the differential silicon mass is

$$F \cdot (X - dX).$$

The moles of MeCl reacted is

$$FX - F(X - dX) = FdX.$$

The moles of silane made per hour in the differential silicon mass is

$$R \cdot dM_{\mathrm{Si}}$$

where

$$R = \frac{\text{moles silane}}{\text{h, mole silicon}}$$

$$dM_{\mathrm{Si}} = \text{differential moles of silicon.}$$

Assuming all the crude is dichlorodimethylsilane, then

$$F \cdot dX = 2 \cdot R \cdot dM_{\mathrm{Si}}. \qquad (1)$$

Rearranging and integrating Eq. (1) gives

$$\int \frac{dX}{R} = \frac{2M_{\mathrm{Si}}}{F}. \qquad (2)$$

From Voorhoeve (Ref. (*2*), p. 229)

$$R = \frac{k_{\mathrm{p}} K_{\mathrm{A}} P_{\mathrm{A}}}{[1 + K_{\mathrm{A}} P_{\mathrm{A}} + K_{\mathrm{B}} P_{\mathrm{B}}]^2} \qquad (3)$$

where

k_{p} = molar reaction rate constant for silane, $\frac{\text{moles silane}}{\text{h, mole silicon}}$

K = adsorption equilibrium constants for MeCl (A), and silane (B), (atm^{-1})

P_{A} = partial pressure, MeCl (atm)

P_{B} = partial pressure, silane (atm)

R = rate of silane production, $\frac{\text{moles silane}}{\text{h, mole silicon}}$.

An expression relating partial pressures, total reactor pressure (P), and X is needed. In general

FX = moles MeCl reacted

$F(1 - X)$ = moles MeCl unreacted

$FX/2$ = moles silane made

$$P_{\mathrm{A}} = \frac{\text{moles MeCl present}}{\text{total moles present}} \cdot P$$

$$P_{\mathrm{A}} = \frac{F(1 - X)}{F(1 - X) + \frac{FX}{2}} \cdot P$$

then

$$P_{\mathrm{A}} = \frac{1 - X}{1 - \frac{X}{2}} \cdot P \qquad (4)$$

and

$$P_{\mathrm{B}} = P - P_{\mathrm{A}}. \qquad (5)$$

Substituting Eqs. (4) and (5) into (3), and substituting the result into Eq. (2) gives an expression which can be numerically integrated. The result is a value for k_{P} in terms of X and P, both of which are known throughout each experiment. Since it is more usual to express normalized rates in terms of grams rather than moles, k_{p} is converted to gram units as follows

$$K_{\mathrm{p}} \frac{\text{grams silane}}{\text{grams silicone, h}} = 4.6k_{\mathrm{p}} \frac{\text{moles silane}}{\text{mole silicon, h}}.$$

If one prefers a closed solution for K_{p}, it can be obtained if the $K_{\mathrm{A}}P_{\mathrm{A}}$ term in Eq. (3) is dropped. The error is small if this is done. Making this change, and substituting Eq. (3) into Eq. (2) gives

$$\frac{2M_{\mathrm{Si}}}{F} = \frac{dX}{\frac{k_{\mathrm{P}} K_{\mathrm{A}} P_{\mathrm{A}}}{[1 + K_{\mathrm{B}} P_{\mathrm{B}}]^2}}$$

eliminating P_{B} and rearranging terms gives

$$\frac{2k_{\mathrm{P}} K_{\mathrm{A}} M_{\mathrm{Si}}}{F} = \frac{[1 + K_{\mathrm{B}}(P - P_{\mathrm{A}})]^2}{P_{\mathrm{A}}} dX. \qquad (6)$$

Expanding terms in the integral of Eq. (4) gives

$$\frac{2k_{\mathrm{p}} K_{\mathrm{A}} M_{\mathrm{Si}}}{F} = \frac{(1 + 2K_{\mathrm{B}}P - 2K_{\mathrm{B}}P_{\mathrm{A}} + K_{\mathrm{B}}^2P^2 - 2K_{\mathrm{B}}^2PP_{\mathrm{A}} + K_{\mathrm{B}}^2P_{\mathrm{A}}^2)}{P_{\mathrm{A}}} dX.$$

Separating the integral into three terms

$$\frac{2k_{\mathrm{p}} K_{\mathrm{A}} M_{\mathrm{Si}}}{F} = \frac{(1 + 2PK_{\mathrm{B}} + P^2K_{\mathrm{B}}^2)}{P_{\mathrm{A}}} dX \text{ (Term I)}$$

$$- (2K_B + 2K_B^2P)\, dX \text{ (Term II)}$$
$$+ K_B^2P_A\, dX \text{ (Term III)}. \qquad (7)$$

Substituting Eqs. (4) and (5) into each term of Eq. (7) and integrating gives

$$\text{Term I} = \frac{1 + 2PK_B + P^2K_B^2}{2P} [X - \log(1 - X)]$$

$$\text{Term II} = (2K_B + 2K_B^2P)X$$

$$\text{Term III} = 2K_B^2PX + 2K_B^2P \log\left(1 - \frac{X}{2}\right).$$

Combining terms results in a straightforward expression for the rate constant:

$$K_p = \frac{(4.6)F(\text{I} - \text{II} + \text{III})}{2K_AM_{Si}} \qquad (8)$$

where

$$\text{I} = \left(\frac{1}{2P} - K_B + \frac{PK_B^2}{2}\right) X$$

$$\text{II} = \left(\frac{1}{2P} + K_B + \frac{PK_B^2}{2}\right) \log(1 - X)$$

$$\text{III} = 2PK_B^2 \log\left(1 - \frac{X}{2}\right).$$

To summarize all the terms used above

F = MeCl feed flow (moles/h)

K = Adsorption equilibrium constants (atm^{-1})
subscript A (MeCl)
subscript B (Silane)

k_p = molar reaction rate constant $\dfrac{\text{moles silane}}{\text{mole silicon, h}}$

K_p = reaction rate constant $\dfrac{\text{grams silane}}{\text{gram silicon, h}}$

M_{Si} = silicon in reactor (moles)

P = total reactor pressure (atm)

P_A = partial pressure MeCl (atm)

P_B = partial pressure silane (atm)

R = normalized silane production rate, $\dfrac{\text{moles silane}}{\text{mole silicon, h}}$

X = fraction of MeCl conversion.

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