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Mechanism and Kinetics of the Metal-Catalyzed Synthesis of Methylchlorosilanes

I. The Synthesis of Methylchlorosilanes in a Fluid Bed

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In this paper a fluid-bed performance of the copper-catalyzed synthesis of methylchlorosilanes from silicon and methyl chloride is described. A contact mass, prepared by reaction of copper(I) chloride and silicon, is employed. The use of standardized procedure allowed reproducible experimentation. The rate and the selectivity of the reaction are studied in relation to the temperature and the silicon conversion. The attainable silicon conversion is 65 to 70% for the particular contact mass studied. The silane products contain an average of 85 wt % dimethyldichlorosilane. The variation of the reaction rate and of the selectivity with the silicon conversion is shown to be related to the surface area of the η phase (Cu_3Si) in the contact mass. The rapid falloff of the reaction velocity after some characteristic silicon conversion is explained by a sudden decrease of the length of the silicon–η interphase boundary at the surface of the contact-mass particles.

I. INTRODUCTION

The synthesis of methylchlorosilanes yields the raw materials for methylsiloxanes, the most widely used type of silicones. The synthesis is commonly carried out by the copper-catalyzed reaction of silicon and methyl chloride (*1*). Other catalysts may be used (*2*). As dimethyldichlorosilane is mainly wanted to produce silicone oils and rubbers, the main reaction should be

$$Si + 2CH_3Cl \rightarrow Si(CH_3)_2Cl_2 \quad (1)$$

This reaction is exothermal, about 80 kcal/mole, dimethyldichlorosilane being liberated. Except for (1), many side and consecutive reactions may take place. The resulting product contains a variety of compounds. The product composition is rather dependent on the reaction temperature (*3, 4*). As the almost exhausted copper-silicon contact mass resulting after the reaction is an extremely active catalyst for the cracking of methyl chloride (*5*), these copper-rich particles have to be withdrawn in any continuous process.

These features have led several authors to the use of a fluidized bed for this synthesis (*6–8*). It was shown in this laboratory (*3, 4, 9*) that with this reactor system it is possible to maintain a constant copper percentage in the contact mass by continuously removing copper-rich fines along with the gaseous products. In the present study an investigation is described in which a contact mass, prepared from copper(I) chloride and silicon, is exhausted at constant temperatures and methyl chloride feed rates.

II. EXPERIMENTAL PROCEDURE

The fluid-bed reactor employed in the present work was described earlier (*4, 9*). The reactor is drawn in Fig. 1. It is employed with a spiral stirrer.

The contact masses used always contained 10 wt % of copper. The silicon was a mixture of 11.7 wt % of a sieve fraction of 50–75 μm, 36.9 wt % of 75–105 μm, 41.4 wt % of 105–150 μm, and 10.0 wt % of 150–210 μm. This silicon mixture contained: Fe, 0.4%; Al, 0.10%; Ca, 0.05%; and Mg, 0.09%.

The contact mass was prepared by reaction (2)

$$4CuCl + n\,Si \rightarrow (n-1)Si + 4Cu + SiCl_4 \qquad (2)$$

The copper(I) chloride used did not contain bivalent copper. The total amount of impurities was less than 0.1%, mainly consisting of earth alkali metals. Emission-spectrometric analysis showed the presence of traces of magnesium and manganese and extremely small quantities of lead and tin. Arsenium, aluminum, antimony, and bismuth were not present. This copper(I) chloride was prepared by a method described in ref. (*9*). To obtain reproducible results it is extremely important to prepare the contact masses by carefully standardized methods. The preparation was carried out in the fluid-bed reactor device. The contact mass was used immediately after preparation.

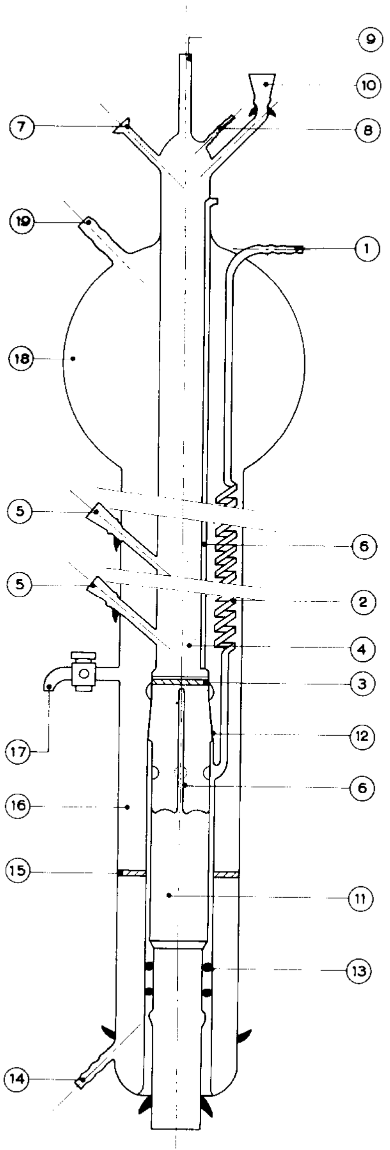

FIG. 1. Fluid-bed reactor. 1. From methyl chloride metering system; 2. preheater; 3. porous plate; 4. reactor with fluidized bed; 5. opening for temperature measurement or contact-mass bleed; 6. Thermocouple well; 7. outlet for products and dust; 8. pressure measuring; 9. passage of stirrer axis; 10. filling opening and outlet for silicon tetrachloride; 11. glass plug with gates for methyl chloride inlet and with 12. ground glass joint; 13. "O" ring seal; 14. inlet pressure air to fluidize the external (heat transport) bed; 15. porous bottom plate external bed; 16. fluidized bed; 17. stopcock; 18. dust chamber external bed; 19. to hydrocyclone; diameter of reactor tube, 38 mm, height 1600 mm.

Preparation of the Contact Mass

Silicon was dried for at least 10 hr in an oven at 180–200°C. Copper(I) chloride, with a particle size of 2–5 μm was passed through a 210 μm sieve. Into a stoppered bottle were weighed 1560 parts copper(I) chloride, 5 parts aluminum powder, and 10 parts zinc powder. The powders were well mixed by rolling the bottle. To the mixture were then added 9095 parts dried and cooled silicon powder. The jar was rolled again until a homogeneous mixture was obtained. This mixture was then poured into the reactor. The reactor was at room temperature and had previously been flushed with nitrogen or argon. When pouring the powders into the reactor segregation of the powder was prevented by rolling the flask and by employing a small height of fall. No gas was being passed through the reactor. Immediately after filling the reactor was closed, except for an outlet for silicon tetrachloride. Argon or nitrogen was passed through at a rate well below the minimum fluidization velocity.

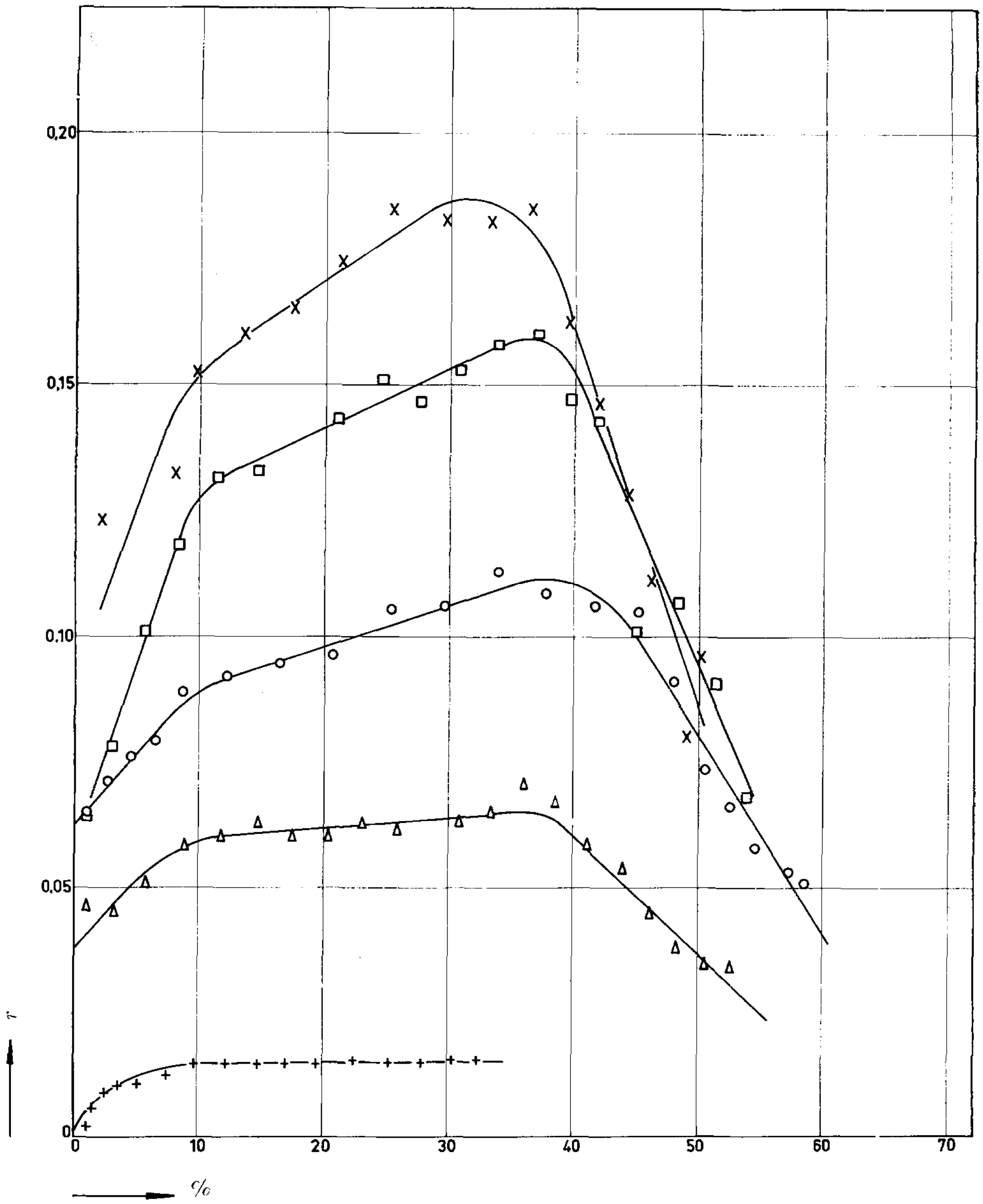

FIG. 2. The reaction rate vs the silicon conversion: +, 281° (F33); △, 312° (F22); ○, 327° (F21); □, 338° (F23); ×, 347° (F24). See Table 1. (Y-axis: r, g CH_3Cl/g Si hr. X-axis: silicon conversion, %).

The reactor was heated at a rate of about 5°/min. Above the initiation temperature of reaction (2) a rapid evolution of silicon tetrachloride occurs. The initiation temperature was always 305°C when freshly prepared, dry copper(I) chloride was employed. The heat supply to the reactor was controlled so as to secure a temperature rise of not more than 20 to 30° when the reaction starts. If the sudden temperature rise is larger, the contact mass is fluidized for a while or preferably stirred. The temperature is then adjusted at 350°C. After heating 2–3 hr at 350° the mass is ready for use.

Complete conversion of the copper(I)

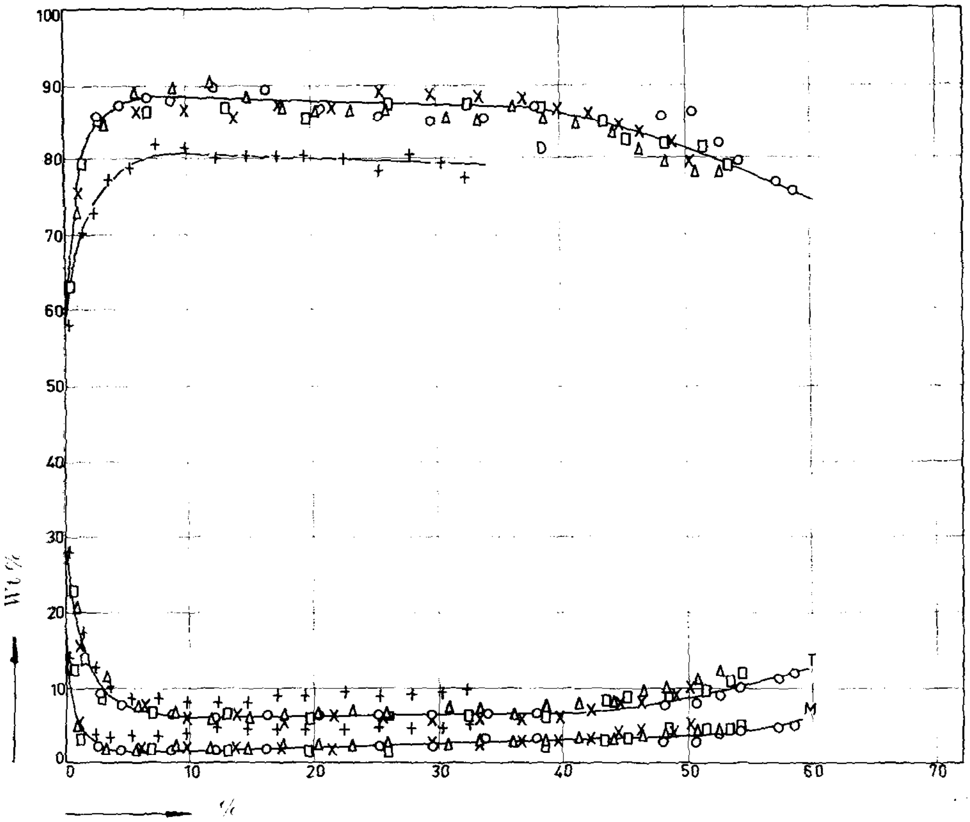

FIG. 3. The composition of the reaction products vs the silicon conversion: +, 281° (F33); △, 312° (F22); ○, 327° (F21); □, 338° (F23); ×, 347° (F24). See Table 1. (Y-axis: product composition, wt %. X-axis: silicon conversion, %).

chloride yields a mass with 1000 parts copper, 5 parts aluminum, and 10 parts zinc (eventually as chlorides) and 8985 parts silicon. The copper is mainly present as η phase (Cu_3Si), as is revealed by röntgenographic analysis (*9,10*). Microscopic study of the contact-mass particles showed that this η phase was incorporated in the silicon as a rough skin (comparable with sand particles pressed in wax). The size of the η-phase particles was about 1 μm.

The minimum fluidization rate of the obtained contact masses is, with nitrogen at 20°C, 1.47×10^{-3} g/cm^2 sec and with methyl chloride at 325°C, 1.05×10^{-3} g/cm^2 sec.

The products of the synthesis consist of copper-rich fines and a gaseous effluent. The fines are collected in a cyclone. The gaseous effluent is continuously distilled in a rectification column which is directly connected to the reactor. Here a separation is effected of silanes and methyl chloride. The silanes are withdrawn from the still at regular intervals and are analyzed gas chromatographically.

All experiments described in this paper were carried out with portions of 330 g contact mass. The methyl chloride feed rate was 117 g/hr (10.3 g/cm^2 hr). This corresponds to three times the minimum fluidization rate of the fresh contact mass. The stirrer turned at 60 rpm.

III. RESULTS

The results of the investigations are collected in Figs. 2–5 and in Tables 1 and 2. The curves of the reaction rate (expressed as grams of methyl chloride converted into silanes per gram of silicon at any time present in the reactor and per hour) in relation to the silicon conversion and with

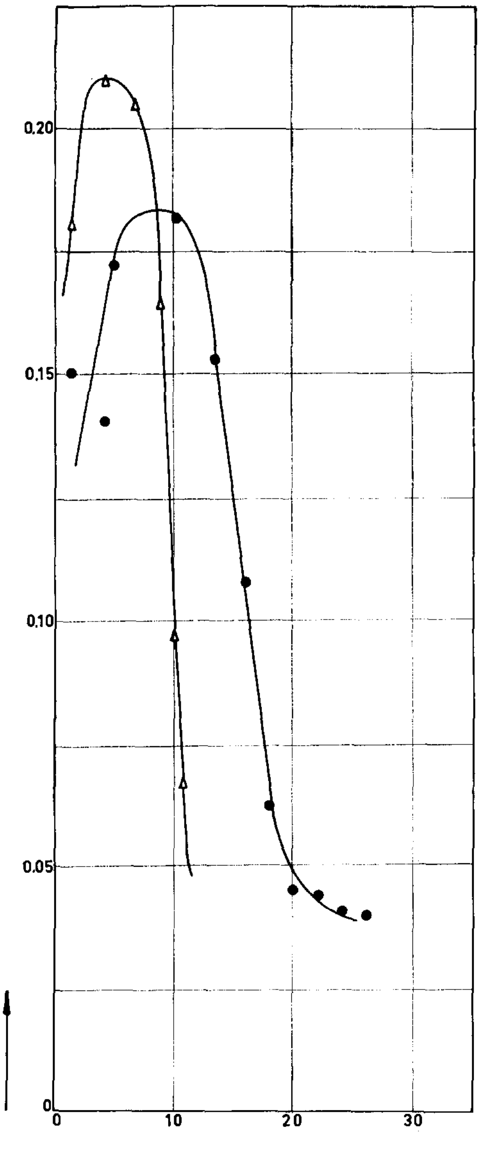

FIG. 4. The reaction rate vs the silicon conversion: ●, 375° (F31); △, 410° (F30). See Table 1. (Y-axis: r, g CH_3Cl/g Si hr. X-axis: silicon conversion, %).

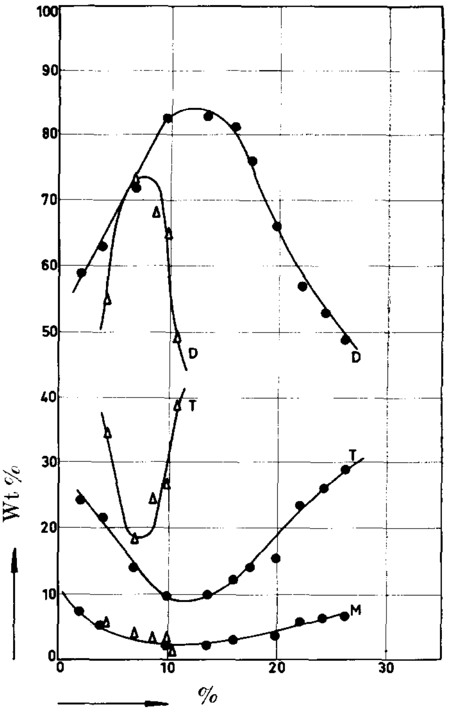

FIG. 5. The composition of the reaction products vs the silicon conversion: ●, 375° (F31); △, 410° (F30). See Table 1. (Y-axis: product composition, wt %. X-axis: silicon conversion, %).

the reaction temperature as a parameter show that in the applied reactor system temperatures between 280° and 350°C are usable. By extrapolation of the curves towards higher silicon conversions, until the reaction rate approaches zero, the maximum attainable silicon conversion may be determined. At temperatures between 300 and 350°C the maximum attainable silicon conversion turns out to be 65 to 70%.* At higher temperatures (375° and 410°C) the contact mass is rapidly inactivated and as a consequence only 20 to 40% of the silicon can be converted. This rapid inactivation of the contact mass is probably due to blocking of the active sites on the surface by the decomposition products of methyl chloride. In accordance with this view the initially rather high selectivity decreases after some time has elapsed at high temperatures (Fig. 5). In the range to 350°C the limit for the silicon conversion shows to be highest for 327° and 338°C (70% silicon conversion). As the reaction rate has achieved a reasonable level in this

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* By adding small amounts of hydrogen sulfide to the methyl chloride feed, 90% of the silicon may be converted into products with 82 wt % dimethyldichlorosilane (*4*, *9*).

TABLE 1

The Synthesis of Methylchlorosilanes in Fluid Bed (Over-all Results). Contact Mass Prepared from Copper(I) Chloride and Silicon

Expt. no.	Temp. (°C)	Duration (hr)	Products (g)	Product composition[a] (wt %)						Silicon[b] conversion (%)	Methyl chloride conversion (%)
				D	T	M	DH	Q	TH		
F33	281	94.5	380	78.5	10.0	4.0	3.5	2.5	1.7	33	3.0
F22	312	50.5	691	85.0	8.0	2.8	2.3	1.3	0.3	54	9.2
F21	327	37.0	756	84.5	8.3	3.2	2.5	1.4	0.3	59	14
F23	338	22.5	680	84.6	7.4	3.1	3.7	1.1	0.2	54	20
F24	347	17.8	649	86.2	7.5	2.4	3.1	1.1	0.1	51	24
F31	375	12.8	324	68.5	17.0	5.0	7.0	2.0	0.3	27	17
F30	410	2.3	130	56.0	32.9	5.6	5.1	0.4	0.3	11	38

Expt. no.	Contact mass after the expt. (g)	Composition of the spent contact mass (wt %)				Dust (g)	Composition of the dust (wt %)				Mass balance (Si + Cu) (%)
		Si	Cu	C	Cl		Si	Cu	C	Cl	
F33	212	86.9	10.5	0.2	0.3	33.6	60.6	24.6	2.3	3.4	97
F22	164	85.8	11.3	0.2	0.5	21.4	30.7	54.5	5.1	5.3	99.8
F21	151	84.8	12.8	0.3	0.7	22.4	29.4	56.0	6.5	6.1	100.1
F23	166	87.1	11.1	0.2	0.6	28.9	36.2	44.1	6.7	9.5	101.2
F24	168	87.5	10.6	0.2	0.5	22.3	27.0	56.6	4.3	8.6	98.1
F31	238	89.6	7.1	—	0.3	22.4	25.5	51.0	4.6	15.7	97.0
F30[c]	265	91.4	6.5	0.3	0.4	~25	36.6	45.1	7.4	8.1	

[a] Throughout this paper the following product code is used: D = dimethyldichlorosilane, T = methyltrichlorosilane, M = trimethylchlorosilane, DH = methyldichlorosilane, TH = trichlorosilane, Q = tetrachlorosilane.

[b] Silicon in silanes and in dust.

[c] At about 20% silicon conversion.

TABLE 2

The Synthesis of Methylchlorosilanes in Fluid Bed (Over-all Results). Contact Mass Prepared from Moist Copper(I) Chloride and Silicon

Expt. no.	Temp. (°C)	Duration (hr)	Product (g)	Product composition[a] (wt %)						Silicon[b] conversion (%)	Methyl chloride conversion (%)
				D	T	M	DH	Q	TH		
F18	348	16.2	865	87.5	5.7	3.1	[3.4[c]]			65	36
F19	338	22.5	733	86.6	7.1	2.7	1.6	[2.1[c]]		56	21
F20	327	39.0	613	83.3	9.9	3.2	2.5	1.2	0.2	55	10.6

Expt. no.	Spent contact mass (g)	Composition of the spent contact mass (wt %)				Dust (g)	Composition of the dust (wt %)				Mass balance (Si + Cu) (%)
		Si	Cu	C	Cl		Si	Cu	C	Cl	
F18	131	—	—	—	—	4.6	—	—	—	—	~98
F19	149	82.4	14.1	1.1	0.8	19.7	—	—	—	—	~98.5
F20	173	85.2	9.3	0.4	0.7	26.6	28.5	62.2	4.9	5.6	97.5

[a] See footnote *a*, Table 1.

[b] Silicon in silanes and in dust.

[c] Total value.

range and as the amount of dimethyldichlorosilanes in the total products is almost a maximum, temperatures between 327° and 338°C appear to be optimal in this system.

It is evident from Fig. 3 that the product composition is hardly dependent on temperature in the range of 280–350°C. At 280° a somewhat lower percentage of dimethyldichlorosilane is found in the products. The reason for this fact is not known, but it need not be significant. Stirred-bed experiments reported earlier yielded at 300°C selectivities of 89% dimethyldichlorosilane in the products (*11*). At high temperatures a high selectivity is found for some time, but the amount of side reactions increases progressively with time, the amount of dimethyldichlorosilane decreasing rapidly along with the reaction rate.

In Table 1 the total amounts of silanes produced in the course of an experiment are reported together with the composition of the over-all product, with the silicon conversion, and with the average methyl chloride conversion. From the compositions of the exhausted contact masses and the corresponding dusts it is clear that the fines are relatively very rich in copper, carbon, and chlorine.

Some data concerning experiments which were carried out with contact masses prepared from moist copper(I) chloride are presented in Table 2. The relevant contact masses were prepared from powders mixed in moist air. Possibly some oxidation of the copper(I) chloride occurred. Most of the moisture present in the mixtures is entrained with the nitrogen flow during the first heating stage in the preparation of the contact mass. Evidently the reactivity of the resulting contact masses is rather high, but unfortunately the results are not reproducible.

IV. THE TEMPERATURE DEPENDENCY OF THE REACTION RATE

To trace the effect of the temperature on the reaction rate it is necessary to calculate initial reaction rates (rates at zero methyl chloride conversion) from the average rates shown in Fig. 2. From the rate equation published in ref. (*12*) and from our own kinetic measurements (*9*, *13*) it appears that at low over-all pressures and not too high conversions the reaction may be considered as first order in methyl chloride. From the average reaction rates in Fig. 2 the initial reaction velocities were calculated, assuming the rate equation to be (3).

$$r = Cp_{\mathrm{CH_3Cl}} \tag{3}$$

The initial reaction rates are calculated for the center part of the curves in Fig. 2 for a definite set of silicon conversions (15, 20, 25, 30, 35%). The results are presented in Table 3.

For each set of values at constant silicon conversion an activation energy for the reaction is calculated. The rates are also averaged at constant temperature between 15 and 35% silicon conversion. The values obtained are illustrated in Fig. 6.

The resulting activation energy is 26.6 kcal/mole. In Fig. 5 the value for 347°C lies under the straight line, indicating that the cracking and blocking reactions already influence the results at 347°. They are still more important at 375° and 410°C.

V. THE EFFECTS BROUGHT ABOUT BY CONVERSION OF THE SILICON

The curves for the reaction rates in the fluid bed as a function of the silicon conversion at 310–350°C are clearly divided into three parts (Fig. 2). The first branch rises sharply until 10% of the silicon is converted. The second fragment of the curves shows a relatively slow, linear increase of the rate between 10 and 35% silicon conversion. After 40% silicon conversion a rapid decrease of the reaction velocity is observed, until at 65 to 70% conversion the reaction rate approaches zero. The corresponding selectivity curves (Fig. 3) show that in the first period, until 5% silicon conversion is reached, the percentage of dimethyldichlorosilane in the products increases strongly, accompanying the sharp rise in reaction rate. After 6% silicon conversion the selectivity remains

TABLE 3

THE TEMPERATURE DEPENDENCE OF THE INITIAL REACTION RATE

Si conv (%)	Temp. (°C)					E_0 (kcal/mole)
	281°	312°	327°	338°	347°	
15	0.014[a]	0.060	0.095	0.135	0.163	
	0.030	0.131	0.207	0.294	0.355	
	0.014	0.062	0.100	0.146	0.179	26.5
20	0.015	0.062	0.099	0.142	0.172	
	0.031	0.127	0.203	0.291	0.352	
	0.015	0.064	0.104	0.153	0.189	26.1
25	0.015	0.064	0.103	0.147	0.180	
	0.029	0.123	0.195	0.282	0.346	
	0.015	0.066	0.108	0.158	0.197	26.7
30	0.016	0.065	0.107	0.153	0.187	
	0.029	0.127	0.186	0.275	0.336	
	0.016	0.067	0.113	0.164	0.204	26.6
35	0.016	0.066	0.112	0.159	—	
	0.027	0.110	0.176	0.265	—	
	0.016	0.068	0.117	0.170	—	27.0
Average	*0.015*	*0.065*	*0.108*	*0.158*	*0.192*	*26.6*

[a] The first number denotes the average reaction rate r (expressed as grams of methyl chloride converted into silanes per gram of silicon in the reactor and per hour). The middle number gives the fraction of the methyl chloride converted into silanes. The number at the bottom denotes the initial reaction rate r_0 (at zero methyl chloride conversion).

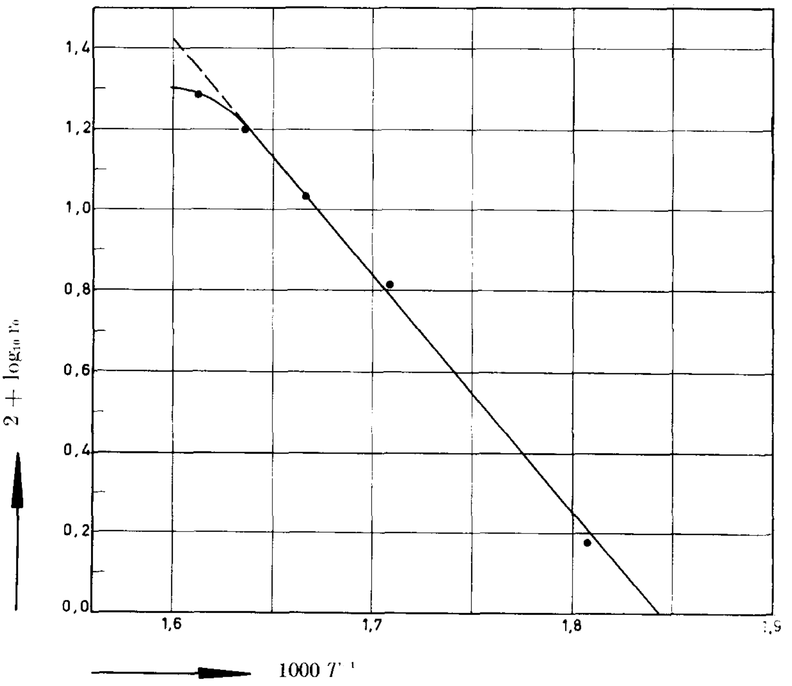

FIG. 6. The temperature dependency of the initial reaction rate. See Table 3.

constant at 87–90% dimethyldichlorosilane until 40% silicon conversion. Beyond this point the selectivity decreases gradually, coinciding with the sharp decrease of the reaction velocity. The boundaries between the three sections of the selectivity and activity curves appear always at about 10 and 40% silicon conversion. The three parts of the curves will now be discussed to gain a better insight into the processes leading to this remarkable course of the synthesis.

The first fragment of each curve shows a sharp increase of both the reaction rate and the percentage of dimethyldichlorosilane in the products. Investigation under the polarization microscope of polished silicon surfaces after reaction with copper(I) chloride showed that the fresh contact mass consists of a silicon substrate which is partly covered by η phase (Cu_3Si). The η phase again is partly covered by a thin layer of free copper, not yet converted into η phase. This result matches with the evidence from microscopic investigation of nonpolished contact-mass particles. Röntgen diffraction also indicates the contact mass to be composed of silicon and η phase with some free copper (Fig. 7(a) and (b). It is obvious that copper and silicon will form η phase at their interface, a relatively copper-rich surface remaining.

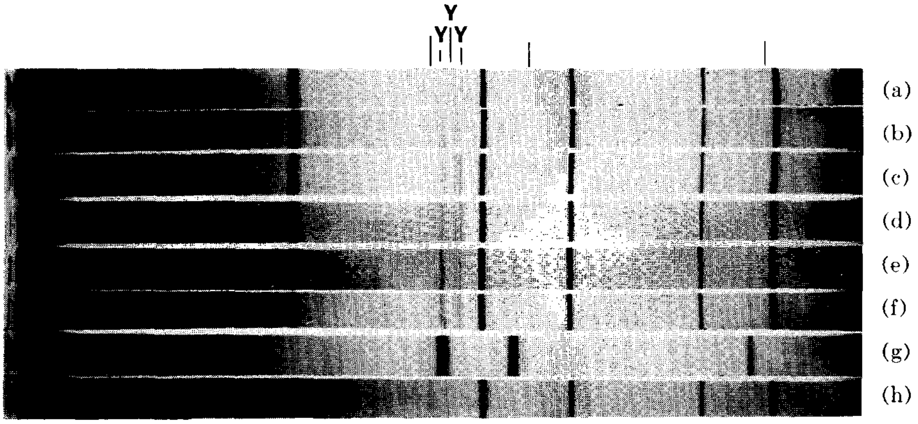

FIG. 7. Röntgen diffraction patterns. Contact masses during the contact-mass preparation and during the first 10% silicon conversion. Guinier camera, Cu K_α radiation. (a) Immediately after the vivid tetrachlorosilane evolution; (b) two hours after (a); (c) during the reaction with methyl chloride after 2.6% silicon conversion; (d) after 5.1% silicon conversion; (e) after 7.6% silicon conversion; (f) after 10.4% silicon conversion; (g) pure copper; (h) pure silicon. The reaction with methyl chloride was carried out at 340°. $Y = \eta$; $| =$ Cu.

In the initial period of the reaction with methyl chloride this copper layer mainly disappears by conversion into η phase or by attrition in the fluid bed. The conversion of copper into η phase is microscopically verified.* In the first reaction period a decrease of the free copper amount in our contact masses could not be shown by X-ray analysis. During the conversion of the first 5% of the silicon the intensity of the copper lines remained about constant [Fig. 7(c,d)].

The increase of the reactivity of the contact mass and the decrease of the rate of formation of side products (Fig. 8) may be attributed to the disappearance of free copper shielding part of the η-phase surface. A second effect which may account for the rise of the reaction rate is the increase in surface area produced by the etching by methyl chloride. Summarizing, the increase in activity during the conversion of the first 10% of the silicon and the rise of the selectivity of the reaction may be attributed to the etching of the surface and to the disappearance of free copper from the active surface.

The second branches of the functions (Figs. 2, 3) representing the selectivity

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* In the ethylchlorosilane synthesis the conversion of copper into η phase in the starting period of the reaction is shown by ref. (*14*).

and reaction rate in relation to the silicon conversion show an almost constant selectivity and a gradual and linear increase of the reaction velocity. Judged from the constant selectivity it is not to be expected that any further change will appear in the ratio of the surface areas of free copper and η phase. However, the amount of free copper and η phase increases relative to the total weight of the contact mass. This is indicated by Fig. 7(e) and (f). Accordingly, the rate of formation of side products is raised beyond 7% silicon conversion (Fig. 8).

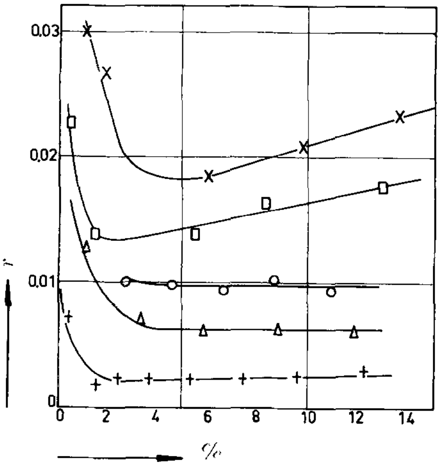

FIG. 8. The specific conversion of methyl chloride into side products vs the silicon conversion: +, 281° (F33); △, 312° (F22); ○, 327° (F21); □, 338° (F23); ×, 347° (F24). (Y-axis: r, g CH_3Cl/g Si hr. X-axis: silicon conversion, %).

The increase of the reactivity of the contact mass is completely accounted for by the radial shrinkage of the silicon particles. With a constant surface area of η phase the reaction velocity per unit weight of silicon will increase with the conversion of the particles. This interpretation is supported by the curves of the reaction velocity expressed as the weight of methyl chloride converted (Fig. 9). The curves representing the second fragments of the function in Fig. 2 show but a small slope.[*]

An explanation of the rather sudden changeover from the second to the third portion of the curves (Fig. 2) has to elucidate the sharp decrease of the reaction rate and the gradual decrease of the selectivity (Fig. 3). The most plausible inference from what has been said above is that the η-phase surface area shows a sudden slump.

As a matter of fact, the catalytic activity of the η phase requires at the surface a grain boundary between η phase and free silicon, as a supply of free silicon atoms to the η-phase surface reacting with methyl chloride is only rapid enough via such a boundary. This implies that free silicon has to be present at the surface of the particles. Initially this is certainly the case. However, in the course of the synthesis process the η-phase grains will cover an ever growing part of the silicon surface. As long as the grain boundaries remain free this will not bear any detrimental effect. But when the η-phase grains reach each other a rapid decrease of the length of the grain boundaries will occur, producing a rapidly decreasing reactivity, diffusion of silicon atoms becoming the rate-controlling process. This may be the explanation of the revealed changes of the contact-mass

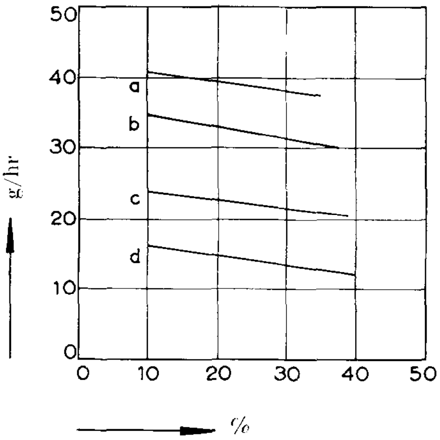

FIG. 9. The conversion of methyl chloride into silanes vs the silicon conversion. The curves were obtained from the center branches of the curves in Fig. 2. a. 347° (F24); b. 338° (F23); c. 327° (F21); d. 312° (F22). (Y-axis: methyl chloride conversion, g/hr. X-axis: silicon conversion, %).

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[*] The negative slope is caused by some attrition, which is relatively more important the longer the experiment lasts.

properties at about 40% silicon conversion. The spread in particle sizes obscures the effects somewhat. The proposed mechanism is in line with the much more gradual decrease of the selectivity of the methylchlorosilane production.

To support the presented interpretation of the facts it may be calculated at which over-all silicon conversion the η-phase grains on the smallest particles (50–75 μm) will start to hinder each other. At that moment the descent of the reaction rate will start. The calculation is based on the model of Fig. 10.

The copper content of the contact mass is known to be 10 wt %. The particle-size distribution of the silicon powder is recorded in the Experimental Procedure section, the specific surface of the mixture being $S_r = 1050$ cm^{-1}. The size of the η-phase particles is microscopically determined to be 1 μm. In the calculation silicon particles are assumed to be spheres, the sphere-shaped η-phase grains being embedded in the silicon surface. The density of the η phase is approximately 8.12 g/ml; the silicon density is 2.42 g/ml. It is simply calculated that the η-phase grains will cover a surface area of 560 cm^2/ml silicon. When all η-phase grains (in closest packing) touch as a consequence of the radial shrinkage of the silicon particles a fraction 0.9 of the silicon surface will be covered.

From the mentioned values it is calculated that this occurs at 55% conversion of the particle. At the moment this happens with the smallest particles (50–75 μm) the sudden falloff of the reaction rate will start. It has to be calculated now at which over-all silicon conversion the particles of

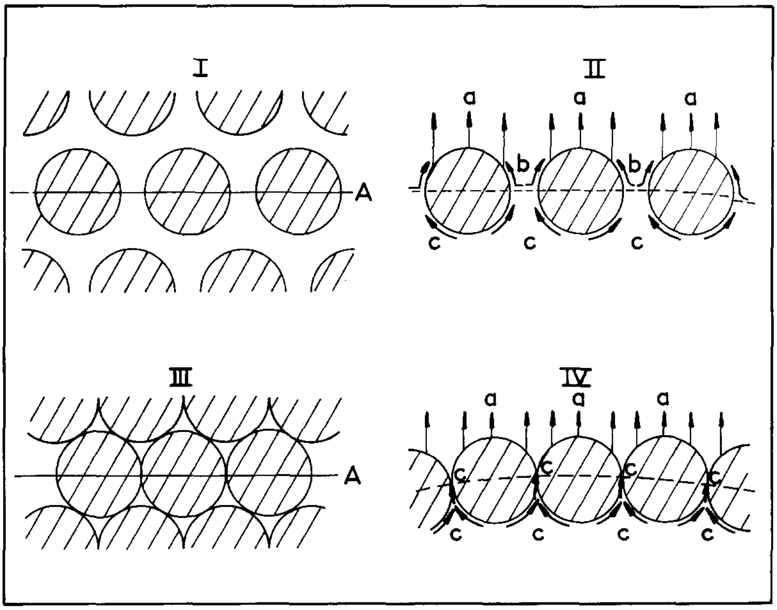

FIG. 10. Model of the surface of a contact mass particle (on scale). Contact-mass data: see the text. I. Idealized structure of the η–Si surface (shaded area is η phase, with silicon in between). II. Cross section along A of the surface I. III. The same particle after 55% conversion. IV. Cross section along A of the surface III. a. Reaction of silicon with methyl chloride; b. surface diffusion of silicon; c. grain-boundary diffusion of silicon.

The transport through a is initially slower than that via b and c. The transport through b and c is proportional with the length of the η-silicon grain boundary at the surface. This length slumps down beyond 55% silicon conversion. Then the transport via b and c may become slower than that via a. After some time b is impossible at all. The whole surface is then covered by η-phase grains.

50–75 μm will be converted to 55%. In this calculation it is assumed that the reaction rate is linearly dependent on the surface area of the particles. It follows then that the conversion of the smallest particles reaches the mentioned value of 55% at about 38% over-all conversion. This is in excellent agreement with the value of 35 to 40% found experimentally (Fig. 2).

From the discussion given above it may be concluded that a decrease of the copper content of the contact mass, with all other mentioned variables unchanged, may provide an opportunity to convert a larger part of the silicon before the rapid slow down of the reactivity starts. The activity of a contact mass with 5 wt % copper, which corresponds to the given model, will not tend to decrease unless 60% of the silicon is converted.

VI. Conclusions

By using standard methods and dry, freshly prepared copper(I) chloride it is possible to obtain a contact mass with reproducible properties. In a fluid bed the selectivity and the activity of such a contact mass vary in a characteristic manner with the silicon conversion. During an important part of the process the activity and the selectivity are on a high level. The optimum reaction temperature is 325° to 340°C. A conversion of 70% of the silicon may be reached. This figure probably may be raised by applying lower copper percentages. The dimethyldichlorosilane content of the products averages 85 wt % and reaches a maximum of 88 to 90%. The selectivity of the process is hardly dependent on temperature between 300 and 350°C. The temperature dependence of the initial reaction rate may be described with the aid of an Arrhenius equation, the activation energy being 26.6 kcal/mole. The variation of the activity of the contact mass and the selectivity of the methyl chloride conversion in the course of the synthesis can readily be explained by a simple model of the structure of the contact mass and its transformation during the conversion of the silicon.*

References

1. Rochow, E. G., *J. Am. Chem. Soc.* **67**, 963 (1945).
2. Voorhoeve, R. J. H., and Vlugter, J. C., *Rec. Trav. Chim.* **82**, 605 (1963).
3. Vlugter, J. C., and Voorhoeve, R. J. H., Conf. Accad. Naznl. Lincei: Alta Tecn. Chim. (1961), 81 (Published in 1962).
4. Voorhoeve, R. J. H., and Vlugter, J. C., *Chem. Weekbl.* **59**, 617 (1963).
5. Bayer Farbenfabriken, British Patent 673, 436 (1952); *Chem. Abstr.* **47**, 4898 (1952).
6. de Wit, N. P. M., Thesis, Univ. of Delft, Delft, The Netherlands, 1959.
7. Boon, E. F., Brandt, F. C. J., Kramers, H., Waterman, H. I., and de Wit, N. P. M. *De Ingenieur* **45** (1958), Chap. 89.
8. Andrianov, K. A., Golubtsov, S. A., Trofimova, I. V., and Lobusevich, N. P., *Zh. Priklad. Khim.* **32**, 2332 (1959); *Chem. Abstr.* **54**, 8608 (1960).
9. Voorhoeve, R. J. H., Thesis, Univ. of Delft, Delft, The Netherlands, 1964.
10. Kolster, B. H., Vlugter, J. C., and Voorhoeve, R. J. H., *Rec. Trav. Chim.* **83**, in press (1964).
11. Joklík, J., and Bažant, V., *Coll. Czech. Chem. Comm.* **26**, 417 (1961).
12. Joklík, J., Kraus, M., and Bažant, V., *Coll. Czech. Chem. Comm.* **26**, 427 (1961).
13. Voorhoeve, R. J. H., Geertsema, B. J. H., and Vlugter, J. C., to be published.
14. Krylov, V. D., Turetskaya, R. A., and Lelchuk, S. L., *Zh. Fiz. Khim.* **37**, 1377 (1963); *Chem. Abstr.* **59**, 5825 (1963).
15. Voorhoeve, R. J. H., and Vlugter, J. C., literature review, to be published.
16. Voorhoeve, R. J. H., and Vlugter, J. C., see the fourth paper in this series.

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* The mechanism of the reaction of methyl chloride with silicon-copper to yield dimethyldichlorosilane is described in refs. (*9, 15, 16*).