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Mechanism and Kinetics of the Metal-Catalyzed Synthesis of Methylchlorosilanes

III. The Catalytically Active Form of the Copper Catalyst

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The explanation of the mechanism of the copper-catalyzed reaction of methyl chloride and silicon is closely related to the state in which copper is catalytically active. The initial stages of the reactions of methyl chloride and various contact masses are studied. The results indicate that the copper catalyst has to be allied with the silicon in order to allow a selective and rapid formation of dimethyldichlorosilane. This idea is substantiated further by observing silicon-copper contact masses under the polarization microscope during the preparation from copper(I) chloride and silicon, during the reaction with methyl chloride, during a heat treatment producing conversion of free copper into η phase, and during a hydrogen sulfide treatment for selective removal of free copper from a mixture of free copper, silicon, and allied copper. These experiments provide full proof of the proposed assignment of the catalytic activity of copper to the allied state.

1. INTRODUCTION

Prompted by theoretical and practical interest, considerable attention has been paid in the literature to the question of the mechanism of the catalytic action of copper in the synthesis of methylchlorosilanes from silicon and methyl chloride. This problem is related to the question of the catalytically active form of the copper catalyst. An essential difference between the mechanisms, proposed by Rochow and Hurd (*1*) on one side and by Trambouze, Imelik (*2*, *3*), Klebansky, Fikhtengolts (*4*, *5*), Bažant, Joklík, and Kraus (*6–8*) on the other side, is the state in which copper must be present to be effective as a selective catalyst. Rochow and Hurd consider the presence of the metal in the elementary state, not allied, but in the immediate vicinity of elementary silicon, to be sufficient. The other mechanisms so far proposed have an essential adsorption of methyl chloride on the silicon-copper surface of an alloy in common. The assumed orientation of the adsorption is different in the various mechanisms, but in each case the presence of a mixture of silicon and copper on an atomic scale is considered to be indispensable. The mechanism, proposed by Andrianov, Krylov, Vabel, Efremov, Klenina, and Lelchuk (*9–11*), constitutes an intermediate form in which the presence of free copper as well as η phase is assumed to be necessary. In the present paper the mechanism will not be subject to elaborate discussions, as this part of the work will appear in the next article of the present series (*12*).

In the literature some attention has already been devoted to the question of the state in which copper is present in the synthesis of organohalosilanes from silicon and organohalides. It has to be stressed that in drawing conclusions from the experiments, attention should be given to the selectivity of the reactions, as at present we are interested in the formation of diorganodihalosilanes. In case data concerning the selectivity are not communicated, some conclusions concerning the selectivity may follow from the reaction temperature. For instance, the reaction of methyl chloride and silicon-copper yields dimethyldichlorosilane selectively at 260–340°C in systems with high heat transfer coefficients (*13*). The corresponding temperature in the synthesis of ethylchlorosilanes is 200–300°C. Beyond these temperatures the cracking of the alkyl halide plays an important role in the over-all reaction (*14*, *15*).

Some important literature results will be reviewed here. Trambouze *et al.* (*2*, *3*) and Klebansky *et al.* (*4*, *5*) demonstrated that the reactivity of contact masses, prepared from silicon and copper, could be correlated qualitatively with the amount of an intermetallic compound which was detected by X-ray analysis. Trambouze (*3*) first identified this compound as the η phase ($\sim Cu_3Si$) of the copper-silicon system. Active contact masses contained much η phase and only small amounts of free copper, whereas inactive or exhausted masses contained much free copper and hardly any η phase.

Contrary to this, Krylov *et al.* (*10*, *11*) and Andrianov *et al.* (*9*), employing silicon-copper alloys composed of η phase and silicon, found that after an induction period the reaction velocity increased in the initial stages of the reaction with concurrent decomposition of the η phase and formation of finely dispersed free copper. The above-mentioned authors concluded that free copper acts as a catalyst, but that the η phase must be present to provide active, finely divided free copper. However, alternatively it might be concluded that the increase of the activity resulted from the etching of the η-phase surface which, in view of the observed induction period, was probably inactivated by oxidation. As a matter of fact fresh η-phase surfaces do not show an induction period in the reaction with alkyl halides, as we have frequently experienced in the course of investigations published earlier (*14*–*16*).

In the present paper, from an inspection of the experimental evidence from the literature and of our own, it is concluded that copper is present in an alloyed state (which generally is the η phase) whenever it is active as a selective catalyst in the reaction of methyl chloride and silicon.

The experiments to be discussed concern the initial stages of the reaction of methyl chloride and various silicon-copper contact masses, the effects on the reaction of heating the masses in an inert atmosphere, the effects of a hydrogen sulfide treatment, and the results of microscopic investigation of polished pieces of silicon treated with copper(I) chloride vapor.

2. THE INITIAL STAGES OF THE REACTION OF METHYL CHLORIDE AND SILICON-COPPER MASSES

The results obtained in the initial phases of the reaction of methyl chloride and a silicon-copper mass are strongly dependent on the state of the copper catalyst at the start of the process. If the catalyst is added to the silicon powder in the form of a copper powder, as is usual in industry, an induction period of variable duration is frequently observed. In the course of the induction period the organochloride is cracked on free copper, copper(I) chloride being formed [Eq. (1), Rochow and Hurd (*1*)].

$$Cu + RCl \rightarrow CuCl + R\cdot \qquad (1)$$

The organic radical decomposes into carbonaceous products and hydrogen. Consequently copper(I) chloride reacts with silicon [Eq. (2)], producing an active copper-silicon complex which easily gives rise to the formation of the η phase.

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

In this period the reaction products are very rich in chlorine. The formation of the η phase allows the subsequent selective production of diorganodichlorosilanes.

This sequence of reactions explains the induction period and the initially low and afterwards increasing selectivity of the process. In the reaction of ethyl chloride and silicon-copper the appearance of this sequence has been demonstrated by X-ray analysis [Krylov *et al.* (*17*)].

Another type of contact mass is obtained by reaction of copper(I) chloride and silicon, producing a mass consisting of silicon particles, irregularly covered by copper. Most of the copper is present as η phase [Voorhoeve, Lips, and Vlugter (*15*)], but the surface is relatively copper-rich. This is reflected in the first stage of the reaction

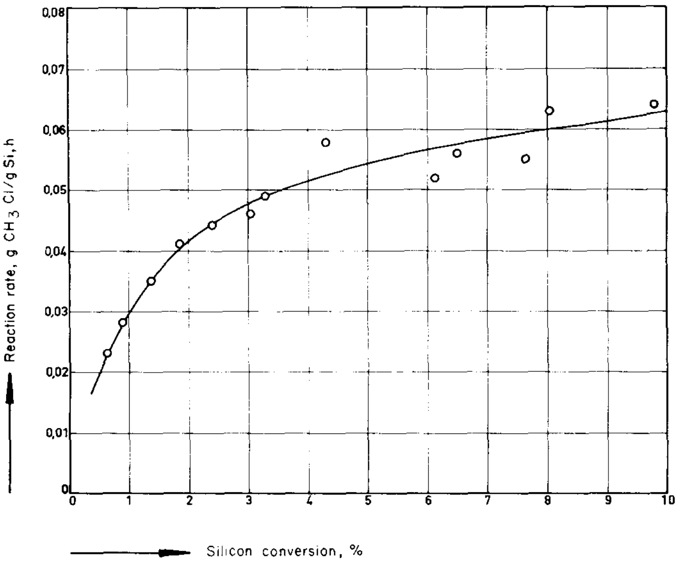

Fig. 1. The rate of reaction of a silicon-rich alloy and methyl chloride. (Expt. Mi-2).

by the appearance of a rather modest selectivity, which is gradually increased to 85–90% (wt % dimethyldichlorosilane in the products) during the conversion of the first 10% of the silicon. By X-ray analysis it could be shown that most of the copper is present as η phase. Microscopic investigation of the contact masses showed that in the initial stage of the reaction the amount of copper in the surface layer of the particles diminished in favor of the amount of η phase. Extensive measurements of this system have been published elsewhere (*14*, *15*, *18*).

Contrary to the experience with silicon-copper masses comprising free copper, contact masses consisting of alloy particles, which contained η phase and silicon exclusively, did not show a variable selectivity in the beginning of the synthesis reaction. Instead the reaction started at a high selectivity level, which remained constant at 90 wt % dimethyldichlorosilane in the products. The course of the reactivity of the alloys in relation to the silicon conversion showed a rise, which was initially rather steep, probably originating from the etching of the surface. Figures 1 and 2 show an example of an experiment carried out at

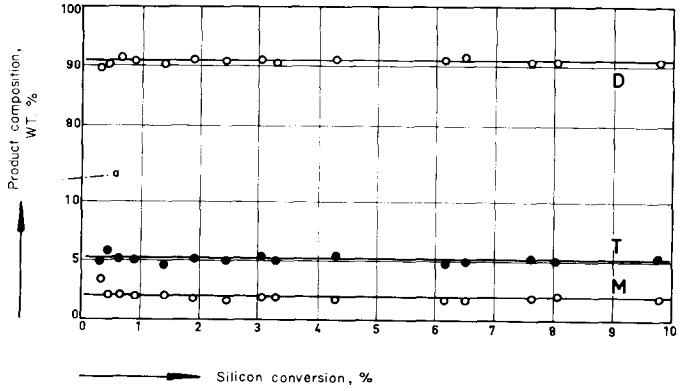

Fig. 2. The reaction of a silicon-rich alloy and methyl chloride. The composition of the products (Expt. Mi-2). a: alteration of the scale.

338°C with an alloy containing 8.3% copper as η phase and in an experimental apparatus described elsewhere (*14*, *16*).

To demonstrate clearly the difference between the behavior of contact masses which contain free, nonallied, copper and those which do not, the selectivity curve of an experiment carried out with an alloy composed of η phase and silicon as a solid reagent and the curve obtained with a contact mass prepared by reaction of silicon and copper(I) chloride are combined in Fig. 3. The striking difference indicates that the contact mass which contained only η phase and silicon yielded at the beginning of the reaction a much more selective course of the process. Herefrom, it may be concluded that pure η phase yields selectively dimethyldichlorosilane, whereas contact masses containing free copper give rise to the formation of cracked products.

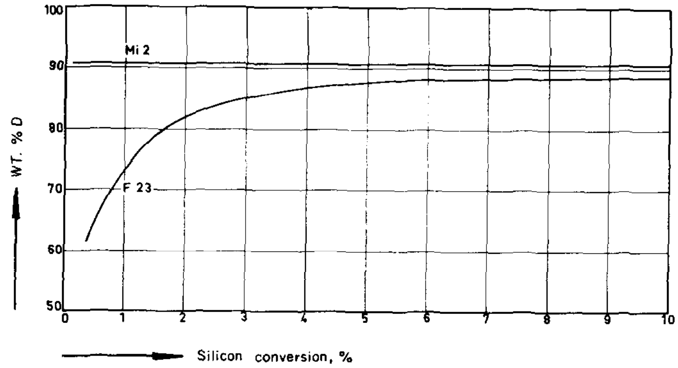

FIG. 3. The amount of dimethyldichlorosilane in the products from contact masses with and without free copper: Mi-2, 338°, contact mass prepared from the melt (no free copper present); F 23, 338° contact mass prepared from copper(I) chloride and silicon (free copper present).

To support further the view that allied copper must be present to guarantee the selectivity of the reaction, attention is directed to experiments in which pure ϵ phase ($\sim Cu_{15}Si_4$), pure η phase ($\sim Cu_3Si$), or an eutectic alloy (30 at. % Si) mainly consisting of η phase were contacted with methyl chloride. From the very beginning the reactions yielded products with about 85 wt % dimethyldichlorosilane, indicating that the alloyed state of copper is the *catalytically active part of the masses* (*16*).

3. Microscopic and Chemical Study of Silicon-Copper Contact Masses*

Direct evidence concerning the state of the copper catalyst in contact masses obtained by reacting silicon particles and copper(I) chloride is gathered by viewing polished samples under the polarization microscope. The polarized-light technique is particularly suitable in this work, because the η phase is the only optically anisotropic phase commonly encountered in the contact masses.

The work described in this section is aimed at obtaining a picture of the phenomena appearing in the preparation of the contact mass, the reaction with methyl chloride, the heating of the masses in inert atmosphere, and the treatment with methyl chloride–hydrogen sulfide mixtures.

The details of the apparatus and the experimentation may be found elsewhere (*14*, *16*). Polished pieces of silicon (99.0%) were used to secure a good picture. The impurities were mainly aluminum (0.1%), calcium (0.1%), and oxygen.

a. The interaction of silicon and copper(I) chloride. In the first series of experiments the results produced by the interaction of a polished silicon surface and solid copper(I) chloride at 350°C were examined. The

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copper(I) chloride reacted preferably at disturbances of the silicon surface, such as polishing grooves. The reaction with the polished silicon was of course much slower than with the unpolished particles usually present in the preparation of the contact mass. After 2.5 hr of contact the polished surface was covered by a number of red fields, the surface layer mainly consisting of free copper. By polishing carefully, it came out that inner layers of the copper had combined with the silicon, producing η phase just under the surface of the copper fields. The following experiments were carried out by contacting the silicon with gaseous copper(I) chloride, which allowed a more even attack of the surface. In Fig. 4 a sample is shown which was obtained by this method in a contact time of 5 hr, the temperature of the silicon being 530–540°C, while the vapor temperature was 490°C. A fine-grained copper field is easily recognized. In Fig. 5 a similar area is shown, obtained in 15 hr and after careful removal of the surface layer. The η-phase crystallites, which show different crystallographic orientations, are distinctly visible. The experiments discussed show that copper is initially formed in the preparation of the contact mass [Eq. (2)]. Subsequently η phase is produced at the interface of copper and silicon [formal Eq. (3)]. These phenomena are illustrated by Fig. 6(a-e).

$$3\,Cu + Si \rightarrow Cu_3Si\ (\eta) \qquad (3)$$

b. The reaction of methyl chloride and a silicon-copper η-phase surface. A sample with a surface consisting of silicon, free copper, and η phase was treated with methyl chloride for 5 hr at 350°C. After this period copper(I) chloride crystals had been formed on the surface by the cracking of methyl chloride. A good deal of the η phase was still present, uncovered by copper(I) chloride.

FIG. 4. Copper deposited on a silicon surface in the reaction with copper(I) chloride vapor. The surface consists mainly of free copper, although some η phase is also present (white spots). Magnification ×300. Polarized light.

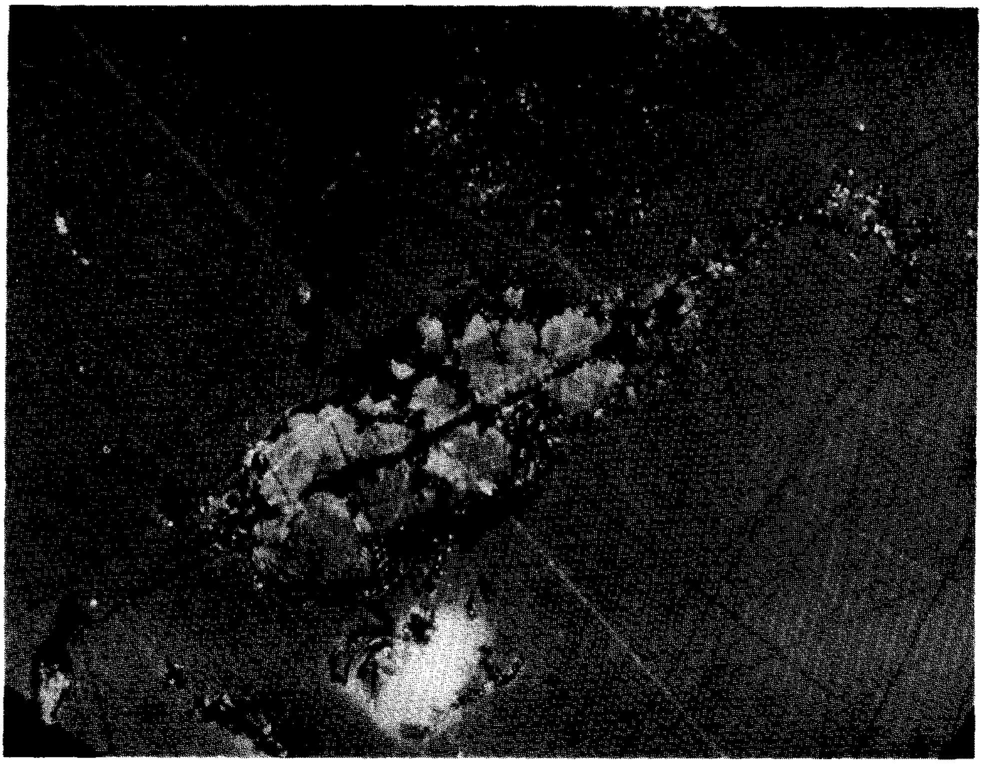

FIG. 5. Surface obtained after polishing a deposit of copper on a silicon surface in the reaction with copper(I) chloride vapor. The different orientations of the η-phase crystallites are perceptible. Magnification, ×400. Polarized light.

On the contrary, much of the free copper was covered by a thick layer of copper(I) chloride. Hence, it seems probable that methyl chloride is mainly cracked on free copper, in accordance with experiences obtained earlier. The reaction is supposed to be:

$$CH_3Cl + Cu \rightarrow CuCl + CH_3\cdot \qquad (4)$$

c. Heating the contact mass in an argon atmosphere. The concept that copper is present in the contact masses in two phases, in an allied, catalytically active form and in a free, catalytically inactive state, has led us to the idea that it should be possible to convert the silicon more effectively into dimethyldichlorosilane by converting free copper into η phase at the start of the process.

Relative experiments were carried out with contact masses prepared from silicon and copper(I) chloride [Eqs. (2) and (3)] in a fluid-bed reactor device described elsewhere (*14*, *15*). Results obtained with such a contact mass were published earlier in this series (*15*). X-ray analysis revealed that the copper is mainly present as η phase, but the results mentioned in Section 3,a indicate that the surface is relatively rich in free copper. Conversion of free copper into η phase was effected by heating the mass at 400°C in an argon atmosphere. A heat treatment of 4 hr resulted in a diminution of the amount of free copper to a value too small to be measured by X-ray analysis. Contacting the silicon-copper mass obtained with methyl chloride (Expt. no. F28, 338°C) showed that the attainable silicon conversion had increased from about 70% to at least 80%. Similar results were obtained by heating the contact mass for 16 hr at 400°C and subsequently reacting with methyl chloride at 333°C (Expt. F25). The results are presented in Fig. 7, which shows the reaction rate, expressed as grams of methyl chloride converted into silanes per gram of silicon

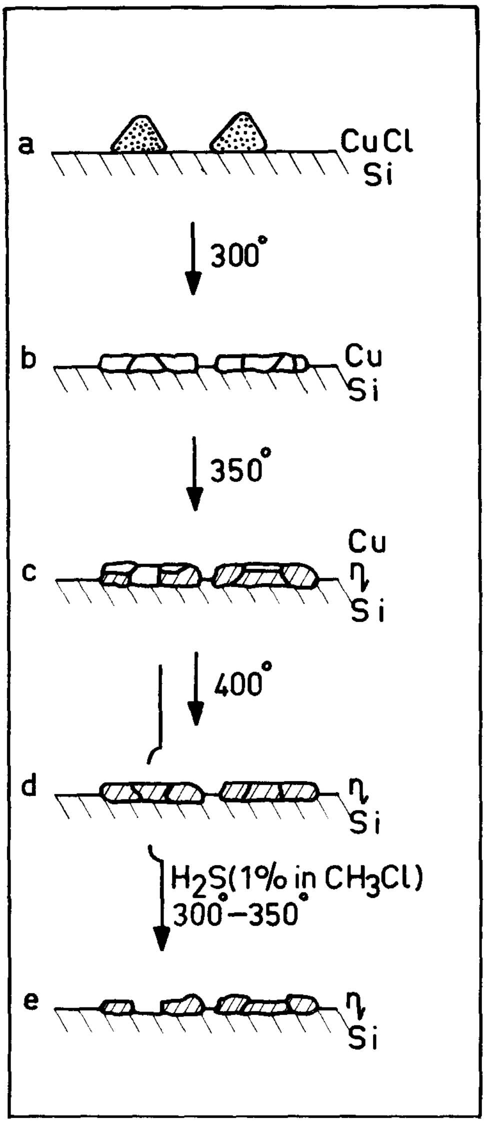

FIG. 6. A model to represent the formation of the surface of a contact mass. (a) A mixture of copper(I) chloride and silicon. (b) Polycrystalline copper has been deposited on the surface. (c) The larger part of the copper is rapidly converted into η phase, but a relatively copper-rich surface remains. (d) All copper has been converted into η phase by a heat treatment in an inert atmosphere. (e) By selectively sulfiding the copper and subsequent erosion of the copper(I) sulfide the η-phase surface has been cleaned.

present in the contact mass and per hour, in relation to the silicon conversion (for comparison, curves have been included for some experiments carried out with contact masses which were not heated prior to the reaction). Except for the initial 5% of the silicon conversion, the selectivity of the conversion of methyl chloride into dimethylchlorosilane was at least 85%. Over-all results of the experiments are presented in Table 1. The effects brought about by heating the contact masses in an argon atmosphere prior to the reaction with methyl chloride were also investigated by polarization microscopy. Polished samples of silicon, which had been covered by a layer of copper and η phase, exhibiting a surface relatively rich in free copper, were heated at 350°C for 1–15 hr. Already after 1 hr part of the free copper in the surface layer was converted into η phase. After 15 hr almost the entire surface consists of η phase. Copper was left at the boundaries of silicon and η phase only. The resulting structure is shown in Fig. 8. The phenomena are depicted schematically in Fig. 6(c-d). The results indicate that conversion of free copper into η phase improves the contact mass and increases the possible silicon conversion in the process of dimethyldichlorosilane formation.

d. Hydrogen sulfide treatment of a surface composed of silicon, copper, and η phase. Direct proof of the concept that only η phase and not free copper is catalytically active in the synthesis of methylchlorosilanes may be obtained by removing or inactivating free copper selectively. This may be done with hydrogen sulfide. Treatment of a contact mass, prepared from copper(I) chloride and silicon, with a mixture of 1 vol % hydrogen sulfide in methyl chloride during 1 hr at 335°C has been shown to produce a rapid increase in the reaction rate, without affecting the selectivity of the reaction (*14*, *18*). These events may be explained by the conversion of free copper, which partly covered the η-phase surface, into flocky, easily removable copper(I) sulfide, thus exposing the η-phase surface. Continuous dosage of hydrogen sulfide keeps the surface continually free from nonallied copper and thus serves to preserve the reactivity of the alloy in the course of the silicon conversion (*14*, *18*).

To check this interpretation of the experimental facts a polished piece of silicon, covered by a layer consisting of η phase and

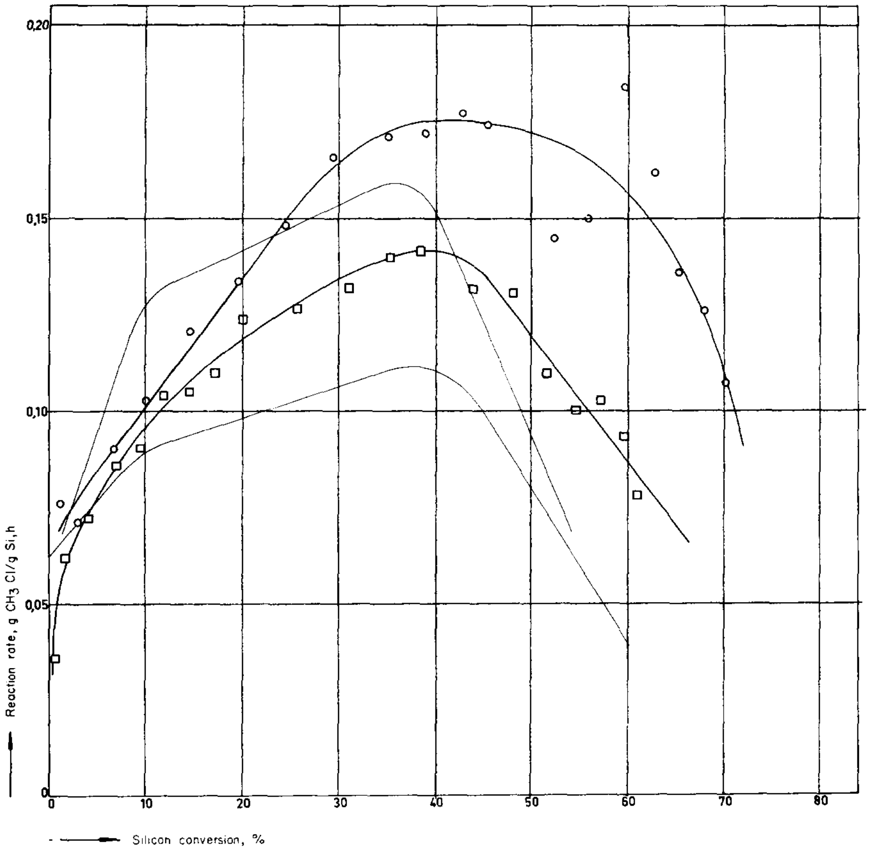

FIG. 7. The relation of the reaction rate and the silicon conversion for contact masses prepared from copper(I) chloride and silicon: □, F25, contact mass heated in argon at 400°C for 16 hr; ○, F28, contact mass heated in argon at 400°C for 4 hr. For comparison, the curves of two experiments with contact masses not treated in argon have been added (F21 and F23).

TABLE 1
Over-all Results of Experiments with Contact Masses Heated in Argon at 400°C and with Untreated Contact Masses[a]

Expt. No.	Temp (°C)	Heating period (hr)	Duration of the process (hr)	Total amount of products (g)	Composition of the products[b] (wt %)						Silicon conversion (%)	Average methyl chloride conversion (%)	Reaction rate at the end of the process (g CH_3Cl/g Si hr)
					D	T	M	DH	Q	TH			
F25	333	16	30.5	785	85.0	7.9	3.4	2.5	1.1	0.3	61	17	0.08
F28	338	4	28.5	872	84.4	8.1	3.4	2.5	1.4	0.2	71	21	0.11
F21	327	—	37.0	756	84.5	8.3	3.2	2.5	1.4	0.3	59	14	0.05
F23	338	—	22.5	680	84.6	7.4	3.1	3.7	1.1	0.2	54	20	0.07

[a] In all experiments 330 g contact mass were used, containing 10 wt % copper. Methyl chloride feed 117 g/hr. For experimental details see refs. (*14*, *15*).

[b] D, dimethyldichlorosilane; T, methyl trichlorosilane; M, trimethylchlorosilane; DH, methyl dichlorosilane; TH, trichlorosilane; Q, tetrachlorosilane.

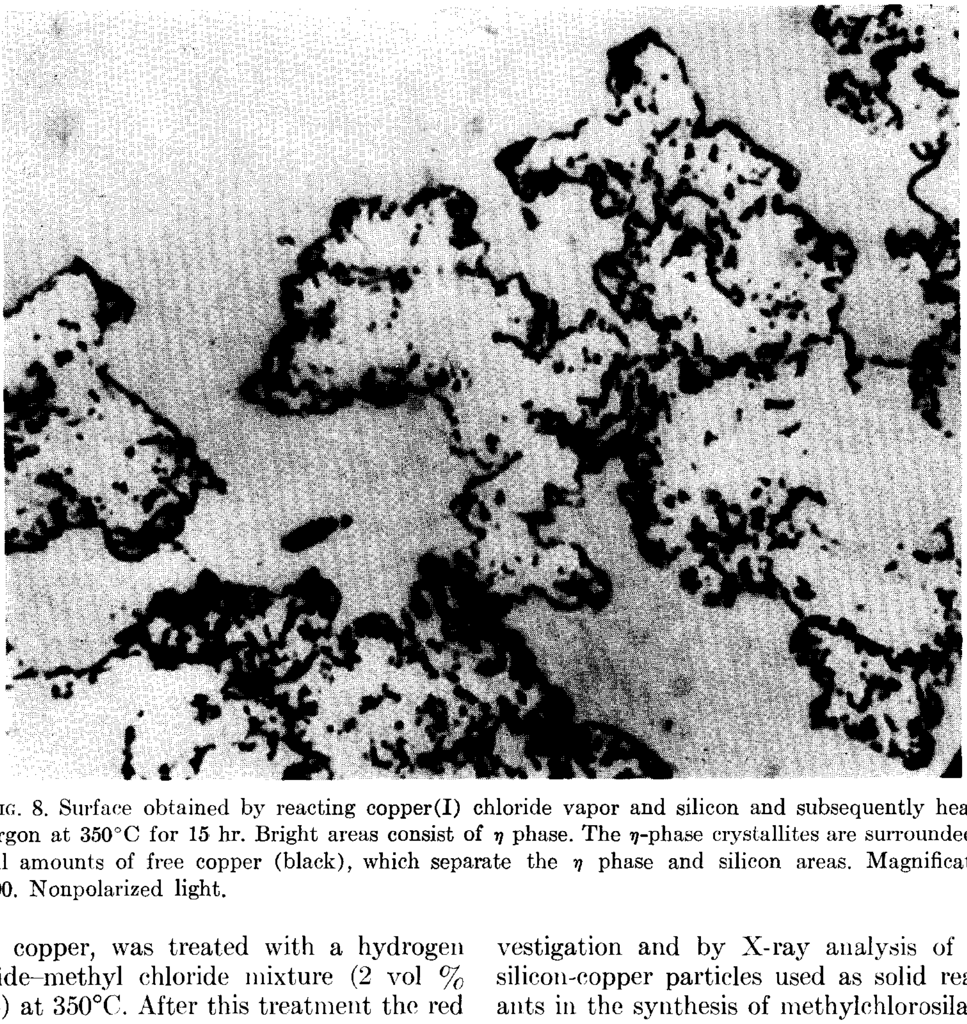

FIG. 8. Surface obtained by reacting copper(I) chloride vapor and silicon and subsequently heating in argon at 350°C for 15 hr. Bright areas consist of η phase. The η-phase crystallites are surrounded by small amounts of free copper (black), which separate the η phase and silicon areas. Magnification, ×800. Nonpolarized light.

free copper, was treated with a hydrogen sulfide–methyl chloride mixture (2 vol % H_2S) at 350°C. After this treatment the red copper was converted into black copper(I) sulfide. The η phase appeared to be unaffected. Removal of the black sulfide by means of a soft cloth, which could easily be done, produced an augmentation of the η-phase area. The latter experiences confirm the explanation of the effects of the hydrogen sulfide treatment which was given above. The phenomena are illustrated schematically by Fig. 6(c) and (e).

It may be concluded that the experiments discussed here are consistent with the view that allied copper is catalytically active in the reaction of silicon and methyl chloride and that free copper is not.

4. SURVEY AND CONCLUSIONS

For comparison and survey the results obtained by chemical and microscopic investigation and by X-ray analysis of the silicon-copper particles used as solid reactants in the synthesis of methylchlorosilanes are summarized in Table 2. From this table and from the discussions in the preceding sections of this paper the following may be concluded:

(1) Silicon and copper, allied as an intermetallic compound, yield a very selective and rapid production of dimethyldichlorosilane from the very beginning of the reaction with methyl chloride.

(2) Intermetallic compounds with up to 80 wt % copper yield initially a very selective production of dimethyldichlorosilane.

(3) When mixtures of copper powder and silicon powder are employed in the synthesis of methylchlorosilanes, the elements are converted into η phase ($\sim Cu_3Si$) through the cracking of methyl chloride in the initial stages of the process.

TABLE 2

THE CATALYTICALLY ACTIVE STATE OF COPPER—SURVEY OF THE EXPERIMENTAL RESULTS

Reaction or treatment	Results obtained by the indicated methods of investigation		
	Chemical analysis	X-ray analysis	Microscopic analysis
(1) Reaction of CuCl + Si	Liberation of heat Evolution of $SiCl_4$	Formation of η phase and some free copper	Formation of η phase with a copper-rich surface Figs. 4 and 5.
(2a) Heating the contact mass for a short period (4 hr at 400°C or 5–10 hr at 350°C	The reaction of this contact mass starts normally; the selectivity and the reactivity remain at a high level for a longer period than without treatment Fig. 7	Hardly any copper traceable; only free silicon and η phase left	Copper is mainly converted into η phase. However, the surface is still relatively rich in copper
(2b) Heating the mass for a longer period (16 hr at 400°C, 15 hr at 350°C)	The reaction with methyl chloride starts with a small rate The formation of side products is constant from the start The attainable silicon conversion is high Fig. 7	No copper detectable	Free copper present at the boundaries of the η-phase grains only Fig. 8
(3a) Reaction with methyl chloride. Contact mass prepared from the melt (η phase + Si)	From the start a constant selectivity is found. Rapid decrease of the selectivity when free Si has been used up Fig. 2	No copper detectable at the start of the reaction. After the reaction, η phase and free copper could be shown	No copper detectable at the start of the reaction
(3b) Reaction with methyl chloride. Contact mass prepared from CuCl + Si	Selectivity and reactivity increase until about 10% silicon conversion Fig. 3	Constant, very small amount of free copper in the contact mass	Decrease of the amount of free copper at the surface Even attack of the surface Cracking of methyl chloride on free copper with formation of CuCl
(4) Sulfiding the contact mass (1–2% H_2S in CH_3Cl for 1 hr)	Activity rises rapidly Selectivity does not alter The attainable silicon conversion is much larger		Selective attack of free copper and conversion into sulfide; η-phase area is increased by removal of the copper layer

(4) Contact masses, prepared from copper(I) chloride and silicon, contain copper mainly as η phase. However, the surface is relatively rich in free copper.

(5) The presence or the formation of free copper in the contact mass diminishes the selectivity and the rate of the reaction of silicon and methyl chloride.

(6) Selective removal of free copper from the contact masses enhances the rate of the reaction by uncovering the surface of the η phase.

(7) Copper catalyzes the selective reaction of silicon and methyl chloride to form dimethyldichlorosilane only if it is present as an intermetallic copper-silicon phase.

REFERENCES

1. Rochow, E. G., and Hurd, D. T., *J. Am. Chem. Soc.* **67**, 1057 (1945).
2. Imelik, B., and Trambouze, P., *Compt. Rend.* **238**, 680 (1954).
3. Trambouze, P., *Bull. Soc. Chim. France*, p. 1756 (1956).
4. Fikhtengolts, V. S., and Klebansky, A. L., *J. Gen. Chem. USSR (Engl. Transl.)* **27**, 2535 (1957).
5. Klebansky, A. L., and Fikhtengolts, V. S., *J. Gen. Chem. USSR (Engl. Transl.)* **26**, 2795 (1956).
6. Bažant, V., *Rozpravy Česk. Akad. Věd., Řada mat.* **71**, S11 (1961).
7. Joklík, J., and Bažant, V., *Coll. Czech. Chem. Comm.* **26**, 417 (1961).
8. Joklík, J., Kraus, M., and Bažant, V., *Coll. Czech. Chem. Comm.* **27**, 974 (1962).
9. Andrianov, K. A., Golubtsov, S. A., Trofimova, I. V., Turetskaya, R. A., and Krylov, V., *Izv. Akad. Nauk. SSSR, Otd. Khim Nauk*, p. 157 (1958); *Chem. Abstr.* **52**, 12752 (1958).
10. Krylov, V. D., and Efremov, Y. N., *Zh. Fiz. Khim.* **31**, 2522 (1957); *Chem. Abstr.* **52**, 8705 (1958).
11. Krylov, V. D., Vabel, Y. I., Jegremov, Y., Klenina, A. M., and Lelchuk, S. L., *Zh. Fiz. Khim.* **33**, 1594 (1959); *Chem. Abstr.* **54**, 8257 (1960).
12. Voorhoeve, R. J. H., and Vlugter, J. C., no. IV of the present series. *J. Catalysis*, in press.
13. Voorhoeve, R. J. H., Geertsema, B. J. H., and Vlugter, J. C., *J. Catalysis* **4**, 43 (1965).
14. Voorhoeve, R. J. H., Thesis, Delft, The Netherlands, 1964.
15. Voorhoeve, R. J. H., Lips, J. A., and Vlugter, J. C., *J. Catalysis* **3**, 414 (1964).
16. Kolster, B. H., Vlugter, J. C., and Voorhoeve, R. J. H., *Rec. Trav. Chim.* **83**, 737 (1964).
17. Krylov, V. D., Turetskaya, R. A., and Lelchuk, S. L., *Zh. Fiz. Khim.* **37**, 1377 (1963); *Chem. Abstr.* **59**, 5825 (1963).
18. Voorhoeve, R. J. H., and Vlugter, J. C., *Chem. Weekbl.* **59**, 617 (1963).