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THE INFLUENCE OF OXYGEN ON THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES

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Summary

The influence of oxygen on the direct synthesis of methylchlorosilanes in a fluidised bed with copper as a catalyst has been studied. At 320°C and a pressure of 1 atmosphere the oxygen content in the feed gas was varied from 1 to 5000 ppm. It was found that the oxygen sharply reduces the rate of reaction but hardly influences the product composition. The maximum degree of conversion of the silicon is about 70% if no oxygen is present; at an oxygen concentration of 2000 ppm the conversion decreases to 50 percent.

Introduction

The direct (or Rochow) synthesis [1,2] is an important process for the production of methylchlorosilanes, the precursors of methylsilicones. The synthesis is carried out commercially in a fluidised bed with silicon (purity $> 98\%$), copper functioning as a catalyst. By adding promoters like zinc or antimony to the contact mixture the degree of selectivity to give the most desired product, dimethyldichlorosilane, reaches a value of about 90 mole percent. But for an economic production of silanes it is also necessary that the greatest possible percentage of the silicon introduced in the reactor be converted into silanes.

Because of the deactivation of the silicon—copper contact mixture this is only possible to a limited extent without formation of worthless by-products. On an industrial scale it is possible to convert 80-90 percent of the silicon into silanes [3]. In laboratory scale experiments on the direct synthesis usually no fresh contact mixture is supplied, and a decreasing reactivity and selectivity are observed when 40-70 percent of the silicon has been converted [4,5a].

Various factors affect the degree of usage of the silicon. During the synthesis a gradual deactivation of the contact mixture surface occurs. This deactivation may be caused by a number of factors. For example, the deposition of carbon and carbonaceous products may block part of the surface [4,6]. Furthermore the activity can be decreased by a decreasing content of promoters on the contact mixture surface, e.g. as caused by the evaporation of $ZnCl_2$ [7a], by the accumulation in the reactor of elements present as contaminants in the silicon (for example iron), by the increase of free copper on the surface, causing enhanced cracking, or by the blocking of the reactive sites by reaction of the contact mixture with traces of oxygen, yielding silicon and copper oxides.

The poisoning of the contact mixture by oxygen was the subject of this investigation. It is known that even minor quantities of oxygen are detrimental to the synthesis of silanes [5b] but quantitative data are hardly known. Van Dalen investigated the direct synthesis both with methyl chloride freed from oxygen and with unpurified methyl chloride, containing at least 30 ppm oxygen [7b]. No differences could be observed but a pulse of oxygen caused a temporary decrease in reactivity. Lobusevich et al. [8] stated that if 7400 ppm oxygen was added to the methyl chloride the reactivity decreased by 30 percent as compared to the reactivity when no oxygen is present; at the same time the selectivity to dimethyldichlorosilane decreased from 53 to 46 percent.

Experimental

Type of experiments performed

In order to obtain information on the influence of oxygen a number of experiments were conducted (Z1-Z10, see Table 1); in these the oxygen con-

TABLE 1

THE INFLUENCE OF OXYGEN ON THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES

Experiment	MeCl flow (ml/min at STP)	Average temperature (°C)	Duration (min)	Time of O_2 feed (min)	O_2 feed (ppm)
Z1	600	340	780	0 - 780	1
Z2	570	316	870	0 - 870	1
Z3	600	314	840	0 - 240	2
				240 - 545	200
				545 - 840	1
Z4	550	318	780	0 - 250	1
				250 - 780	500
Z5	550	316	840	0 - 235	1
				235 - 840	2630
Z6	550	316	720	0 - 720	1
Z7	550	316	840	0 - 305	1
				305 - 840	4750
Z8	550	316	840	0 - 605	450
				605 - 840	1
Z9	380	325	900	0 - 235	1
				235 - 900	1000
Z10	550	316	840	0 - 310	1
				310 - 580	3400
				580 - 840	1
Z11	380	335	4740	0 - 3500	2000
				3500 - 4740	5
Z12	380	318	4500	0 - 4500	350

centration in the feed gas was varied from 1 to 5000 ppm. Additional experiments (Z11, Z12) were performed to investigate the influence of the oxygen concentration on the maximum degree of conversion of the silicon.

Apparatus

The experiments were carried out in the apparatus shown in Fig. 1. Methyl chloride and nitrogen were supplied via flow meters and freed from oxygen and water by passage through a column containing active copper (BTS-catalyst, type R 3-11, from BASF) and a column containing a 4A molecular sieve, respectively. The oxygen concentration in the purified feed gas always amounted to 0.5-5 ppm. The silanes and unconverted methyl chloride were partially separated by continuous distillation through a Vigreux column. The silanes and some of the methyl chloride were drained from the reboiler; the reflux was maintained by a Dewar vessel containing 15 kg of a CO_2/acetone mixture, which was sufficient to run the experiments for 18 h. The greater part of the unconverted methyl chloride was liquified in a second Dewar vessel (condenser) and stored in a container with vacuum wall. Uncondensable gases were discharged via an eight-way valve and led off through a column containing KOH pellets to a gas meter. Oxygen could be injected in the feed gas through a calibrated stainless steel capillary, situated after the BTS-catalyst and molecular sieve; the flow rate was calculated from the pressure drop across the capillary. The oxygen, injected

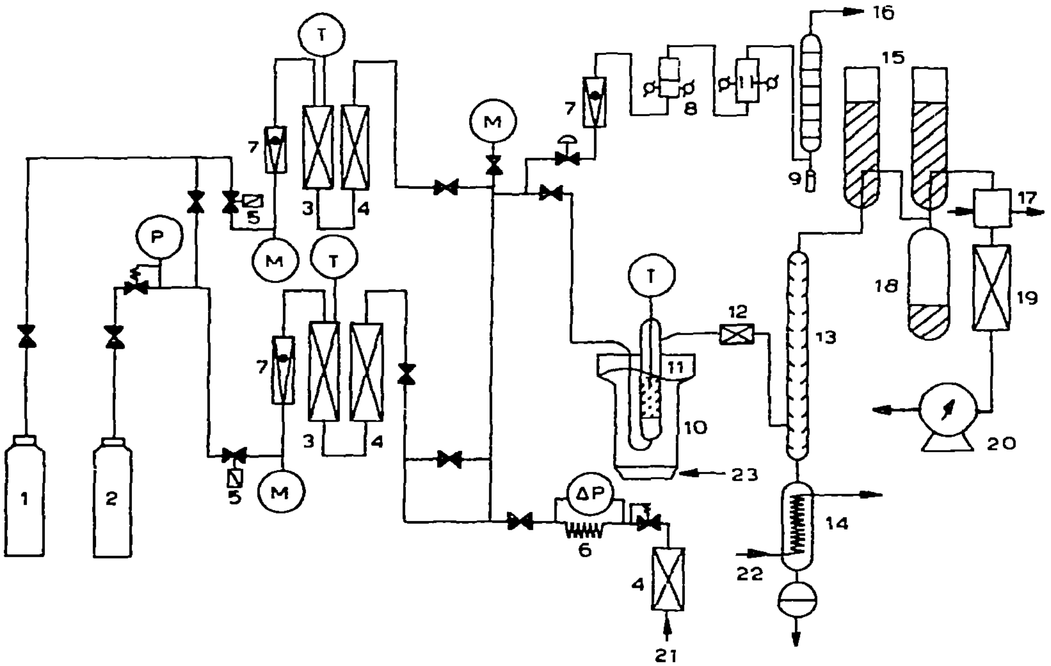

Fig. 1. Laboratory equipment for fluid bed synthesis. 1, Cylinder with nitrogen. 2, Cylinder with methyl chloride. 3, BTS catalyst for oxygen removal. 4, Linde molecular sieve 4A for water removal. 5, Magnetic valve. 6, Capillary for oxygen injection. 7, Flowmeter. 8, Hersch-cell. 9, Flow meter. 10, Fluid bed with silicon. 11, Reactor. 12, Dust trap containing glass wool. 13, Distillation column. 14, Discharge of silanes. 15, Dewar vessels with acetone/CO_2. 16, Vent. 17, Sample tube for gas analysis. 18, Dewar vessel for unreacted methyl chloride. 19, KOH pellets. 20, Gas meter. 21, Air for oxygen injection. 22, Heating water for reboiler. 23, Pressure air for fluid bed. *T* = temperature; *P* = pressure; M = manometer.

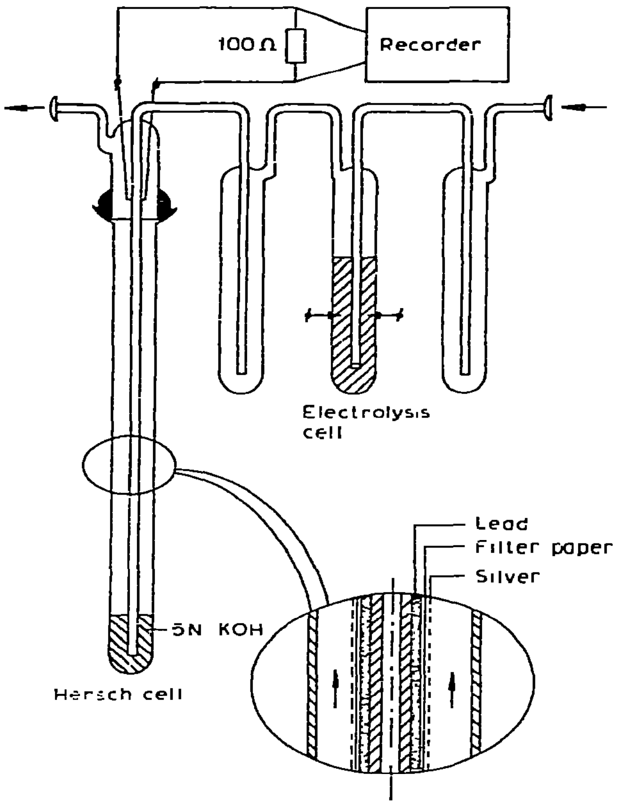

Fig. 2. Hersch-cell apparatus for measuring the oxygen concentration.

as air, was previously dried by a molecular sieve. Before the reactor part of the gas mixture (30 ml/min) was passed through a Hersch-cell (Fig. 2, [9]) to measure the oxygen concentration continuously. The cell was calibrated by electrolysis of water (assuming 100% efficiency), thus adding a known amount of oxygen to a known amount of methyl chloride. Above 400 ppm measuring of the oxygen concentration by the Hersch-cell became difficult, and in this case the amount of oxygen was calculated from the known feed rate of the gases. At 400 ppm the calculated oxygen concentration was equal to the concentration as measured in the Hersch-cell.

The reactor (i.d. 28 and length 600 mm, see Fig. 3) was made of glass and was situated in a fluidised bed containing silicon. The temperature in the synthesis reactor was kept constant to within 2°C by control with a platinum resistance thermometer and was measured by chromel—alumel thermocouples.

Analysis of Reaction Products

The product mixture consisting of silanes and unconverted methyl chloride was analysed by means of gas—liquid chromatography with katharometer detection; separation took place on a 4 m copper column filled with nitrobenzene, 30% on Chromosorb W, at a temperature of 30°C. Hydrogen, dried on a molecular sieve, was used as a carrier gas. The uncondensable gases were

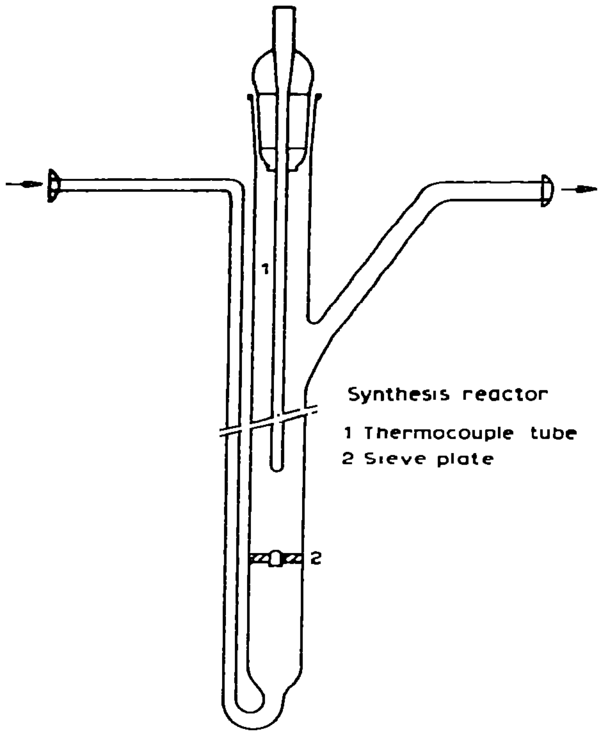

Fig. 3. Synthesis reactor for fluid bed experiments.

separated by gas—liquid chromatography with katharometer detection on a 2 m stainless steel column filled with Linde molecular sieve 5A; helium with 8.5% hydrogen was used as a carrier gas. In this way hydrogen, nitrogen, oxygen and methane were separated; the uncondensable gases in the experiments consisted almost exclusively of methane (with nitrogen and oxygen if air had been added to the feed gas).

Materials used

The silicon used in the experiments was technical silicon, the main impurities being 0.4% Fe, 0.1% Al and 0.3% Ca + Mg (by weight), and before use it was washed with water, dried, and treated with a magnet to remove part of the iron (resulting in an iron content of 0.2-0.3%). All experiments were conducted in a fluidised bed, and because of this an easily fluidized mixture of silicon particles was used [5c]. Copper was introduced as pure copper chloride, prepared by a standard method [5d] resulting in 10 wt % copper in the contact mixture. Pure zinc (0.1 wt %) and aluminium (0.05 wt %) were used as promoters. Methyl chloride, nitrogen and air were fed from cylinders.

Description of the experiments

Before each experiment the contact mixture was prepared in situ: silicon (91 g), CuCl, zinc and aluminium were stored in the reactor and dried at 100—150°C for at least 3 h. Then the temperature was raised, and reaction between silicon and copper chloride took place between 250 and 300°C; when the re-

TABLE 2

COMPOSITION (in wt %) OF CONTACT MIXTURE AND DUST AFTER THE EXPERIMENTS

Experiment	Silicon converted (g)		Cu	Zn	Al	Fe	C	H
Z1	31.1	c.m.[a]	12.0	0.07	0.2	0.4	0.4	0.05
		dust	41	1.6	2.0	3.0	0.4	1.0
Z2	19.6	c.m.	9.3	0.02	0.11	0.45	0.24	0.6
Z3	16.2	c.m.	9.4	0.15	0.22	0.4	0.1	0.2
		dust	33	1.6	2.3	1.2	0.25	1.2
Z4	15.9	c.m.	10.2	0.04	0.2	0.4	0.2	0.6
		dust	27	1.4	3 2	1.2	0.4	1.8
Z5	16.9	c.m.	10.0	0.04	0.2	0.4	0.4	0.1
		dust	24	1.2	2.5	1.6	6.4	2.2
Z6	21.1	c.m.	10.7	0.05	0.2	0.3	0.2	0.03
		dust	45	1.7	5.4	3.1	2.8	1.7
Z7	15.5	c.m.	9.8	0 05	0.22	0.4	0.5	0.1
		dust	30	0.7	4.0	3.0	4.0	2.0
Z8	19.8	c.m.	10.1	0.06	0.33	0 4	0.2	0.07
		dust	26	1.0	2.5	1.4	3.3	1.5
Z9		c.m.	10.0	0.04	0.3	0.45	0.2	0.6
Z10	14.5	c.m	9.7	0.05	0.26	0.36	0.35	0.1
		dust	23	1.5	3.5	1.4	3.2	2.3
Z11	48.5	c.m.	20.0	0.05	0.6	0.15	0.4	0.5
		dust	25	0.8	0.9	1.5	0.8	1.8
Z12	58.3	c.m.	25.0	0.04	0.4	0.9	3.7	0.23
		dust	42	1.2	1.0	1.5	6.8	1.4

[a] c.m. = contact mixture.

action had ended the contact mixture was heated for about 16 h under a stream of purified nitrogen before starting the experiment.

The experiments were conducted at temperatures between 315 and 340°C; reactivities were converted to a standard temperature of 320°C by use of the overall energy of activation of 26 kcal/mole. The product composition does not vary in this temperature region [5e]. More information of the experiments is tabulated in Table 1; in this Table an oxygen concentration between 1 and 5 ppm indicates that no air was fed to the reactor. After each experiment the amount of carbon, hydrogen, copper, aluminium, zinc and iron were determined in the contact mixture and the entrained dust (see Table 2).

Results and Discussion

The results of some experiments without supply of oxygen are shown in Fig. 4. The rate of reaction in the first part of the stable region of the synthe-

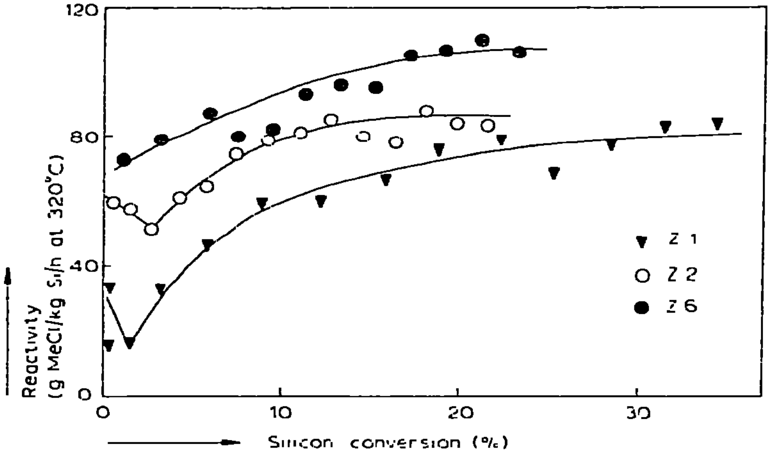

Fig. 4. Reactivity at 320°C as function of the silicon conversion; ppm O_2 = 1.

sis reaches a value between 80 and 110 g methyl chloride/kg Si/h at 320°C and the selectivity to dimethyldichlorosilane (D) a value of 90 mole percent. If methyl chloride with an oxygen concentration up to 1000 ppm is used no influence on the product composition is observed. The concentration of dimethyldichlorosilane remains at a constant level of 90 percent; the percentages of trichloromethylsilane (T) and trimethylchlorosilane (M) being 3-4 percent. The rate of reaction on the contrary, decreases very sharply between 1 and 1000 ppm oxygen and at 1000 ppm declines to a value of 65 percent of the value when no oxygen is present. When 350 ppm oxygen is fed to the reactor

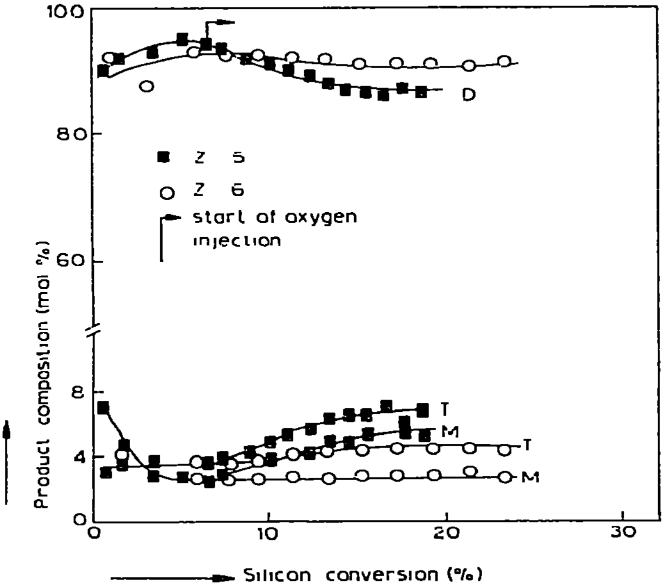

Fig. 5. Product composition as function of the silicon conversion.

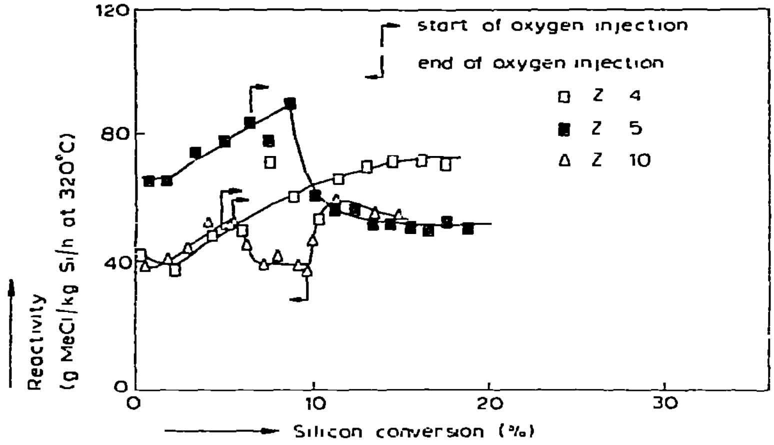

Fig. 6. Reactivity at 320°C as function of the silicon conversion.

the same degree of conversion of the silicon as in an oxygen free experiment can be reached (Fig. 8).

An oxygen concentration higher than 1000 ppm brings about a slight decrease in selectivity (Z5; Fig. 5); this decrease becomes greater as the oxygen content in the feed gas increases and amounts to 10 percent at 5000 ppm oxygen. The percentages of trichloromethylsilane and trimethylchlorosilane remain equal to each other, and reach higher values as the percentage of dimethyldichlorosilane decreases. When more than 1000 ppm oxygen is used the rate of reaction decreases less sharply than from 1 to 1000 ppm, as can be seen in Fig. 9. If poisoning of the contact mixture is continued for some hours the former level (no oxygen present) of selectivity is reached; the reaction rate on the other hand, remains low and does not reach the level of an oxygen-free experiment (Z10; Fig. 6). If 2000 ppm oxygen is present in the

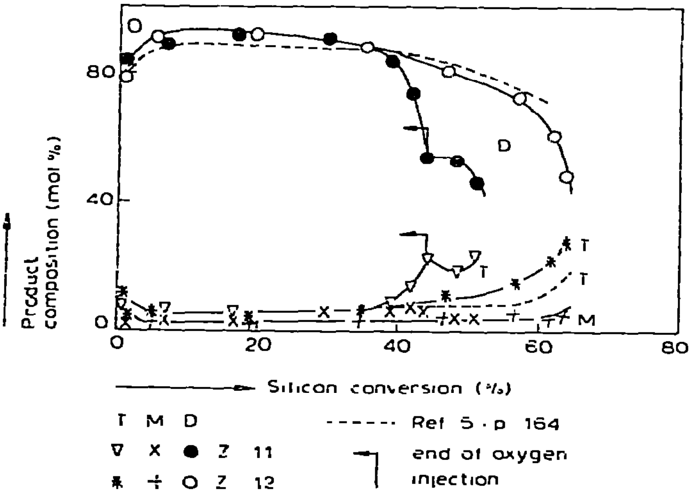

Fig. 7. Product composition as function of the silicon conversion.

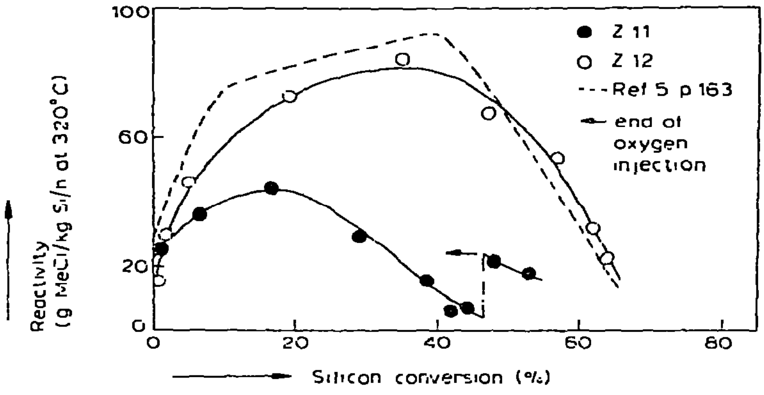

Fig. 8. Reactivity at 320°C as function of the silicon conversion

feed gas the reaction rate remains very low (Fig. 8) and the selectivity starts decreasing at 35 percent conversion of the silicon; stopping the oxygen injection does not restore the normal reactivity and selectivity (Fig. 7). A remarkable feature of the experiments is the constant rate of reaction when much oxygen was fed to the reactor.

The results of the experiments described above agree very well with the results obtained by Lobusevich et al.[8] with a contact mixture containing silicon, 10 percent copper and 0.005 percent antimony. Lobusevich found that adding 7400 ppm oxygen to the feed gas results in a decrease in selectivity of 14 percent; in the experiments described here the decrease at 5000 ppm amounted to 11 percent. Also the decrease in the reaction rate of 30 percent observed by Lobusevich agrees reasonably with the 50 percent decrease at 5000 ppm found in our experiments.

Kinetics

The kinetics of the direct synthesis of methylchlorosilanes in the presence of oxygen can be analysed with the aid of these experiments if we assume that the fluidised bed reactor can be described as an ideal tubular re-

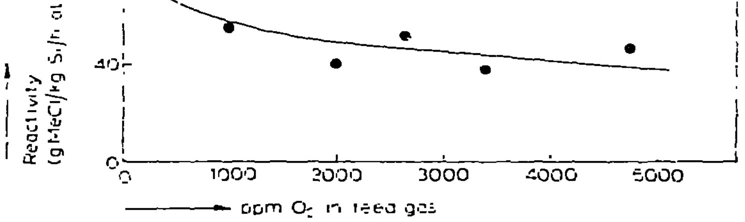

Fig. 9. Reactivity at 320°C as function of the oxygen concentration in the feed gas.

actor. It has been demonstrated earlier [10] that this is indeed the case under the applied conditions. Further it is assumed that the influence of oxygen in the temperature region of 315-340°C is the same for all temperatures (the adsorption equilibrium constant of oxygen on the contact mixture surface is assumed to be constant), and that minor changes in the product composition do not alter the overall kinetics.

During the synthesis, at constant oxygen feed rate, the equilibrium $O_2\ (g) \rightleftharpoons O_2\ (ads)$ will be established in the reactor with the equilibrium constant $K_{O_2} = R_{adsO_2} (R_{desO_2})^{-1}$. If both for methyl chloride and oxygen a Langmuir type adsorption is assumed, then for description of the synthesis four models must be considered; methyl chloride may adsorb via a single or dual site mechanism on the contact mixture surface [7c, 5f] and also for oxygen one can assume the same possibilities; the overall rates of reaction for the four models can then be described by eqns. 1-4:

$$R = kK_m P_m\ [1 + K_m P_m + K_{O_2} P_{O_2} + K_p P_p]^{-1} \tag{1}$$

$$R = kK_m P_m\ [1 + K_m P_m + (K_{O_2} P_{O_2})^{1/2} + K_p P_p]^{-1} \tag{2}$$

$$R = kK_m P_m\ [1 + (K_m P_m)^{1/2} + K_{O_2} P_{O_2} + K_p P_p]^{-2} \tag{3}$$

$$R = kK_m P_m\ [1 + (K_m P_m)^{1/2} + (K_{O_2} P_{O_2})^{1/2} + K_p P_p]^{-2} \tag{4}$$

k = reaction velocity constant (g MeCl/kg Si/h);
K = adsorption equilibrium constant; m = methyl chloride; O_2 = oxygen;
p = products; P = pressure;
R = reactivity at 320°C and 20% silicon conversion.

Because of the small conversion of methyl chloride during the experiments (see Table 3) the reactor can be considered as an ideal differential reactor with a constant pressure of methyl chloride; further, because of the small conversion, the concentration of products will not be very high and will not influence the synthesis [11], so in eqns. 1-4 K_pP_p can be neglected. The average methyl chloride partial pressure in each experiment is given in Table 3; this

TABLE 3

MAXIMUM METHYL CHLORIDE CONVERSIONS

Experiment	ξ MeCl (%)[a]	P_{MeCl} (average)(atm)
Z 1	15.4	0.93
Z 2	7.0	0.97
Z 3	5.9	0.98
Z 4	6.5	0.98
Z 5	4.4	0.98
Z 6	9.2	0.97
Z 7	4.0	0.97
Z 8	6.5	0.98
Z 9	9.7	0.96
Z 10	3.3	0.98
Z 11	10.2	0.95
Z 12	10.2	0.96

[a] ξ = highest conversion of methyl chloride in reactor during experiment.

pressure has been corrected for the presence of oxygen and nitrogen and the conversion of methyl chloride; as can be seen from Table 3 one can assume an average partial pressure of methyl chloride of 0.97 atmosphere for all experiments.

Thus eqns. 1-4 may be simplified to:

$$R^{-1} = C_1 + C_2 K_{O_2} P_{O_2} \qquad (5)$$

$$R^{-1} = C_3 + C_4 (K_{O_2} P_{O_2})^{1/2} \qquad (6)$$

$$R^{-1/2} = C_5 + C_6 K_{O_2} P_{O_2} \qquad (7)$$

$$R^{-1/2} = C_7 + C_8 (K_{O_2} P_{O_2})^{1/2} \qquad (8)$$

with C_i = constant.

If one of these equations applies, the experimental results, plotted according to one of eqns. 5-8, should yield a straight line. The plots (Fig. 10) indicate clearly that only 6 and 8 fit the results in a satisfactory manner. Further discrimination between these two models is not possible; the standard deviation for eqn. 6 amounts to 8.27 and for eqn. 8 to 8.00 g MeCl/kg Si/h. In Fig. 9 the

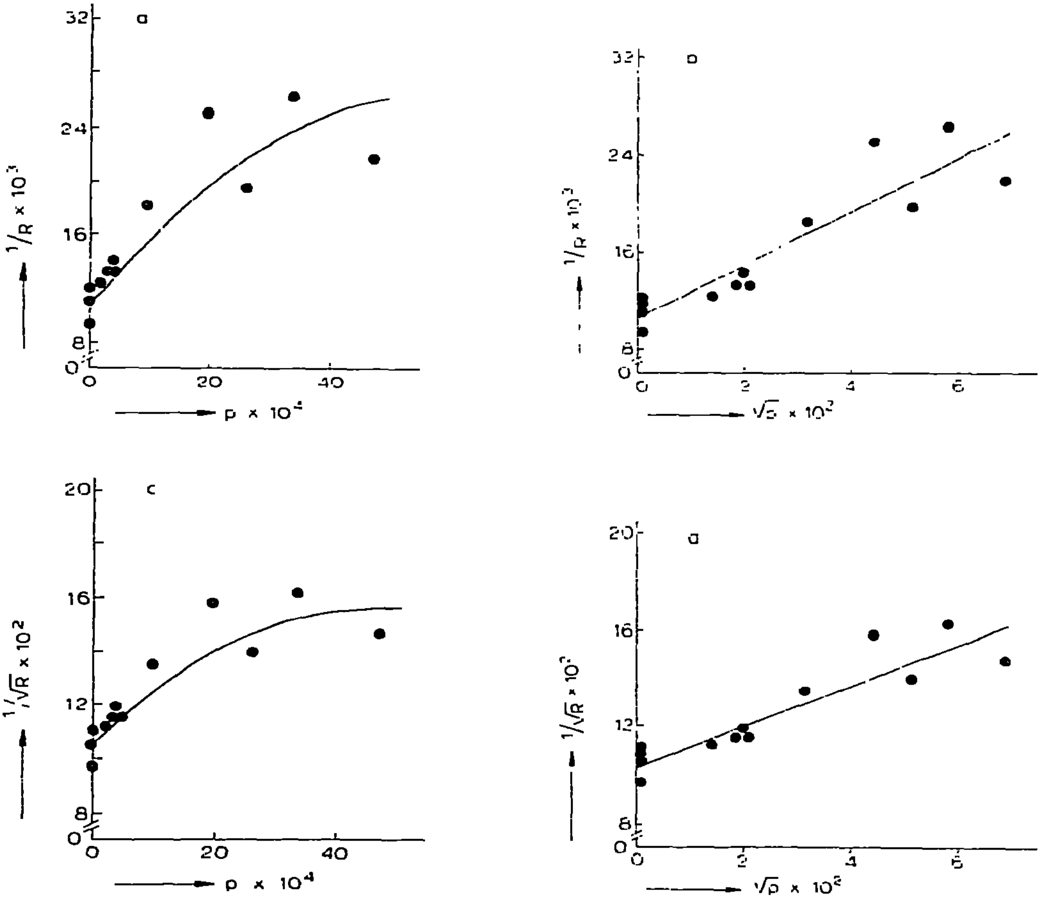

Fig. 10 Testing of models. a, eqn. 5; b, eqn. 6; c, eqn. 7; d, eqn. 8.

reaction rate is plotted against the oxygen pressure according to eqn. 6:

$$R = [0.01064 + 0.21253(P_{O_2})^{1/2}]^{-1}$$

$$\text{with } 0.01064 = (1 + K_m P_m)(kK_m P_m)^{-1}$$

$$0.21253 = (K_{O_2})^{1/2}(kK_m P_m)^{-1} \quad (P_m = 0.97 \text{ atm})$$

The constants in this equation were determined by means of the method of least squares. Assuming $K_m = 0.029$ atm^{-1} [7c] it follows that $K_{O_2} = 421$ atm^{-1}. The results obtained in our experiments agree qualitatively very well with the results obtained by Meyer and Vrakking on the adsorption of oxygen on a clean silicon surface [12]. A very stable surface species upon O_2 adsorption, exhibiting oxide structure, has been found in their investigations.

Conclusions

In the direct synthesis of methylchlorosilanes with copper as a catalyst and zinc and aluminium as promoters the selectivity to dimethyldichlorosilane is only slightly dependent on the oxygen concentration in the range of 1-5000 ppm O_2. The decrease in selectivity becomes greater as the amount of oxygen increases and amounts to 11 percent at 5000 ppm. The reactivity is strongly dependent on the oxygen concentration and decreases between 1 and 5000 ppm by a factor 2. Also the maximum conversion of the silicon is strongly dependent on the oxygen concentration and decreases as the concentration of oxygen increases.

The influence of oxygen on the direct synthesis can be described by a Langmuir type dual site adsorption of oxygen on the contact mixture surface. The very high adsorption equilibrium constant results in a high coverage of the surface, so the reaction rate decreases sharply when even only small quantities of oxygen are present. Another possibility for the poisoning effect of oxygen is the reaction with hydrogen (always present in small quantities due to the cracking of methyl chloride) to form H_2O, as proposed by Lobusevich et al.

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