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THE DIRECT SYNTHESIS OF METHYLDICHLOROSILANE AND DIMETHYLCHLOROSILANE

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Summary

The synthesis of methylchlorosilanes with a silicon—hydrogen bond, based on the reaction of silicon and methyl chloride with copper as a catalyst, has been investigated at a temperature of 332°C and a pressure of 1 atmosphere. By adding hydrogen to the gas phase, an overall selectivity of methyldichlorosilane and dimethylchlorosilane of over 80 mol% has been achieved together with a small quantity of by-products. The action of hydrogen consists of a reaction with the CuCl reaction intermediates; reaction of hydrogen with CuCl and silicon or with CuCl and chemisorbed methyl chloride also takes place. Metal chlorides such as $CdCl_2$ and $ZnCl_2$, which usually are promoters in the synthesis of methylchlorosilanes, do not promote the formation of the hydrogen-containing products.

Introduction

Methylchlorosilanes with a silicon—hydrogen bond are interesting starting materials for the production of silicones [1]. The reactive Si—H bond facilitates the production of complex substances, which normally cannot be synthesised directly, by addition, substitution and condensation reactions. Products containing the Si—H bond are, however, only obtained in minor quantities from the product mixture of the synthesis of methylchlorosilanes [1]. Of several methods which have been tried to increase this content [2-10], the most attractive seems to be the addition of HCl or H_2 to the methyl chloride gas phase. The production is invariably reported to be accompanied by the formation of considerable amounts of highly chlorinated, worthless by-products.

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In this paper the conditions are discussed which favour a high level of Si—H containing products, together with a low level of by-products, by using hydrogen as a reactant.

Theoretical aspects of the synthesis

From the literature it is known that copper, as well as silicon, exhibit a poor capacity for adsorbing hydrogen [11]. Nothing is known about the adsorption on a silicon/copper contact mass (probably containing η-phase) and it is therefore assumed that hydrogen enters into the products via a gas-solid reaction, not preceded by chemisorption on the catalyst. According to the reaction scheme of the direct synthesis of methylchlorosilanes [12], the most probable and energetically most advantageous route is then the reaction of hydrogen with the CuCl reaction intermediates, or the reaction of hydrogen with CuCl and, e.g., chemisorbed methyl chloride or silicon. The following steps may then occur on the surface:

$$2\ \mathrm{CuCl} + \mathrm{H_2} \rightarrow 2\ \mathrm{Cu} + 2\ \mathrm{HCl} \qquad (1)$$

$$\mathrm{HCl} + \mathrm{Cu} \rightarrow (\mathrm{HCl})\mathrm{Cu} \qquad (2)$$

$$\mathrm{SiCl} + (\mathrm{HCl})\mathrm{Cu} \rightarrow \mathrm{HSiCl_2} + \mathrm{Cu} \qquad (3)$$

$$\mathrm{HSiCl_2} + (\mathrm{MeCl})\mathrm{Cu} \rightarrow \mathrm{MeHSiCl_2} + \mathrm{CuCl} \qquad (4)$$

$$\mathrm{MeSiCl_2} + (\mathrm{HCl})\mathrm{Cu} \rightarrow \mathrm{MeHSiCl_2} + \mathrm{CuCl} \qquad (5)$$

Side reactions may also occur, resulting in the formation of molecules containing more than one Si—H bond. These steps are rather unlikely because the HCl concentration on the surface will be low.

From the mass balance it follows that, if reactions 1-5 take place, a surplus of methyl groups will occur on the contact mixture surface which can be counterbalanced by the formation of $\mathrm{Me_3SiCl}$ or ethane. Also the formation of one molecule of DH* can be accompanied by the formation of one molecule of $\mathrm{CH_4}$ or MH; the latter can be formed via reactions 6 and 7.

$$\mathrm{CuCl} + \mathrm{H_2} + \mathrm{Si} \rightarrow \mathrm{HCl} + \mathrm{Cu} + \mathrm{SiH} \qquad (6)$$

$$\mathrm{SiH} + 2\ (\mathrm{MeCl})\mathrm{Cu} \rightarrow \mathrm{Me_2SiHCl} + \mathrm{CuCl} + \mathrm{Cu} \qquad (7)$$

According to the reaction scheme, the concentration of CuCl reaction intermediates should be as high as possible in order to achieve high production of Si—H containing substances. Although the addition of promoters such as $\mathrm{ZnCl_2}$ and $\mathrm{CdCl_2}$ increases the number of active reaction centres [12], the concentration of CuCl is reduced by reaction 8, so the use of high concentrations

$$\mathrm{MCl}_{n-1} + \mathrm{CuCl} \rightarrow \mathrm{MCl}_n + \mathrm{Cu} \qquad (8)$$

of protomers does not seem to be advisable. Further, a high pressure of

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* D = dimethyldichlorosilane, M = trimethylchlorosilane, T = trichloromethylsilane, DH = dichloromethylsilane, MH = dimethylchlorosilane.

hydrogen should be applied because of the competing reactions 1, 6 and 9, reactions 1 and 6 must be favoured. Also the existence of chlorine-contain-

$$CuCl + Si \rightarrow SiCl + Cu \qquad (9)$$

ing reaction intermediates (other than CuCl), capable of reaction with hydrogen, should exert a favourable effect.

Experimental

Experiments performed

Experiments were performed in order to investigate the synthesis of Si—H containing methylchlorosilanes both with and without promoter (exp. 1-3). In experiment 3 $CdCl_2$ was used as the promoter instead of $ZnCl_2$ because liquid $ZnCl_2$ in high concentrations causes agglomeration of the contact mixture particles. In experiment 4 silver was added as a possible chlorine acceptor from CuCl because AgCl is more stable with regard to silicon than CuCl [13]. In experiment 5 the total effect of addition of silver and promoters has been investigated.

All experiments were carried out in a fluidised bed. During the synthesis the pressure of hydrogen was varied from time to time in order to investigate its influence.

Apparatus

The apparatus which was used has been described earlier [14]. By means of a Hersch-cell the oxygen content in the reaction gases was measured continuously. Oxygen removal from methyl chloride was effected by a column containing active copper (BTS-catalyst). Hydrogen was led through a column containing a Pd-catalyst for oxygen and a molecular sieve 4A for water removal.

Materials used and experimental procedure

In the experiments 100 g contact mixture was used with silicon and copper as in ref. 14. $CdCl_2$ was added as a powder with a particle diameter $<50\ \mu$. Silver, zinc and aluminium were added as fine metallic powders.

Before the start of the experiments the components were mixed and dried for 16 h at 50-100°C under a stream of pure nitrogen. Then the mixture was

TABLE 1

SUMMARY OF EXPERIMENTAL DATA

Experiment	Composition of the contact mixtures at the start of the experiments (wt%)					Average tempera-ture (°C)	Average oxygen content (ppm)
	Cu	Ag	Cd	Zn	Al		
1	10					332	10
2	10			0.1	0.05	332	4
3	10		2.0			332	
4	9.4	5.7		0.1	0.05	332	10
5	9.2	5.6	2.7	0.1	0.05	333	6

TABLE 2

IDENTIFICATION OF DH AND MH BY NMR SPECTROSCOPY

		$\delta(CH_3)$			$\delta(H)$	
		found	lit. [15]		found	lit. [15]
MH	doublet.	0.50	0.507	septuplet:	4.88	4.886
DH	doublet:	0.87	0.880	quartet:	5.58	5.581

heated and reaction of silicon and copper took place at 300-330°C. Thereafter the contact mixture was heated for 16 h at 300°C.

In the first hours of the synthesis pure methyl chloride was fed to the reactor in order to achieve a proper distribution of the copper catalyst over the silicon surface. Some data concerning the experiments have been collected in Table 1.

Identification and analysis of reaction products

Identification of MH took place by NMR spectroscopy. From the product mixture distillation fractions in the range 35-40°C were isolated. The chemical shifts of the hydrogen atoms of the products of these fractions relative to TMS can be found in Table 2. The products were identified as DH and MH.

In the experiments the analysis of the reaction products was performed by means of gas-liquid chromatography [14]; for MH a calibration factor of 1.0 relative to D was assumed.

Results and discussion

The results of the experiments have been collected in Table 3. An example of a complete synthesis can be found in Figs. 1 and 2 (experiment 2).

By use of a contact mass without promoter (experiment 1) higher reaction rates can be achieved than in experiments in which promoters are used. In preliminary experiments without a promoter it was found, however, that it is very difficult for such a contact mixture to become active. In these experiments the reaction rate amounted to only 40 g MeCl $kgSi^{-1}$ h^{-1} (T 330°C) at a $MeCl/H_2$ ratio of 1/1. Such a reaction rate is low by comparison with experiment 1. The selectivity was always high: 70-80% of Si—H containing products were obtained.

In experiment 2 a contact mixture with a small content of promoter, 0.1 wt% Zn and 0.05 wt% Al, has been used. In the first 30% of silicon conversion the selectivity of Si—H containing products is not as high as in experiment 1 because of the reduction of the CuCl concentration by the action of the promoter. As the synthesis proceeds, the amounts of DH and MH gradually increase, probably because of the evaporation of promoter. This effect was observed in all experiments in which a promoter was used. As can be seen in Fig. 1, an increase in the pressure of hydrogen increases the amounts of DH and MH in the end product. The overall reaction rate of this experiment can be

TABLE 3

EXPERIMENTAL RESULTS CONCERNING THE SYNTHESIS OF Si—H CONTAINING PRODUCTS

Experiment	Silicon conversion (%)	$P(H_2)$(atm)	P(MeCl)(atm)	DH (%)[a]	MH (%)	D (%)	M (%)	T (%)	Other products (%)	Overall rate g MeCl kg Si^{-1} h^{-1}
1	20	0,55	0,45	37,6	32,7	23,4	2,9	3,4	0,0	75
	40	0,55	0,45	23,8	30,8	33,1	2,3	9,9	0,1	100
	55	0,75	0,25	45,7	33,1	12,5	1,5	6,9	0,3	75
	65	0,55	0,45	51,1	24,4	17,3	2,1	4,8	0,3	85
2	25	0,55	0,45	30,8	17,5	45,8	1,2	4,7	0,0	40
	50	0,75	0,25	56,7	28,5	10,3	1,2	2,7	0,6	40
	60	0,75	0,25	70,3	17,5	5,0	1,2	2,7	3,3	50
3	45	0,54	0,46	8,1	2,2	80,4	4,0	5,3	0,0	50
	70	0,69	0,31	0,3	4,0	88,0	3,7	4,0	0,0	65
4	30	0,55	0,45	17,7	12,4	63,2	3,3	3,2	0,2	60
	55	0,75	0,25	58,2	19,8	15,3	1,8	4,0	0,9	45
5	30	0,55	0,45	6,1	5,5	76,7	5,5	6,2	0,0	60
	55	0,75	0,25	7,8	10,5	70,6	2,5	8,5	0,1	60
	75	0,55	0,45	3,5	11,7	62,4	3,0	19,4	0,0	50

[a] All percentages are molar.

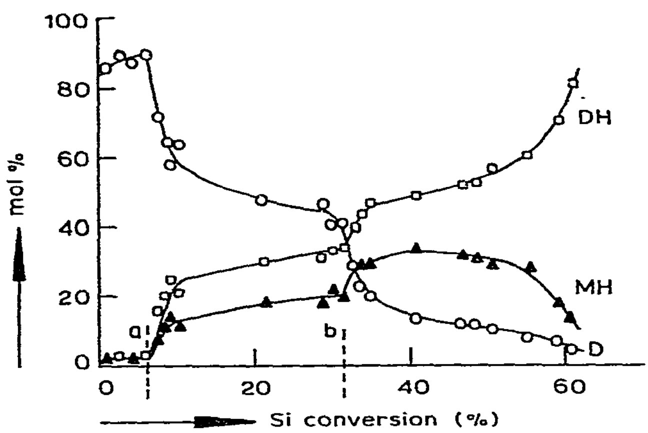

Fig. 1. Product composition of the direct synthesis of DH and MH with low content of promoter. a, pressure change from $P(\text{MeCl}) = 1$ atm to $P(\text{MeCl}) = 0.45$ and $P(\text{H}_2) = 0.55$ atm. b, pressure change from $P(\text{MeCl}) = 0.45$ and $P(\text{H}_2) = 0.55$ atm to $P(\text{MeCl}) = 0.25$ and $P(\text{H}_2) = 0.75$ atm. The percentages of M and T have not been inserted in this figure.

found in Fig. 2. The production of T is very low because side reactions, e.g. the reaction of CuCl with SiCl, are suppressed.

Experiment 3, in which CdCl_2 was used as the promoter in a high concentration (3%), shows poor production of DH and MH. This holds even for a silicon conversion of 70%. Evidently in this experiment the concentration of CuCl is reduced to very small amounts by its reaction with cadmium subchloride.

In experiment 4 the influence of silver has been investigated. By comparison with experiment 2 a decrease in the formation of Si—H containing products is observed. Only in experiment 5 is a small positive influence of silver observed, although its activity remains poor.

From the experiments it may be concluded that the addition of metal chlorides which are promoters for the synthesis of dimethyldichlorosilane, do

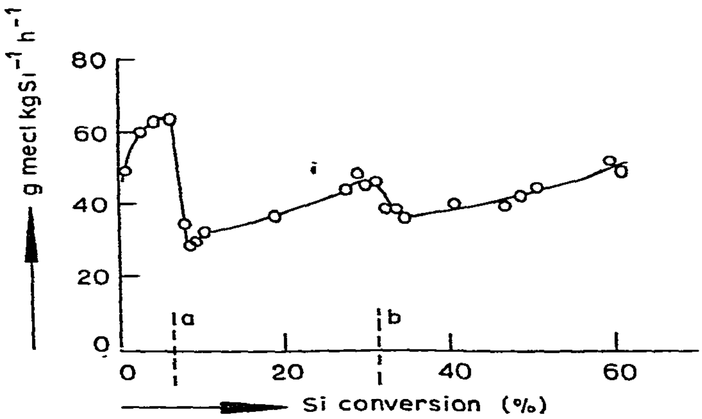

Fig. 2. Overall reaction rate of the direct synthesis of DH and MH with low content of promoter. For the meaning of a and b see Fig. 1.

not promote the synthesis of DH and MH. The influence of metals or metal salts which have been used by other investigators [6,7,9,10] could be such that they promote cracking of methyl chloride; this effect results in the formation of Si—H containing products. This cracking is, however, detrimental for the activity of the contact mass and should therefore be avoided.

Conclusions

The synthesis of methylchlorosilanes containing a silicon—hydrogen bond has been investigated with copper as the catalyst and a gas phase composed of methyl chloride and hydrogen. An overall selectivity of Si—H containing products of over 80 mol% has been achieved.

Hydrogen reacts from the gas phase with two CuCl reaction intermediates or with CuCl and, e.g., free silicon or chemisorbed methyl chloride. The formation of both MH and DH takes place. The addition of metal chlorides which are promoters for the synthesis of D, does not favour the formation of Si—H containing products due to the reduction of the CuCl concentration, nevertheless a small amount of promoter is needed in order to achieve an active contact mixture.

The addition of silver to a contact mixture with little promoter decreases the concentration of DH and MH. If much promoter is present, silver brings about a slight increase in the selectivity to DH and MH.

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