

## Thermodynamic assessment of the copper catalyzed direct synthesis of methylchlorosilanes

Jörg Acker<sup>a,\*</sup>, Klaus Bohmhammel<sup>b</sup>

<sup>a</sup>Lausitz University of Applied Sciences, Department of Biological, Chemical and Process Engineering, Großenhainer Straße 59, D-01968 Senftenberg, Germany

<sup>b</sup>Freiberg University of Mining and Technology, Department of Physical Chemistry, Leipziger Straße 29, D-09596 Freiberg, Germany

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### ABSTRACT

The copper catalyzed direct synthesis of methylchlorosilanes is a reaction of enormous complexity. Although, there is a general acceptance about a silylenoide based reaction mechanism, many details of the reaction are not yet fully understood. The present work is a comprehensive thermodynamic study on the reaction system of the direct synthesis. The calculations are based on a broad database containing the elements, all silanes, chlorosilanes, methylsilanes, and methylchlorosilanes with one Si atom, hydrocarbons and chlorinated hydrocarbons as well as other relevant compounds in the system Si–C–H–Cl. A calculation of the reaction between silicon and methylchloride, excluding only SiC as an unlikely reaction product, results in the total decomposition of methylchloride and the formation carbon, methane, hydrogen, trichlorosilane, and silicon tetrachloride. The systematic suppression of certain reaction products from the calculation yields finally into a product distribution close to the experimentally observed ones. The chosen approach to remove certain compounds from the calculation is equivalent to the introduction of unspecific kinetic constraints arising from a hypothetically total and selective blocking of certain reaction pathways. From this, three major kinetically determined reaction pathways are identified: (i) the formation of carbon, hydrocarbons, hydrogen, and hydrogen chloride due to the cleavage of the C–H bond in methyl chloride, (ii) the formation of hydrogen-containing methylchlorosilanes that occurs only in the presence of hydrogen or hydrogen chloride, and (iii) the competition between the thermodynamically favored chlorosilanes and the kinetically favored methylchlorosilanes. The presence of transition metals (regardless whether Cu, Fe, or Ni) during the direct synthesis gives no thermodynamic preference for the formation of methylchlorosilanes. The metals effect is to open a kinetically controlled reaction pathway to the formation of methylchlorosilanes far away from the formation of chlorosilanes or from other thermodynamically more favored compounds. Furthermore, processes related to the induction period, the addition of hydrogen to the direct synthesis, constrained equilibria between methylchlorosilanes, and the limits of the applied calculation procedure are discussed in detail.

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### 1. Introduction

The reaction of silicon with methyl chloride in the presence of copper as catalyst is designated as the direct synthesis of methylchlorosilanes. This reaction, independently discovered by E.G. Rochow at General Electric Company and R. Müller in Germany, is the basis for today's industrial organosilicon chemistry. The history of organosilicon chemistry and the direct synthesis is described in the excellent review by Seyferth [1].

The direct synthesis has to be considered as a kinetically determined reaction, which can be driven by the choice of a catalyst and by the addition of certain promoters to an optimum between reactivity (reaction rate) and selectivity (yield) with respect to the

desired main product dimethyldichlorosilane (Table 1). Although significant contributions for the understanding of essential steps of the mechanism had been made [2–23], such as the silylene mechanism investigated by Lewis et al. [11] and other authors [11,12,15,20–22], we are far away from a comprehensive model or a quantitative description of this reaction. This can be mainly attributed to the complexity of the direct synthesis. The enormous complexity arises from a large number of factors generating and influencing the observed wide-ranging product distribution and the yields that vary (i) with the catalyst, its method of preparation and added promoters, as well as (ii) with the temperature and pressure. (iii) Hydrodynamics inside the reactor plays a role, since the reactor type and reactor geometry seem to influence the yield of the products. Further parameters are (iv) the residence time of the products, (v) local inhomogeneities in the catalyst composition, promoter distribution, and temperature distribution that can form

\* Corresponding author. Tel.: +49 3573 85 839; fax: +49 3573 85 809.  
E-mail address: [jaecker@fh-lausitz.de](mailto:jaecker@fh-lausitz.de) (J. Acker).

**Table 1**  
Typical product ranges in direct synthesis [18]

| Product   | Yield (mol%) |
|---|--------------|
| (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> | 83–93        |
| CH <sub>3</sub> SiCl <sub>3</sub>                 | 3–10         |
| (CH <sub>3</sub> ) <sub>3</sub> SiCl              | 1–5          |
| CH <sub>3</sub> SiHCl <sub>2</sub>                | 0.1–1        |
| (CH <sub>3</sub> ) <sub>4</sub> Si                | 0.01–0.5     |
| (CH <sub>3</sub> ) <sub>2</sub> SiHCl             | 0.01–0.5     |

sites of different reactivity and selectivity and causing side reactions, (vi) transport phenomena, depletion and enrichment of catalyst constituents, particularly in the induction and the final period, and finally (vii) the unknown role of known or unintentionally introduced impurities and dopants in the used silicon and/or the catalyst. That list underlines the difficulty in the research on the direct synthesis to compare published results which have been produced under different reaction conditions.

It would be of interest for the discussion of the direct synthesis, to have a deeper understanding about the ongoing reactions in the absence of any hindrances caused by kinetics, transport phenomena, or hydrodynamics. Furthermore, the identification of kinetic hindrances, i.e. thermodynamically allowed but not occurring or somehow suppressed chemical reactions, should be helpful for the understanding. Thermodynamics is the tool to evaluate the processes occurring in such a complex reaction system. Thermodynamic equilibrium calculations of complex chemical systems on the basis of Gibbs free energy minimization can give answers on numerous questions: about the thermodynamically stable reaction products and their yield, whether a chemical reaction proceeds endothermically or exothermically, on the impact of reaction parameters like temperature, pressure, or reactant ratios, whether a reaction proceeds irreversibly or leads to equilibrium, and whether observed reaction temperatures are thermodynamically determined. By comparing the calculations with experimental results kinetic hindrances can be identified, or at least, hints can be given.

It will be shown early in this paper, that a simple thermodynamic calculation of the system Si–C–H–Cl is insufficient to model the direct synthesis. Certain reaction pathways have to be closed in the calculations to get a more realistic model of the direct synthesis. A procedure to introduce unspecific constraints into the thermodynamic calculations is presented, from which general conclusions about possible reaction pathways of the direct synthesis can be drawn. The mentioned procedure was already successfully applied to the calculation of the hydrochlorination of silicon [24].

The present paper should be seen as an attempt of a thermodynamic assessment of the complex reaction system of direct synthesis based on an earlier, less comprehensive study [25].

## 2. Thermodynamic calculations

### 2.1. Calculation mode and database

The thermodynamic modeling of the direct synthesis was performed using the software package ChemSage 4.1 [26]. The equilibrium is calculated by minimization of the Gibbs energy of the global reaction system for all compounds in all phases included in the used data set. Hence, the data set should contain as many compounds as possible that can be meaningfully related to the reaction. A preselection of compounds for the data set, such as the main products only, is not sufficient. In the present case of the Si–H–Cl–C, system the data set includes the elements, monosilane, chlorosilanes, methylsilanes, and methylchlorosilanes containing one silicon

atom, saturated and unsaturated hydrocarbons and chlorohydrocarbons with up to four carbon atoms, as well as hydrogen chloride and silicon carbide. All data for the compounds mentioned above were taken from the HSC database [27]. Because of the lack of data, disilanes and polymer compounds consisting of (Si–CH<sub>2</sub>) units are not included in the data set. Thermodynamic data for the silicide phase were taken from the following sources: nickel silicides [28], iron silicides [29], copper silicides [30], pure metals and metal chlorides [27].

The gas phase is considered as ideal mixture without any intermolecular interactions. If not otherwise stated, the total pressure was set to 10<sup>5</sup> Pa. In the case of pure silicon as solid reactant, the composition and the structure of the solid phase remain unchanged during the reaction. The modeling of the direct synthesis with a metal silicide phase as solid neglects any kinetic hindrances stemming from the change of the solid phase composition due to silicon depletion (e.g. diffusion or segregation phenomena).

For the sake of a comprehensive description of a modeled reaction, a wide range of the molar reactant ratio has to be considered. The calculations are usually performed for a single reaction between a fixed amount (e.g. 1 mol) of one reactant (e.g. silicon) and a varying amount (e.g. from 0 to 2 mol) of another reactant (e.g. methyl chloride) denoted as “incoming amount”. This implies that the amounts of formed products must be given as absolute values in mol. Such representation gives a comprehensive picture of the reaction particularly if solid products (e.g. carbon) or non-silane products (e.g. hydrogen, hydrogen chloride, or hydrocarbons) are formed. Yields are usually calculated only for the silane products and, if not otherwise stated, the given in mol% throughout this paper.

The performed calculations consider a chemical reaction as a bulk reaction. Surface area and surface morphology known as important parameters in any heterogeneous reaction are not modeled. The calculated results can not be related to technical parameters such as space velocity (incoming volume methyl chloride per time and per mass of catalyst) or space–time yield (yield of product per time and per mass of catalyst). Therefore, a given stoichiometry in the calculation does not automatically correspond to the actual molar reactant ratio at the catalyst surface in a heterogeneous reaction.

To study the reactivity of an individual transition metal silicide phases in the direct synthesis, the solid phase is introduced into the calculation in a manifold excess with respect to the gaseous reactant. It has already shown for the hydrochlorination of silicon, that the composition of the considered silicide phase is practically not changed during the reaction. On the other hand, the composition of the gaseous reaction products can undergo dramatic changes by variation of the transition metal and the metal-to-silicon ratio [31]. In the absence of any reactant excess, hints about the ongoing reaction due to solid phase depletion, processes at the initial or final period of reaction, or possible local equilibrium can be derived.

### 2.2. Constrained thermodynamic equilibrium calculations

A thermodynamic calculation of a chemical reaction is the sole search for the global Gibbs energy minimum of the total system neglecting any kinetic behavior or mass transport effects. However, information about possible reaction pathways can be derived from thermodynamic equilibrium calculations, by introducing the following boundary condition. If the thermodynamically most stable reaction product is suppressed by the calculation, the compound with the next higher stability is calculated as main product. Repeated suppression of the respectively most stable product generates an order of product stability. Hence, the real product distribution can be matched with the calculated ones by a consec-

utive suppression of in reality unlikely or not occurring calculated reaction products. In other words, the chemical system is more and more narrowed until an agreement with experimental data is found. The reduction of the number of compounds in such a system restricts the number of possible reaction pathways.

A simplified explanation is given by Scheme 1. The procedure applied to a hypothetical reaction between A and B corresponds to a selective blockade of the reaction pathway that leads to the global minimum of Gibbs free energy of the total reaction system (pathway I). This favors another reaction pathway (pathway II) yielding into a new local minimum of Gibbs free energy of generally higher energy than the global minimum. If this pathway is closed again, the next possible pathway III yields to products which are thermodynamically more unfavored and more kinetically favored than those of pathway II.

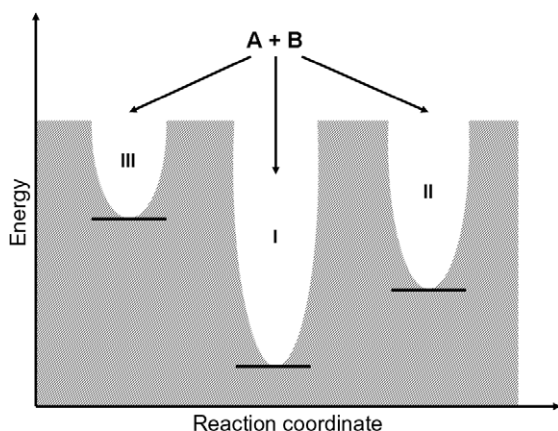
All calculated reactions leading to new local minima follow the basic principle of any thermodynamic calculation: they proceed instantaneously without any kinetic hindrances. Therefore, the total blocking of a reaction pathway gives general information about the behavior of the newly established, narrowed or constrained, reaction system and does not include any information about rate constants, diffusion processes or mechanism in terms of parallel or consecutive reactions.

Since the solid phase consists of pure silicon, only the gas phase composition needs to be discussed. If transition metal silicides are calculated as solid reactants the depletion of silicon is assumed to proceed strictly thermodynamically without any kinetic hindrances. Effects arising from diffusion processes and silicide phase formation hindrances are neglected [24,25]. Their modeling would require comprehensive experimental data as well as the application of sophisticated models known from metallurgical research.

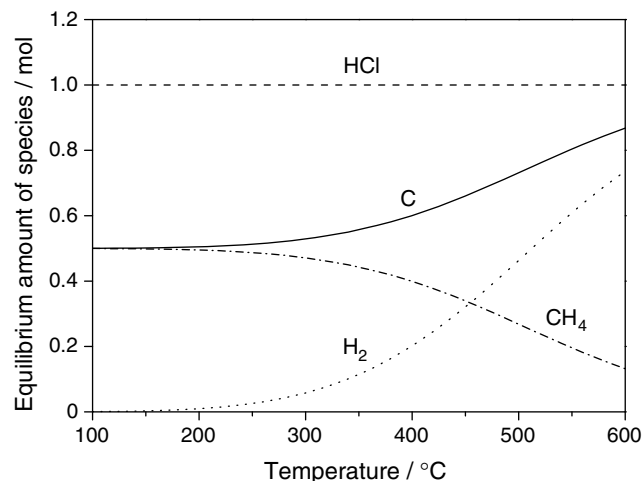
### 3. Results and discussion

#### 3.1. Thermal behavior of methyl chloride

Gaseous methyl chloride is a thermodynamically metastable compound. It decomposes exothermically (molar reaction enthalpy,  $\Delta_R H = -41.9 \text{ kJ mol}^{-1}$ ) into C, CH<sub>4</sub>, and HCl. Methane undergoes a further cleavage into carbon and hydrogen with increasing temperature (Fig. 1).



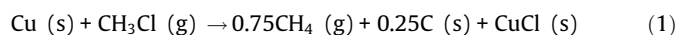
**Scheme 1.** A chemical reaction A + B leads into the global Gibbs free energy minimum by the following reaction pathway I. By selectively closing of that pathway, e.g. by the suppressing of the major reaction product, the new reaction pathway II is favored, although this pathway results in a local energy minimum. A further suppression of products forces the system to follow pathway III into an energetically more unfavored local minimum. An ongoing suppression leads finally into a state, in which the reaction does not proceed. The number of components involved in the calculation decreases from pathways I to III.



**Fig. 1.** Calculated product distribution of the thermal decomposition of 1 mol methyl chloride.

#### 3.2. Reaction of methyl chloride with metals

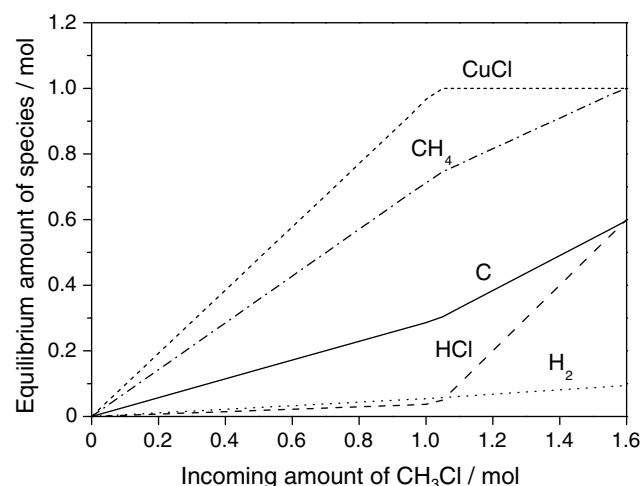
The reaction between copper and methyl chloride is part of the induction period of direct synthesis. Fig. 2 shows the solid and gaseous reaction products calculated for an increasing molar methyl chloride-to-copper ratio at 300 °C. The proceeding exothermic reaction ( $\Delta_R H = -106.1 \text{ kJ mol}^{-1}$ ) is described by the equation:



In any case, even in the presence of a large excess of hydrogen (not shown in the figure) CuCl is the main reaction product. Hydrogen chloride is not formed while elemental copper is present.

No reaction occurs if the reaction pathway of methane formation is closed. This behavior can be associated with the end of the induction period at which the formation of hydrocarbons turns mainly into methylchlorosilane formation. From this can be assumed, that surface species (e.g. silylenes) or a chemical surface modification (e.g. the formation of a surface reaction layer [31]) established during the induction period act as a kinetic barrier of C-H bond cleavage.

Calculations performed with iron and nickel agree fully with that for copper.



**Fig. 2.** Calculated product distribution of reaction between 1 mol copper and methyl chloride at 300 °C.

### 3.3. Reaction behavior of dimethyldichlorosilane

Dimethyldichlorosilane is a thermodynamically metastable compound that decomposes into silicon tetrachloride, hydrocarbons, and carbon. The exclusion of the latter two decomposition products results into the known – kinetically determined – stability of the methyl groups. The thermal decomposition of dimethyldichlorosilane at 300 °C yields to a mixture of 44.5% dimethyldichlorosilane, 35.7% trimethylchlorosilane, 18.7% silicon tetrachloride, 0.9% tetramethylsilane and a negligible fraction of 0.2% methyltrichlorosilane (Fig. 3). The extent of decomposition decreases with increasing temperature, since the decomposition is exothermal. Hydrogen-containing methylchlorosilanes  $\text{CH}_3\text{-SiHCl}_2$ ,  $(\text{CH}_3)_2\text{HSiCl}$ ,  $(\text{CH}_3)_3\text{SiH}$ , and  $\text{HCl}$  are formed in presence of hydrogen, however, only above 375 °C in significant amounts (the sum of all side products including  $\text{Si}(\text{CH}_3)_4$  and  $\text{CH}_3\text{SiCl}_3$  amounts to 4.6%). The presence of silicon or methyl chloride causes no significant change from the product distribution shown in Fig. 3.

If the formation of chlorosilanes, hydrocarbons, and carbon is excluded from the calculation, then the product distribution is determined by the reversible equilibrium in Eq. (2) (Fig. 4).

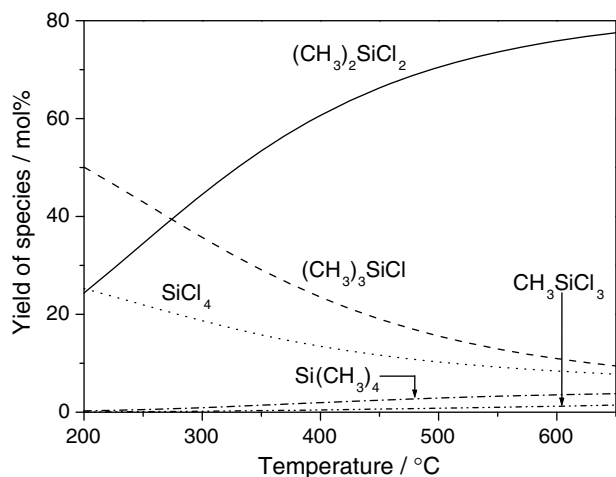


Fig. 3. Calculated product distribution of the thermal decomposition of dimethyldichlorosilane. The formation of C,  $\text{H}_2$ , and hydrocarbons is suppressed.

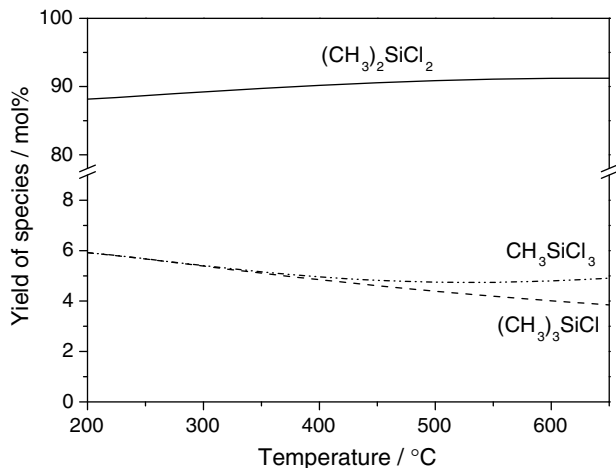
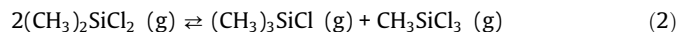


Fig. 4. Calculated product distribution of the thermal decomposition of dimethyldichlorosilane. The formation of C,  $\text{H}_2$ , hydrocarbons, and chlorosilanes is suppressed.



This redistribution proceeds almost independently of temperature yielding to 5.4% methyltrichlorosilane and 5.4% trimethylchlorosilane. The equilibrium constant is calculated to  $3.7 \times 10^{-3}$  at 300 °C. The negligible temperature dependence is explained by a small reaction enthalpy of  $-6.3 \text{ kJ mol}^{-1}$ . The reaction is fully reversible so that an equimolar mixture of  $(\text{CH}_3)_3\text{SiCl}$  and  $\text{CH}_3\text{SiCl}_3$  gives an identical product distribution as stated out above.

The equilibrium in Eq. (2) is at 300 °C not very sensitive to the addition of hydrogen. Only a small shift in the product composition to 7.8%  $(\text{CH}_3)_3\text{SiCl}$  and 3.3%  $\text{CH}_3\text{SiCl}_3$  is found at 300 °C. The only indication for the presence of hydrogen is the formation of hydrogen chloride and 4.5%  $\text{CH}_3\text{HSiCl}_2$  at the same temperature. An addition of silicon has no impact on the product distribution at 300 °C.

### 3.4. Modeling of the direct synthesis

Silicon carbide is the most stable reaction product if the calculation is running with all compounds in the database. Suppression of this never observed product leads to the product distribution shown in Fig. 5. Methyl chloride is fully decomposed into methane, carbon, and hydrogen chloride. The latter reacts with silicon partially to silicon tetrachloride and trichlorosilane. This calculated product distribution agrees widely with the experimental one, if methyl chloride is passed over silicon in the absence of metals [2,32].

The suppression of the carbon formation prevents the total decomposition of methyl chloride and leads to large amount of hydrocarbons (Fig. 6). However, suppressing the carbon formation is not a guarantee for the stability of the methyl groups. It rather guarantees that the total number of C–H bonds in the reaction system is constant. With respect to this limitation a redistribution of a fraction of the C–H bonds leading to  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  is thermodynamically allowed if this reduces the Gibbs energy of the total system. The suppression of carbon opens the pathway to the formation of dimethyldichlorochlorosilane, which is present in a higher yield than the simultaneously formed trimethylchlorosilane. The yields of the formed silanes of 45.6%  $\text{SiCl}_4$ , 37.0%  $(\text{CH}_3)_2\text{SiCl}_2$ , and 17.3%  $(\text{CH}_3)_3\text{SiCl}$  should be expected to correlate with the reversed order of the Gibbs energy of formation at 300 °C as follows as  $\text{SiCl}_4$  ( $-852.4 \text{ kJ mol}^{-1}$ ) <  $(\text{CH}_3)_2\text{SiCl}_2$  ( $-655.2 \text{ kJ mol}^{-1}$ ) <  $(\text{CH}_3)_3\text{SiCl}$  ( $-564.3 \text{ kJ mol}^{-1}$ ). However,  $(\text{CH}_3)_3\text{SiCl}$  with a Gibbs formation energy of  $-807.8 \text{ kJ mol}^{-1}$  at 300 °C is missing. Its absence is a con-

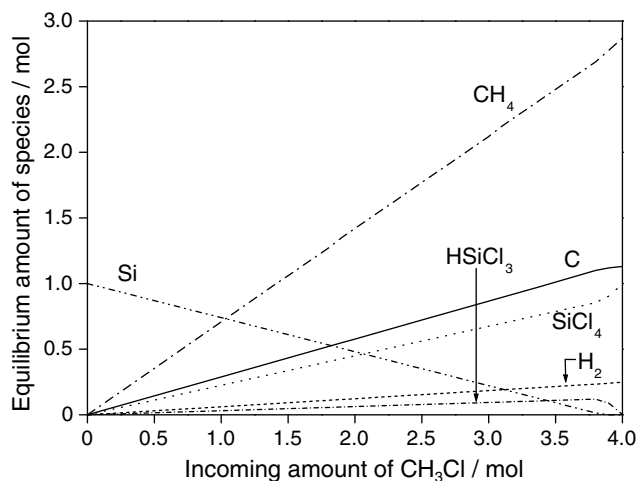


Fig. 5. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC is suppressed.



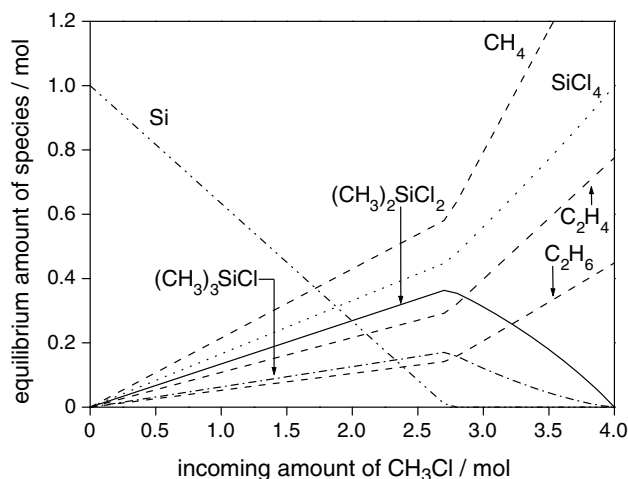


Fig. 6. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC and C is suppressed.

sequence of the constant number of methyl groups and the requirement of Gibbs free energy minimization. Roughly speaking, the formation of the thermodynamically most preferred silane, SiCl<sub>4</sub>, generates formally four methyl groups. These methyl groups have to be distributed between the possible methylchlorosilanes and hydrocarbons under the condition that the Gibbs energy of the total system is minimized. Therefore, the absence of the remarkable stable (CH<sub>3</sub>)<sub>3</sub>SiCl is a result of the constraint calculation condition leading to a slightly lower value of Gibbs energy than in the presence of (CH<sub>3</sub>)<sub>3</sub>SiCl. The maximum yield of (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> is reached at a molar methyl chloride-to-silicon ratio of 2.7 instead of 2.0 due to the large extent of methyl chloride decomposition. Above the ratio of 2.7, silicon tetrachloride and the decomposition products of methyl chloride determine the product distribution.

A simultaneous suppression of SiC and chlorosilanes leads to the results shown in Fig. 7. The hydrogen-containing methylchlorosilane CH<sub>3</sub>SiHCl<sub>2</sub> is formed at molar methyl chloride-to-silicon ratios up to 2.1 as the only silane compound and as main reaction product. The formed hydrogen results from a partial decomposition into methane and carbon. At reactant ratios above 2.1, a H vs. Cl exchange at the silane molecule occurs and methyltrichloros-

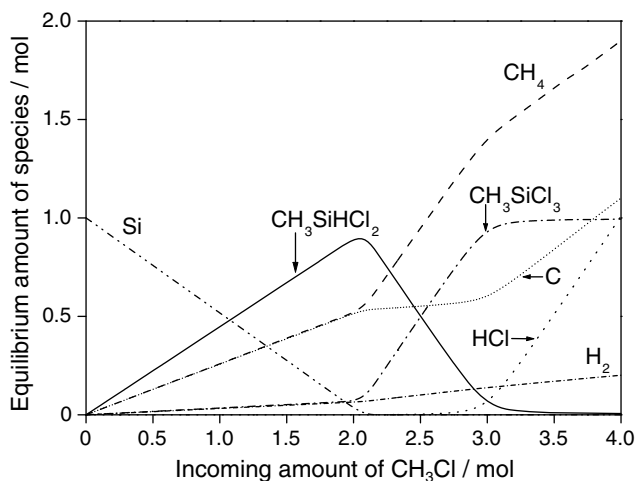
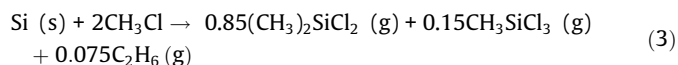


Fig. 7. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC and chlorosilanes is suppressed.

ilane becomes the only silane product into which all silicon is converted. The excess methyl chloride is fully decomposed into methane and carbon as dominant products.

The removal of carbon, silicon tetrachloride, and trichlorosilane (dichlorosilane plays no role) from the calculation makes dimethyldichlorosilane the main product with a yield of 88.5% at molar methyl chloride-to-silicon ratios up to 2.0 (Fig. 8). Side reactions leading to hydrocarbons are suppressed as well, mainly due to the lack of chlorosilanes as a sink of chlorine necessary for methyl chloride suppression. At reactant ratios higher than 3.0, silicon is entirely converted into methyltrichlorosilane. The excess methyl chloride decomposes into hydrocarbons and hydrogen chloride.

Given by the molar carbon-to-hydrogen ratio of 1:3, the formed hydrocarbons can be formally summarized as C<sub>2</sub>H<sub>6</sub>. Then, the following net equation becomes valid:



This points to a reaction pathway of methyltrichlorosilane formation parallel to that of dimethyldichlorosilane by linking the yield of methyltrichlorosilane with that of hydrocarbons and the amount of deposit coke as consequence of methyl chloride decomposition [11,33].

The suppression of SiC, carbon, and hydrocarbons rules out any decomposition of methyl chloride (Fig. 9). Therefore, excess methyl chloride remains unreacted and any silane yield is stable for molar methyl chloride-to-silicon ratios above 2. This pathway favors the formation of dimethyldichlorosilane (45.0%) and trimethylchlorosilane (36.1%) and makes, under the given constraints, silicon tetrachloride (the compound with a more negative Gibbs formation energy) less stable.

If silicon carbide, carbon, and hydrocarbons are suppressed from the calculation a product mixture of 89.2% dimethyldichlorosilane, 5.4% methyltrichlorosilane, and 5.4% trimethylchlorosilane results (Fig. 10). This is in close agreement to the known product distribution in the stationary period of the direct synthesis (Table 1). A considerably exothermic reaction enthalpy of  $-277.3 \text{ kJ mol}^{-1}$  is calculated at 300 °C. Therefore, the heat transport should significantly affect the product distribution.

The calculated reaction enthalpy is found at the lower limit of a range between  $-270$  and  $-420 \text{ kJ mol}^{-1}$  that was estimated from the different values of published formation enthalpies of methylchlorosilanes [34].

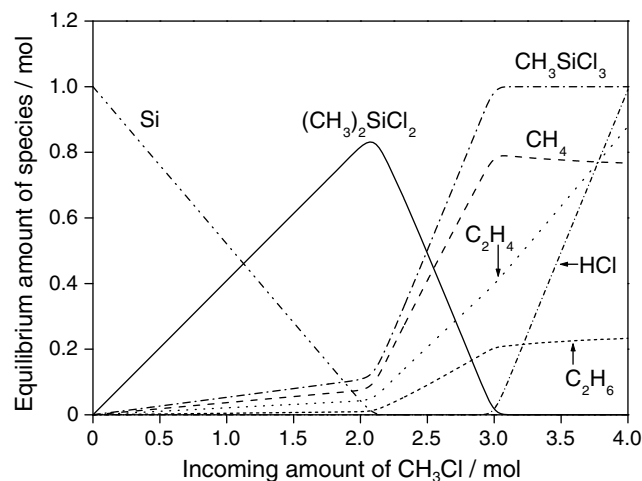


Fig. 8. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC, C, and chlorosilanes is suppressed.

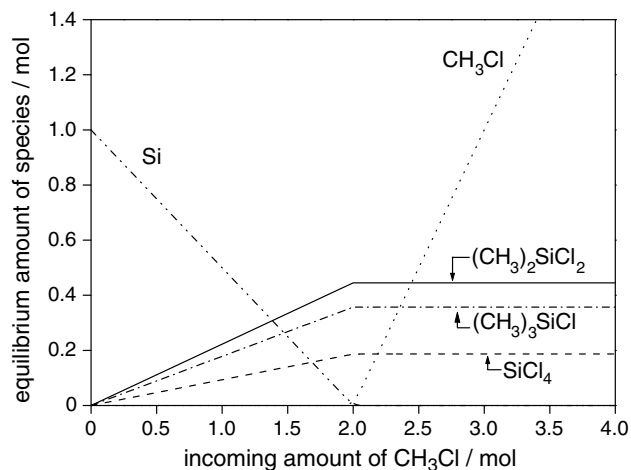


Fig. 9. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC, C, and hydrocarbons is suppressed.

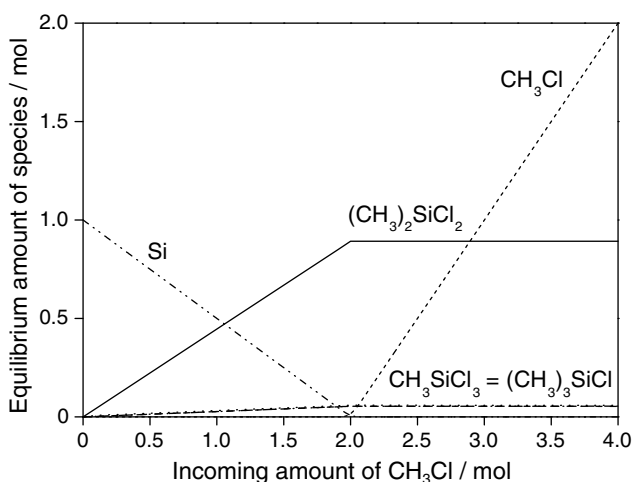


Fig. 10. Calculated product distribution of the reaction between 1 mol silicon and methyl chloride at 300 °C. The formation of SiC, C, hydrocarbons, and chlorosilanes is suppressed.

### 3.5. Modeling of the influence of hydrogen on the direct synthesis

The product distribution of direct synthesis can be influenced by the addition of hydrogen depending on the molar ratios between silicon, methyl chloride, and hydrogen. If a stoichiometry of 1 mol silicon and 2 mol methyl chloride is set at 300 °C, then the product distribution changes by subsequent addition of hydrogen almost linearly to finally 82.5% dimethyldichlorosilane, 2.8% methyltrichlorosilane, 8.7% trimethylchlorosilane, and 6.0% methyldichlorosilane at 4 mol hydrogen. Hydrogen chloride is the only non-silane byproduct.

The product distribution is found to be more sensitive with respect to the variation of the amount of silicon. In Fig. 11, the products formed by an increasing amount of silicon added to a fixed gas mixture of 2 mol methyl chloride and 3 mol hydrogen are illustrated. For incoming amounts of silicon below 1 mol, silicon is fully converted into the main products trimethylchlorosilane and dimethyldichlorosilane as in accordance to DeCooker et al. [35], and minor fractions of tetramethylsilane. Hydrogen chloride is the major non-silane side product. Above 1 mol of incoming silicon, hydrogen-containing and highly methylated chlorosilanes are dominant. Above 1.25 mol silicon, the product yield becomes con-

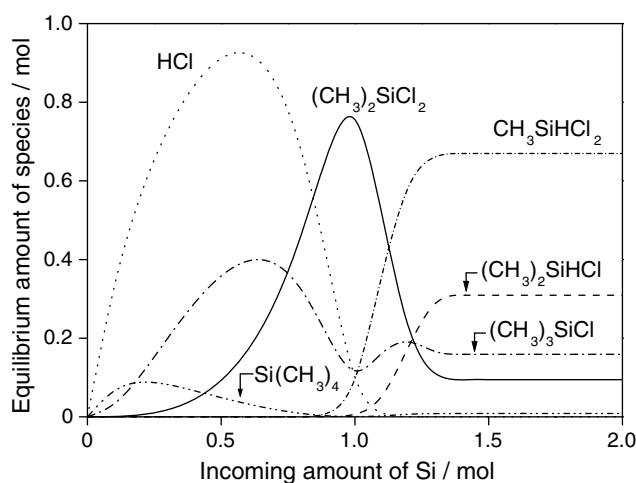
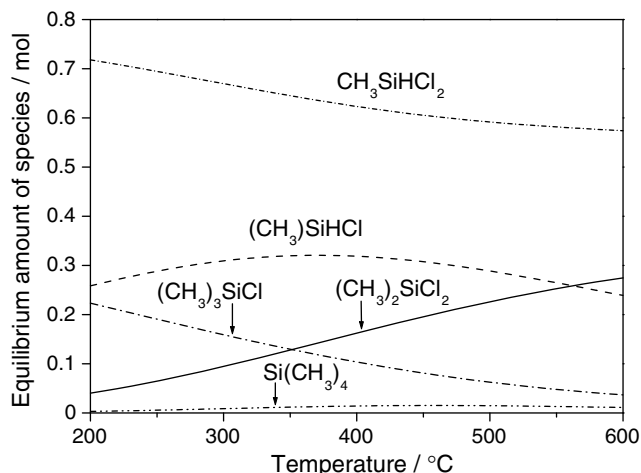


Fig. 11. Calculated product distribution of the reaction of 2 mol methyl chloride and 3 mol hydrogen with an increasing amount of silicon at 300 °C. The formation of SiC, C, hydrocarbons, and chlorosilanes is suppressed.

stant and independent on the amount of incoming silicon and the reaction is considered to be in a stationary regime. As already shown in Fig. 10, the formation of dimethyldichlorosilane is mainly forced by the suppression of SiC, carbon, hydrocarbons, and the chlorosilanes. The same is valid for Fig. 11 at incoming amounts of silicon of around 1 mol. Here, the Gibbs formation energy of dimethyldichlorosilane contributes about 85% to the global Gibbs energy minimum. The wider variety of silane products evolving above 1 mol silicon is similarly explained as for Fig. 6. With a Gibbs formation energy of  $-617.1 \text{ kJ mol}^{-1}$  at 300 °C CH<sub>3</sub>SiHCl<sub>2</sub> is slightly less favored than (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>; and (CH<sub>3</sub>)<sub>2</sub>SiHCl ( $-483.1 \text{ kJ mol}^{-1}$  at 300 °C) should even lesser expected in the product mixture than Si(CH<sub>3</sub>)<sub>4</sub>. However, exceeding the molar methyl chloride-to-silicon ratio of 2 in the presence of hydrogen opens the pathway to the hydrogen-containing silanes CH<sub>3</sub>SiHCl<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>SiHCl simply by a shift in law of mass action. Their resulting contribution to the total Gibbs energy overcompensates considerably the contribution of the obviously more stable (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> and CH<sub>3</sub>SiCl<sub>3</sub>.

The addition of hydrogen leads to a remarkably increased temperature dependence of the product distribution in the stationary regime. Fig. 12 displays an overview about the formed products between 200 °C and 600 °C for a molar reactant mixture of 2 mol methyl chloride, 3 mol hydrogen, and 1.5 mol silicon. The temperature dependence is furthermore expressed by the reaction enthalpy that amounts to  $-298.8 \text{ kJ mol}^{-1}$  at 300 °C. This enthalpy is equivalent to an adiabatic temperature (that can be related as a measure for local overheating of the solid reactant) of 1099 °C starting from an initial reaction temperature of 300 °C. The same reactant mixture without added hydrogen gives an enthalpy of  $-277.6 \text{ kJ mol}^{-1}$  and 1627 °C as adiabatic temperature. The lower adiabatic temperature in the presence of hydrogen is originated by the heat capacity of the introduced hydrogen, since it leaves the reactor mainly unreacted. This defines hydrogen as a medium to support an effective heat transfer.

If the reaction runs in the non-stationary regime, i.e. the product distribution depends on the amount of silicon (Fig. 11), hydrogen has no significant impact on the temperature dependence of the product distribution. Reaction enthalpy and adiabatic temperature for a molar reactant mixture of 2 mol methyl chloride, 3 mol hydrogen, and 1 mol silicon at 300 °C are calculated to  $-276.3 \text{ kJ mol}^{-1}$  and 1099 °C, respectively, in the absence of hydrogen the values are  $-277.6 \text{ kJ mol}^{-1}$  and 1445 °C, respectively. Again, the heat capacity of hydrogen lowers the adiabatic temperature and therefore the probability of local overheating.



**Fig. 12.** Temperature dependence of the product distribution for the reactions of 2 mol methyl chloride, 3 mol hydrogen, and 1 mol silicon. The formation of SiC, C, hydrocarbons, and chlorosilanes is suppressed.

There are two detailed reports in the literature [11,35] about the effect of hydrogen addition to the direct synthesis. The experimental data given therein, e.g. temperatures, reactant ratios, pressure, etc., were used to calculate the theoretical product distributions by means of the constrained thermodynamic equilibrium.

In Tables 2 and 3 a fair accordance between the experimental data of DeCooker et al. [35] and the calculated results is shown. Lewis et al. reported about a series of direct synthesis experiment with a reactant gas flow consisting of methyl chloride and hydrogen in varying mixing ratios and under different pressures [11].

The calculated products distributions for the reaction conditions given by Lewis et al. are summarized in Table 4. Here, the main reaction product, methylchlorosilane, and its calculated yields are in good agreement with the experimental results. Furthermore, the calculation is at least successful to identify the other

products, however, fails fully to reproduce their yields. In general, the calculated product mixture is higher in their total content with respect to hydrogen and methyl groups than in the experiments.

### 3.6. The influence of metals on the direct synthesis

Calculations were performed with transition metal silicide phases of Fe, Ni, and Cu as the solid reactants in the direct synthesis. As expected, the silicides act as sources of silicon and undergo Si depletion, so that their composition is shifted to metal-rich phases during the reaction. Fig. 13 depicts this for the case of NiSi<sub>2</sub> as solid reactant. Of special interest is the product gas phase composition. The calculated product distributions for all silicide phases of nickel, iron, and copper are identical to the calculated ones in case of pure silicon in any stage in the suppression of side products (Fig. 10). A relationship between the molar metal-to-silicon ratio of a silicide phase and the product distribution (as shown for the trichlorosilane synthesis [31]) does not exist. Furthermore, the final reaction product formed from the silicide phase is the pure metal and not the expected metal chloride as shown for the reaction of metals with methyl chloride with suppressed C–H bond cleavage in Fig. 13 (Section 3.2).

## 4. Discussion

### 4.1. Calculation of the induction period of direct synthesis

Experimental studies on the induction period of direct synthesis have shown, that methyl chloride reacts and decomposes on copper already at temperatures of 185 °C [36] and 200 °C [37] yielding the gaseous reaction products H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The absence of hydrogen chloride is explained by the formation of CuCl. Contrarily, Joklik and Bazant [38] found that methyl chloride decomposition in contact with copper at 300 °C proceeds to a negligible extent only, whereas under the same conditions in the presence of AlCl<sub>3</sub> a full decomposition occurs. The decomposition of methyl chloride leads to the deposition of carbon (coke) at the surface of

**Table 2**  
Experimentally determined [35] and calculated product distribution for the direct synthesis with added hydrogen

| Silicon conversion (%) | p(H <sub>2</sub> ) (atm) | p(CH <sub>3</sub> Cl) (atm) | Yield (mol%)                       |                                       |   |                                      |                                   |        |
|------------------------|--------------------------|-----------------------------|------------------------------------|---------------------------------------|---|--------------------------------------|-----------------------------------|--------|
|                        |                          |                             | CH <sub>3</sub> SiHCl <sub>2</sub> | (CH <sub>3</sub> ) <sub>2</sub> SiHCl | (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> | (CH <sub>3</sub> ) <sub>3</sub> SiCl | CH <sub>3</sub> SiCl <sub>3</sub> | Others |
| <i>Experimental</i>    |                          |                             |                                    |                                       |   |                                      |                                   |        |
| 20                     | 0.55                     | 0.45                        | 37.6                               | 32.7                                  | 23.4  | 2.9                                  | 3.4                               | 0      |
| 40                     | 0.55                     | 0.45                        | 23.8                               | 30.8                                  | 33.1  | 2.3                                  | 9.9                               | 0.1    |
| 65                     | 0.55                     | 0.45                        | 51.1                               | 24.4                                  | 17.3  | 2.1                                  | 4.8                               | 0.3    |
| <i>Calculated</i>      |                          |                             |                                    |                                       |   |                                      |                                   |        |
| –                      | 0.55                     | 0.45                        | 52.7                               | 24.6                                  | 10.1  | 11.8                                 | –                                 | 0.9*   |

Experiments were performed in a fixed-bed reactor at 332 °C using a copper–silicon contact mass with 10 wt% copper (\* only tetramethylsilane was calculated as side product).

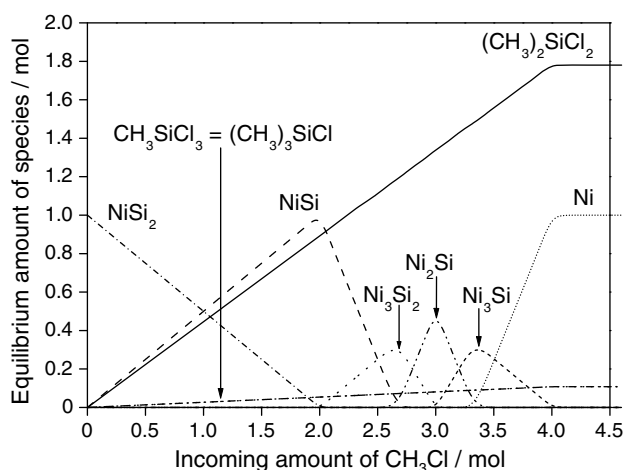
**Table 3**  
Experimentally determined [35] and calculated product distribution for the direct synthesis with added hydrogen

| Silicon conversion (%) | p(H <sub>2</sub> ) (atm) | p(CH <sub>3</sub> Cl) (atm) | Yield (mol%)                       |                                       |   |                                      |                                   |        |
|------------------------|--------------------------|-----------------------------|------------------------------------|---------------------------------------|---|--------------------------------------|-----------------------------------|--------|
|                        |                          |                             | CH <sub>3</sub> SiHCl <sub>2</sub> | (CH <sub>3</sub> ) <sub>2</sub> SiHCl | (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> | (CH <sub>3</sub> ) <sub>3</sub> SiCl | CH <sub>3</sub> SiCl <sub>3</sub> | Others |
| <i>Experimental</i>    |                          |                             |                                    |                                       |   |                                      |                                   |        |
| 50                     | 0.75                     | 0.25                        | 56.7                               | 28.5                                  | 10.3  | 1.2                                  | 2.7                               | 0.6    |
| 60                     | 0.75                     | 0.25                        | 70.3                               | 17.5                                  | 5.0   | 1.2                                  | 2.7                               | 3.3    |
| <i>Calculated</i>      |                          |                             |                                    |                                       |   |                                      |                                   |        |
| –                      | 0.75                     | 0.25                        | 53.3                               | 28.7                                  | 7.3   | 9.9                                  | –                                 | 0.8*   |

Experiments were performed in a fixed-bed reactor at 332 °C using a contact mass with 10 wt% copper, 0.1 wt% Zn, and 0.05 wt% Al (\* only tetramethylsilane was calculated as side product).

**Table 4**  
Experimentally determined [11] and calculated product distribution for the direct synthesis with added hydrogen using a contact mass prepared from technical grade silicon and cuprous chloride

| Reaction conditions                               |              |               |              |               |              |            |              |            |
|---|--------------|---------------|--------------|---------------|--------------|------------|--------------|------------|
| T (°C)  | 307          | 307           | 306          | 329           |              |            |              |            |
| p (bar)   | 1.4          | 2.1           | 2.8          | 2.8           |              |            |              |            |
| H <sub>2</sub> (L/min)                            | 0.39         | 1.08          | 0.92         | 1.33          |              |            |              |            |
| CH <sub>3</sub> Cl (L/min)                        | 0.42         | 0.73          | 0.59         | 0.71          |              |            |              |            |
| Reactor   | Fixed bed    | Fluidized bed | Fixed bed    | Fluidized bed |              |            |              |            |
| Yield (mol%)                                      |              |               |              |               |              |            |              |            |
| Product   | Experimental | Calculated    | Experimental | Calculated    | Experimental | Calculated | Experimental | Calculated |
| CH <sub>3</sub> SiHCl <sub>2</sub>                | 44.94        | 43.37         | 51.52        | 43.77         | 44.27        | 43.82      | 36.22        | 43.93      |
| (CH <sub>3</sub> ) <sub>2</sub> SiHCl             | 4.75         | 28.15         | 18.36        | 32.71         | 0.69         | 34.08      | 4.03         | 35.05      |
| (CH <sub>3</sub> ) <sub>3</sub> SiCl              | 2.37         | 16.83         | 1.72         | 14.47         | 1.40         | 13.72      | 1.59         | 13.13      |
| (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> | 31.70        | 10.19         | 15.76        | 7.61          | 34.19        | 6.93       | 42.80        | 6.44       |
| CH <sub>3</sub> SiH <sub>2</sub> Cl               | 8.68         | 0.22          | 0.00         | 0.34          | 7.74         | 0.39       | 1.22         | 0.43       |
| CH <sub>3</sub> SiCl <sub>3</sub>                 | 6.38         | 0.02          | 9.75         | 0.01          | 9.33         | 0.01       | 13.05        | 0.01       |
| HSiCl <sub>3</sub>                                | 1.17         | 1.23          | 2.89         | 1.08          | 2.38         | 1.04       | 1.09         | 1.01       |

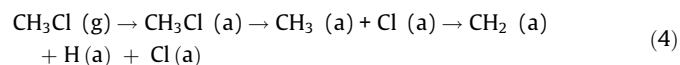


**Fig. 13.** Calculated product distribution of the reaction of 1 mol NiSi<sub>2</sub> with increasing amount of methyl chloride at 300 °C. The formation of SiC, C, hydrocarbons, and chlorosilanes is suppressed.

the contact mass. Wessel and Rethwisch [39] showed by means of temperature programmed oxidation, that a certain type of carbon, the so called  $\beta$ -coke, deactivates the contact mass by blocking the silane forming reactive silicon sites. Based on the studies by Frank et al. [5] and Wessel and Rethwisch [39] it was concluded, that methyl chloride decomposition occurs preferably at sites consisting of elemental copper instead of sites consisting of alloyed copper, e.g. Cu<sub>3</sub>Si.

The thermodynamic calculation is able to reflect the experimental results. The formation of CuCl in the presence of a copper catalyst and the more or less complete cleavage of the CH<sub>3</sub> group of methyl chloride, a thermodynamically metastable compound (Fig. 1), proceed strictly thermodynamically (Fig. 2).

The cleavage of the methyl group on a copper surface in the ultra-high vacuum proceeds according to Ali et al. [36] via radical intermediates as formally shown in Eq. (4) (g – gaseous, a – adsorbed). The identified decomposition products H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> are considered as the consequence from the further reactions of the adsorbed radical intermediates [36]. The further cleavage of the adsorbed intermediates yields to the deposition of elemental carbon.



However, the thermodynamic calculations presented here are only able to enable or to close the reaction pathway of methyl group cleavage. A fractional decomposition, which is assumed to be responsible for the formation of minor fractions of methylchlorosilane or dimethylchlorosilane cannot be computed. The consequences become obvious when the thermodynamically driven regime of the induction period turns into the kinetically determined stationary period of the direct synthesis.

#### 4.2. General aspects on the calculation of the stationary period in direct synthesis

The direct synthesis of methylchlorosilanes is a heterogeneous catalyzed reaction yielding to thermodynamically metastable reaction products. The reaction pathway to the thermodynamically favored compounds such as silicon carbide, methane, carbon, and silicon tetrachloride is closed in the stationary period of the direct synthesis. Qualitatively, this becomes obvious by the quite positive free formation enthalpies of the actually formed methylchlorosilanes compared to those of silicon carbide or silicon tetrachloride. Particularly, the absence of silicon tetrachloride (a formation of SiC at 300 °C is unlikely) as the silane compound having the most negative Gibbs energy of formation of all compounds underlines the kinetic character of the reaction.

The calculations were performed in runs of subsequent suppression of the respective most stable reaction product until the obtained product distribution matches the experimental ones. This procedure revealed three major reaction pathways: (i) The C–H bonds of the methyl group persist if the formation carbon and hydrocarbons is excluded. (ii) Methylchlorosilanes are formed only if the formation of silicon tetrachloride is suppressed. (iii) Hydrogen-containing methylchlorosilanes are only formed if hydrogen or hydrogen chloride is present during the reaction. Both can be added externally or formed by decomposition of the methyl group of methyl chloride.

A product distribution of 90% dimethyldichlorosilane, 5% methyltrichlorosilane, and 5% trimethylchlorosilane, which is close to the experimental ones (Table 1), is only obtained if carbon, hydrocarbons, and chlorosilanes are concertededly suppressed from the calculation (Fig. 10). According to this agreement the applied approach appears sufficient for a thermodynamic description of the stationary period of the direct synthesis.

This statement needs a detailed discussion in case of the calculation of the direct synthesis in the presence of hydrogen. With respect to the data of DeCooker et al. [35], the calculations are in remarkable agreement with the experimentally found product



distributions (Tables 2 and 3). Taking the total hydrogen balance over all formed products, the calculated products are in very good agreement with that of the experiments. Differences occur only in the methyl and chlorine contents in Table 3. Here, the calculated product distributions have in total a higher methyl content and lower chlorine content compared to the experimental yields. Regarding the data of Lewis et al. [11] (Table 4), only the calculated product molecules agree with the experimentally found ones, the computed yields for the individual compounds are far away from being satisfying. Generally, the calculated products have in total a higher methyl group and hydrogen content and are lower chlorinated than found in the experiments. The disagreement in Table 4 shows, that under the given reaction conditions additional complex processes occur, which are not adequately modeled by the total blocking of certain reaction pathways.

The major lack in the calculation is the total exclusion of compounds, like carbon, hydrogen, hydrocarbon, and chlorosilanes from the calculation. It can be assumed, that some of the suppressed compounds are formed to less extents (possibly as function of the catalyst and/or in the presence of promoters), which is sufficient for them to be converted in subsequent reactions into the experimentally observed side products. This is particularly valid for a fractional cleavage of the methyl groups according to Eq. (4), which generates a source of hydrogen, hydrogen chloride, and  $\text{CH}_2$  radicals as further potential reactants. In addition it is possible, that under some reaction conditions (particularly for a long residence time) redistribution equilibria [11] between minor and major reaction products play a major role, whereas in other cases their influence can be neglected. Of particular interest is the product molecule  $\text{CH}_3\text{SiH}_2\text{Cl}$  (Table 4) that is formed in an considerable yield only in the fixed-bed reactor. Its presence in the fixed-bed reactor experiments points to redistribution reactions as suggested by Lewis et al. [11] yielding to significant changes in the product distribution.

It has to be kept in mind, that any heterogeneous reaction is strongly influenced by local equilibria at the surface of the solid reactant. The common observed variation of the product distribution with the utilization of silicon (e.g. in Table 2) stands for the time dependent change of contact mass activity due to changes in the local surface composition as well as for an inhomogeneous distribution of the residence time of all involved gaseous compounds. Therefore, the variation of the product distribution as function of the molar reactant ratio, expressed as incoming amount of methyl chloride or silicon in the present work, has to be considered over a wide range.

Furthermore, the effect of contact mass deactivation by coking is likewise left out of consideration. A similar case of an insufficiently calculated influence of hydrogen in a direct reaction is found for the hydrochlorination of silicon. At the present state it is not possible to model the known H vs. Cl exchange in the presence of aluminum [25]. Another effect lying outside from the capabilities of the applied calculations is found in the silicide-catalyzed hydrochlorination of silicon tetrachloride to trichlorosilane [40,41]. In lab experiments it was observed, that  $\text{HSiCl}_3$  is not formed in the expected thermodynamic yield. A further experiment was performed with two subsequent reactors filled with silicide catalyst each. The first reactor was held at a constant reaction temperature of 850 °C, the temperature of the second one was varied. It turned out, that the experimentally obtained yield agreed exactly with the thermodynamically calculated one, if the reaction temperature of the second reactor was used. So it turned out, that the reverse reaction, i.e. the hydrochlorination of trichlorosilane, dominates the trichlorosilane yield at low temperatures.

These examples show exemplarily the control of the product distribution by the reaction conditions, the difficulties to assess

and to compare experimental results as well as to address the origin of changes in the product distribution.

#### 4.3. The role of metals in the direct synthesis

Fig. 10 shows, that the product distribution of 90% dimethyldichlorosilane, 5% methyltrichlorosilane, and 5% trimethylchlorosilane is already achieved in the absence of any catalyst. To clarify the role of the metal, calculations in the presence of the silicide phases of copper, iron, and nickel were performed. It should be noted, that the equilibrium silicide phases are used for the purpose of modeling only and not considered to be the catalytic active phases in direct synthesis.

Fig. 13 stands exemplarily for the results of any of the studied metals. As expected, the silicide phases are the source of silicon and are gradually depleted of silicon. Nickel and not nickel(II)chloride is the final reaction product in this calculation, since the formation of carbon, hydrocarbons, and hydrogen is suppressed (Eq. (1) and Fig. 2). Surprisingly, neither the metals nor the compositions of the used silicide phases have any influence on the product distribution. Furthermore, the sequences of the suppression of unwanted reaction products in the absence of any metal (Figs. 5–9) as well as the final product distribution as shown in Fig. 10 are identical. According to this calculation, metals seem to have no kinetic impact on the direct synthesis.

The use of silicide phases introduces a new source for silicon into the reaction having a lower chemical potential i.e. the chemical activity of the bound silicon compared to pure silicon. This should result into a general shift of the global minimum of the reaction system, leading to a changed product distribution and/or changed yields. This expectation was found to be valid in the calculation of the hydrochlorination of transition metal silicides [31]. It was shown, that the metal itself and the metal-to-silicon ratios of the considered silicide phases influence the yields for silicon tetrachloride and trichlorosilane. Generally, the yield of silicon tetrachloride increases with the affinity of the metal towards chlorine (expressed by the molar formation enthalpy of the metal chloride,  $\Delta_f H(\text{MCl}_x)$ ) ( $\text{Fe} > \text{Ni} > \text{Cu}$ ) and with the metal content in the silicide phase. Copper is a remarkable exception. It is the only metal that gives dichlorosilane as a thermodynamically determined reaction product. In analogy to the described relationship, Falconer et al. found a similar correlation between the chlorine content of the formed products and the metal–chlorine bond strength for the direct synthesis [5]. Now the question arises, why the thermodynamic calculation is able to reflect this behavior for the hydrochlorination but not for the direct synthesis.

The answer can be given by a closer look at the chemistry of dimethyldichlorosilane.

#### 4.4. Redistribution reactions of dimethyldichlorosilane

If all side-reactions leading to the formation of carbon, hydrocarbons, and silicon tetrachloride are suppressed from the equilibrium calculations, the resulting product distributions of the thermal decomposition (Fig. 4) and the direct synthesis (Fig. 10) are identical. Moreover, the presented thermodynamic model of the direct synthesis with its implemented constraints is exclusively described by the gas phase equilibrium of Eq. (2). This explains the apparent independence of the product distribution on the chemical potential of silicon in the solid phase as in the case of metal silicides (Fig. 13).

This defines the role of the metals in the direct synthesis as catalysts that choose a distinct reaction pathway to a kinetically controlled regime of methylchlorosilane formation far away from all thermodynamically favored reactions leading to C–H-bond cleav-

age and chlorosilane formation. The variation of product distributions with the added metal catalysts depends on the extent to adjust the required kinetically determined state. Beside this strong kinetic contribution, a thermodynamic contribution is still present as derived from the found correlation between the chlorine content in the final product mixtures and the metal–chlorine affinity. However, the exceptional role of copper in the direct synthesis and in the hydrochlorination of silicon is of different nature. In the latter case the formation of dichlorosilane is thermodynamically determined [31] whereas in the direct synthesis copper seems to be an excellent catalyst that opens a kinetically determined reaction pathway to the thermodynamically unfavored dimethyldichlorosilane.

The conclusion, that the direct synthesis is determined by Eq. (2), invites to two interesting speculations. It might be assumed at first, that copper is such an effective catalyst (presumably by preferential stabilization of  $\text{CH}_3\text{SiCl}$  silylenoids) that the yield of dimethyldichlorosilane is 100%. Then, the observed side products methyltrichlorosilane and trimethylchlorosilane are the inevitable consequence of Eq. (2). The second speculation is based on the reversibility of Eq. (2). A high yield of dimethyldichlorosilane might also be achieved by the use of catalysts or promoters that drive the reaction to form methyltrichlorosilane and trimethylchlorosilane as the only products.

The redistribution equilibrium of dimethyldichlorosilane was studied by Sauer and Hadsell [42] and Zemany and Price [43] in the presence of  $\text{AlCl}_3$  as catalyst in an autoclave at pressures between 1 and 76 atm, temperatures between 300 °C and 375 °C, and reaction times up to 48 hours. The thermal treatment of dimethyldichlorosilane gave a final composition of approx. 77.2% dimethyldichlorosilane, 11.1% trimethylchlorosilane, and 11.8% methyltrichlorosilane [42]. The commutation reaction between an equimolar mixture of trimethylchlorosilane and methyltrichlorosilane led to a final composition of approx. 77.7% dimethyldichlorosilane, 10.6% trimethylchlorosilane, and 11.7% methyltrichlorosilane, accounting for the reversibility of Eq. (2) [42]. Almost identical results for Eq. (2) were obtained by Golosova et al. [44]. The role of the strong Lewis acid  $\text{AlCl}_3$  as catalyst of this equilibration according to Eq. (2) is supported by Meier and May [45] by passing a mixture trimethylchlorosilane and methyltrichlorosilane through a  $\text{AlCl}_3$ – $\text{NaCl}$  melt at 400 °C.

The questions remain, whether the equilibration proceeds under the conditions of the direct synthesis and whether the practically observed product distributions can be explained by the redistribution reaction. The latter question points to the equimolar formation of trimethylchlorosilane and methyltrichlorosilane according to Eq. (2) in contrast to the common observation in direct synthesis, that the yield of methyltrichlorosilane is generally higher than that for trimethylchlorosilane. Apart from the work done by Sauer and Hadsell [42], Zemany and Price [43], Golosova et al. [44], and Meier and May [45], there are clear experimental results, that the reaction according Eq. (2) performed in the presence of  $\text{AlCl}_3$  containing catalysts, in an autoclave at high pressures, and for reaction times of several hours does not necessarily result in an equimolar formation trimethylchlorosilane and methyltrichlorosilane [46]. Independent of the reaction conditions and catalysts, the yields of methyltrichlorosilane were found to exceed by a factor ranging from 1.3 up to 4.7.

Joklik and Bazant [38] studied the reaction between dimethyldichlorosilane and gaseous  $\text{AlCl}_3$  at temperatures of 280 °C and 300 °C under atmospheric pressure. From the found maximum yield of 15.4% exclusively formed methyltrichlorosilane they concluded, that dimethyldichlorosilane is not involved in the reaction of Eq. (2) under the conditions of the direct synthesis. Compared to  $\text{AlCl}_3$  used alone, a  $\text{CuCl}$ – $\text{AlCl}_3$  catalyst was found to have an extraordinary catalytic activity [46]. The  $\text{CuCl}$ – $\text{AlCl}_3$  catalyst (mo-

lar ratio 1:2) reduces the activation energy between 264 °C and 304 °C from a value of 88  $\text{kJ mol}^{-1}$  for  $\text{AlCl}_3$  to 27  $\text{kJ mol}^{-1}$  as well as increases the reaction rate by a factor of  $10^6$ . However, the experiments were conducted in a closed reaction vessel that had brought to a certain reaction temperature, so that the residence time for the equilibration is far away from that of the direct synthesis. As consequence it has to be concluded, that Eq. (2) has an only negligible impact on the product distribution of the direct synthesis. The major side products trimethylchlorosilane and methyltrichlorosilane are likely to be formed in parallel silylene insertion reactions [11,33,47].

The constrained equilibrium calculation of the direct synthesis is a satisfying approximation for the direct synthesis that delivers the thermodynamic limit, and therefore, a defined criterion for the discussion of experimental results, e.g. how close a product distribution does reach the thermodynamic equilibrium.

#### 4.5. The impact of the reactor design

One essential parameter (beside the residence time) in such discussions is the actual temperature during the reaction. Reactions performed in fixed-bed reactors, having a higher probability of local overheating than fluidized-bed reactors, exhibit a lower selectivity for dimethyldichlorosilane, a higher temperature dependence of the product distribution, and a higher degree of methyl chloride decomposition leading to the formation of carbon and hydrogen-containing methylchlorosilanes. Reactors having a good heat transfer characteristics can form dimethyldichlorosilane in yields up to 90% [47]. It seems that the latter reaction conditions are closer to the constrained equilibrium calculations of the direct synthesis, since side products stemming from methyl group cracking are suppressed from formation.

The opposite seems to be valid for the direct synthesis in the presence of hydrogen. A reasonable matching of the calculated yields is obtained only for the fixed-bed reactor experiments in Tables 2 and 3 and for the major reaction product from the fixed-bed reactors in Table 4. It appears that the constrained equilibrium is a valid approximation for such experimental conditions if hydrogen is present. It is assumed, that side-reactions play a major role for the final product distribution in this reaction system, which are otherwise suppressed in a reactor with a more efficient heat transfer and shorter residence time (Table 4). This is consistently with the higher temperature dependence of the product distribution discussed with respect to Fig. 12.

## 5. Conclusion

The present paper describes a thermodynamic model of the direct synthesis based on the minimization of the Gibbs energy of the total reaction system. Unspecific kinetic hindrances in terms of a total and selective blocking of certain reaction pathways are introduced. The consequent suppression of the thermodynamically favored reaction products yields to the formation of dimethyldichlorosilane as the major reaction product and to a calculated product distribution close to the experimentally observed ones. Furthermore, this procedure led to the identification of three major reaction pathways. In thermodynamic terms, copper plays no role in the reaction, so that its known catalytic effect seems to be mainly of kinetic nature by opening a certain reaction pathway to the formation of the thermodynamically unfavored methylchlorosilanes. The constrained equilibrium is considered as the thermodynamic limit for the direct synthesis, serving as a benchmark to evaluate and discuss experimental results. However, the method of total and selective blocking of certain reaction pathways has to be seen as too stiff and too unspecific to model the direct synthesis

in all known aspects and its wide variety of product distributions even at quite comparable reaction conditions. Particularly, the consequences of a partial cleavage of the methyl group of methyl chloride are not adequately modeled. As example, the calculation of the minor reaction products in direct synthesis in the presence of hydrogen makes clear, that side effects have an enormous impact on the product distribution so that more sophisticated approaches have to be developed to obtain a deeper insight into the complex reaction system.

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