

Compensation effect in trichlorosilane synthesis

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Abstract

In a recent publication [J. Acker, K. Bohmhammel, J. Phys. Chem. B 106 (2002) 5105], the reactions between transition metal silicides and hydrogen chloride were studied by isothermal calorimetric measurements. The obtained apparent activation energies and pre-exponential factors show clearly a linear dependence that is attributed to the compensation effect. An isokinetic temperature of 696.9 ± 22.1 K was determined. According to Larsson's model of selective energy transfer, a characteristic frequency of 969.3 ± 46.5 cm^{-1} is calculated. The occurrence of the compensation effect is discussed in terms of chemisorption, precursor formation, and the involvement of surface species in essential reaction steps.

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1. Introduction

Considering that the temperature dependence of rate constants for a series of closely related reactions (indexed by i) is valid described by the Arrhenius equation (Eq. (1))

$$k_i = A_i \exp\left(\frac{-E_{A,i}}{RT}\right) \quad (1)$$

then, the linear relationship between the activation energies $E_{A,i}$ and the logarithm of the pre-exponential factors $\ln A_i$ according to the empiric relationship in Eq. (2) is denoted as compensation effect.

$$\ln A_i = a \left(\frac{E_{A,i}}{T_{\text{iso}}}\right) + b, \quad a \text{ and } b \text{ are constants} \quad (2)$$

The term “compensation” can be explained by the Eyring theory of reaction: a positive slope in Eq. (2) corresponds to a decreasing pre-exponential factor (entropy of the activated complex ΔS^\ddagger) with decreasing activation energy (enthalpy of the activated complex ΔH^\ddagger), i.e. a compensation of a loss of freedom in the

transition state by a reduced enthalpy of the transition state while the free energy remains constant.

Another common phenomenon, the isokinetic effect, is defined by a point of intersection for a family of Arrhenius lines representing a series of closely related reactions i in the $\ln k$ vs. $1/T$ plane. A relationship between compensation and isokinetic effect is found by rewriting Eq. (2) as

$$\ln A_i = \frac{E_{A,i}}{RT_{\text{iso}}} + \ln k_{\text{iso}} \quad (3)$$

and inserting into Eq. (1) gives finally

$$\ln k_i = \ln k_{\text{iso}} - E_{A,i} \left(\frac{1}{RT} - \frac{1}{RT_{\text{iso}}}\right) \quad (4)$$

Deduced from the coordinates of the point of intersection in the Arrhenius plane ($\ln k_{\text{iso}}$; T_{iso}) as well as from a slope of $1/T_{\text{iso}}$ and an intercept of $\ln k_{\text{iso}}$ at $E_{A,i} = 0$ in the $E_{A,i}$ vs. $\ln A_i$ plane both effects become synonymous, as shown theoretically in detail by Linert and Jameson [1]. In contradiction, Liu and Guo [2] showed that compensatory and isokinetic behavior are not necessarily in relationship to each other.

Compensation effect and isokinetic effect are phenomena which are very often found for homogeneous and heterogeneous reactions. In spite of the overwhelm-

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ing number of papers dealing with this effect, its origin and theoretical explanation are still matter of an ongoing debate (for reviews, see Refs. [1–3]). Few selected concepts with relevance for the present paper are briefly introduced here.

From point of view of heterogeneous catalysis, Larsson [4–6] developed the selective energy transfer model. According to this model, a characteristic single frequency vibration ω of a catalyst system and a vibration ν for the adsorbed reactant molecules on the catalyst are bound together as a damped oscillator of classical mechanics. As closer the vibration frequency of the reactant molecules come to the vibration of the catalyst as more effective is the energy transfer from the catalyst into the vibrational states of the adsorbed molecules. The efficiency of energy transfer is linked to the pre-exponential factor A in Eq. (2). The chemical reaction of the adsorbed molecule proceeds in case of perfect resonance $\omega = \nu$. This yields to the following expression for T_{iso} :

$$\Theta_{\omega=\nu} = T_{\text{iso}} = \frac{Nh\nu}{2R} = 0.715\nu \quad (5)$$

According to Patterson and Rooney [7] and Rooney [8] the compensation effect arises from a multi-step reaction.

$$k_{\text{exp}} = \frac{kT}{h} \prod K K^{\ddagger} \quad (6)$$

In his model of the extended Eyring equation (Eq. (7)), the equilibrium constant of the activated complex K^{\ddagger} can be separated from the product of the equilibrium constants $\prod K$ of all preceding reaction steps, like adsorption or chemisorption. Expanding the term $\prod K K^{\ddagger}$ of Eq. (6) (according to $\Delta G_i = RT \ln K_i$) gives:

$$\begin{aligned} \sum \Delta G^0 + \Delta G^{\ddagger} \\ = \sum \Delta H^0 + \Delta H^{\ddagger} - T(\sum \Delta S^0 + \Delta S^{\ddagger}) \end{aligned} \quad (7)$$

As stated above, compensation occurs for a constant $\sum \Delta G^0 + \Delta G^{\ddagger}$ by an inverse variation between the enthalpy and entropy.

$$\Delta(\sum \Delta H^0 + \Delta H^{\ddagger}) = T\Delta(\sum \Delta S^0 + \Delta S^{\ddagger}) \quad (8)$$

Therefore, the compensation effect is explained by equilibrium thermodynamics as a balance between a thermodynamic contribution of the activated complex and a thermodynamic contribution of all preceding reaction steps.

Finally, compensatory behavior itself can arise from adsorption and chemisorption of gases on solids [9,10].

As the first author in silicon chemistry, Lieske et al. [11,12] reported about the compensation effect in the reaction between silicon and methyl chloride (Table 1). This reaction is referred as direct synthesis throughout

this paper. He found that the reaction run with different contact masses (i.e. mixtures between silicon and copper containing various catalyst precursors and promoters, such as cuprous chloride, copper chloride, copper oxide; zinc, tin, and antimony) clearly obey the linearity between pre-exponential factor and activation energy according to Eqs. (2) and (3). Recently, Larsson and Lieske [13] applied Larsson's model of selective energy transfer [6] on the data of Refs. [11,12] and calculated an isokinetic temperature of 606 ± 20 K. The corresponding "heat bath" frequency of $850 \pm 30 \text{ cm}^{-1}$ was associated to an excitation of the Si-CH₃ rocking mode of catalytically active intermediates at the silicon surface.

Recently, Poco et al. [14] discussed similarities of compensation behavior in direct synthesis and isokinetic behavior found in wet chemical anisotropic etching of silicon in alkaline solutions [15] on a common base as anisotropic reaction with reaction rates different for the different crystallographic planes of silicon. Direct synthesis [16,17] and copper silicide formation [18,19] (as dominant step in activation of contact masses by reaction between silicon and cuprous chloride CuCl) were found to be anisotropic. The paper by Poco et al. [14] leads to the interesting statement that "the anisotropic character of these reactions seems to be responsible for the existence of compensation effect, which means that more than one active surface are present, each one related to a crystallographic plane".

Our present report refers to a recent kinetic study [20] about the reaction between transition metal silicide phases and hydrogen chloride by means of calorimetric methods.

2. Experimental and kinetic modeling

Kinetic data on direct reactions of silicon (the reaction between silicon with methyl chloride, hydrogen chloride or alcohols) are commonly obtained from the time-dependency of the amount of formed products. The data presented here are based on the thermokinetic evaluation of isothermal calorimetric measurements. All measurements were performed in a DSC 111 (Setaram, France). A flow cell is filled with a silicide sample. An empty flow cell serves as reference cell. A constant flow of argon is passed through both cells all the time. After having established a certain temperature and a stable baseline of heat flow, the reaction is initiated by opening a sample valve having a reservoir of a constant volume which is filled with dry hydrogen chloride. The argon flow introduces the hydrogen chloride into the sample cell. The heat flow (heat per time) between sample and reference cell is measured.

An investigation of a silicide phase starts at a temperature, which is too low for a chemical reaction. In subsequent runs with fresh samples, the reaction

Table 1

Overview about the relevant parameters belonging to isokinetic effect in alkaline etching of silicon and the compensation effect in direct synthesis and trichlorosilane synthesis

	Alkaline etching of silicon	Direct synthesis	Hydrochlorination
Temperature range of experimental data (K)	303–363	553–633	474–877
Range of activation energies (kJ mol ⁻¹)	31.7–86.9	22.6–95.1	41.6–196.3
T_{iso} (K)	628	603 ± 20	696.9 ± 22.1
Heat bath frequency (cm ⁻¹) ^a	873	850 ± 30	969.3 ± 46.5
Reference	[15]	[12,13]	Present study

^a According to Eq. (5).

temperature is increased with each run until the heat flow signal becomes structured.

In order to prevent uncontrolled depletion of silicon, the amount of silicide sample was chosen in such a way that always a manifold excess of silicon (depending on the stoichiometry of the silicide phase) with respect to hydrogen chloride is given. This ensures furthermore that only the adjacent metal-rich silicide phase according to the phase diagram is formed (one exception exists: the reaction between NiSi and hydrogen chloride yields Ni₂Si instead of Ni₃Si₂ due to a nucleation hindrance of Ni₃Si₂ below 600 °C [21,22]). Only the expected silicide phases were found after reaction, metal chlorides were not formed. The use of defined silicide samples and a minimal, but controlled depletion of silicon serves as the necessary condition that all derived kinetic data can be attributed to the pure silicide phases.

For kinetic evaluation, the heat flow curves of the reactions are fitted by the Avrami–Erofeev equation (Eq. (9)), a common thermokinetic model that describes a spherical grain formation and growth of a new solid phase in a matrix phase.

$$\text{rate} = \frac{dq}{dt} = q_{\text{total}} k^3 \frac{1}{3} t^2 e^{-(kt)^3} \quad (9)$$

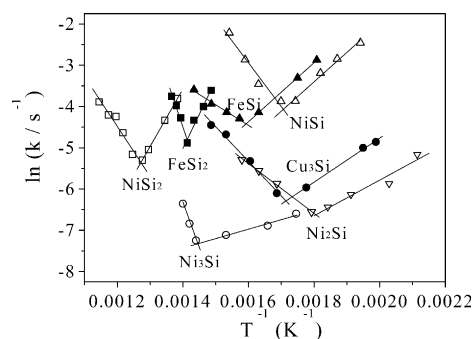


Fig. 1. Arrhenius plot of the reaction between various transition metal silicide phases and hydrogen chloride. (Reprinted with permission from Ref. [20]. Copyright 2002 American Chemical Society.)

This thermokinetic model describes a reaction by a first-order rate law; therefore, the obtained rate constants are independent from the composition of the reactants. The resulting activation energies do not have to be normalized to the stoichiometry of the considered silicide phase.

Main assumption of the thermokinetic model is that the entire reaction is valid described by a single rate constant which has no relationship to the real reaction mechanism. This criterion is practically satisfied up to moderate reaction temperatures while a uniform heat flow peak is obtained. The evaluation fails at the temperature at which a structured signal (peak splitting or shoulders) is observed.

A serious argument against the compensation effect is a lack of reliable experimental data. The used calorimetric system provides a constant temperature within 0.02 K. But, due to the exothermic reaction the temperature inside the reaction cell can temporarily rise up to several Kelvin above the isothermal temperature. The total error of the measurements, including reproducibility and data fitting, is below 10% [20].

3. Results

The Arrhenius diagram in Fig. 1 shows two activation energies for each silicide phase, an apparent positive activation energy at higher temperature and an apparent negative activation energy at lower temperature (all experimental results are summarized in Table 2). The point of intersect defines a characteristic temperature, denoted as T_{start} , which is a unique parameter for a silicide phase at a given hydrogen chloride partial pressure. T_{start} was identified as parameter to describe and to compare the reactivity between various silicide phases [20]. By plotting activation energies vs. pre-exponential factors for all studied silicide phases (Fig. 2) the linear dependence is obtained, which is characteristic for the compensation effect.

Table 2
Kinetic parameters of the reactions between transition metal silicide phases with hydrogen chloride

Silicide phase	Reaction start temperature, T_{start} (°C)	Minimum rate constant $\ln k_{\text{min}}$ at T_{start}	$E_{A+}(\text{app})$ (kJ mol^{-1}) ($T > T_{\text{start}}$)	Pre-exponential factor $\ln A_+$ ($T > T_{\text{start}}$)	$E_{A-}(\text{app})$ (kJ mol^{-1}) ($T < T_{\text{start}}$)	Pre-exponential factor $\ln A_-$ ($T < T_{\text{start}}$)
Ni ₂ Si	270	-6.63	49.9±1.8	4.23±0.36	-35.7±7.0	-14.43±1.66
Cu ₃ Si	310	-6.29	69.8±5.0	8.11±0.95	-44.3±2.4	-15.43±0.55
Cu ₃ Si+Zn ^a	n.d.	n.d.	80.0±20.5	8.56±3.94	n.d.	n.d.
NiSi	313	-4.07	88.1±13.0	14.00±2.53	-59.2±5.1	-16.22±1.14
FeSi	355	-4.42	41.6±3.9	3.55±0.71	-59.4±0.6	-15.80±0.13
Ni ₃ Si	418	-7.33	186.1±9.2	24.56±1.82	-19.6±3.5	-10.75±0.71
α-FeSi ₂	435	-4.82	196.3±22.1	28.55±3.70	-137.6±17.1	-28.19±2.98
NiSi ₂	513	-5.38	100.9±15.1	10.08±2.17	-115.8±0.7	-23.07±0.12

The errors are given as 1s. The symbols are: $E_{A+}(\text{app})$ —apparent positive activation energy, $E_{A-}(\text{app})$ —apparent negative activation energy, $\ln A_+$, $\ln A_-$ —pre-exponential factors belonging to $E_{A+}(\text{app})$ and $E_{A-}(\text{app})$, respectively. $\ln A_+$ and $\ln A_-$ were not published before. (Reprinted with permission from Ref. [20]. Copyright 2002 American Chemical Society.) n.d., not determined.

^a Cu₃Si alloyed with 1.5 at.% Zn.

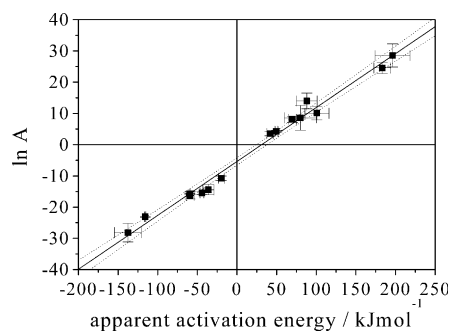


Fig. 2. Pre-exponential factor—apparent activation energy compensation plot of the data from Table 2 (confidence interval: 95%).

4. Discussion

4.1. Rate constants, apparent activation energies, and models

One has to be careful in the interpretation of thermokinetic data and to ask what effects can cause the measured calorimetric reaction signal. It depends on the magnitude of released heat and on the reaction rate, whether a reaction is or is not detected by a calorimeter [23]. If a reaction is faster than the response time of the calorimeter, the signal of reaction is convoluted by the response function of the calorimeter. A reaction signal is hardly to separate from the baseline, if the reaction rate is slow and the reaction heat is too low.

For complex reaction, as in the present case, a calorimetric signal is caused by the sum of reaction enthalpies of all proceeding reactions (adsorption or chemisorption, precursor formation, formation of silanes, etc.). A sudden introduction of hydrogen chloride to a native silicide sample causes a calorimetric signal that is mainly determined by processes at the very early stage of reaction, like chemisorption, surface reactions

and processes related to an initial bulk depletion. All these processes are usually attributed to the induction period of reaction. Therefore, our thermokinetic data represent initial rate constants of the induction period of hydrochlorination of transition metal silicides and not the steady-state period of a continuous silane formation.

In light of this discussion, the turn from negative to positive apparent activation energies with increasing temperature, the most remarkable feature in Fig. 1, becomes understandable. Below T_{start} , adsorption/chemisorption and precursor formation are dominating. The measured reaction heat increases slightly with increasing reaction temperature [20]. If the reaction temperature comes close to or higher than T_{start} , reaction rate and heat of reaction increase stronger. Above T_{start} the measured reaction heat results from the highly exothermic formation of chlorosilanes (trichlorosilane and silicon tetrachloride). Therefore, the reaction of any silicide phase with hydrogen chloride reaches an identical state at T_{start} , at which the formation of gaseous products just starts. This corresponds to the model of a characteristic temperature of onset temperature of reaction mentioned by Galwey [3] as a possible explanation for the compensation effect.

All activation energies discussed throughout this paper are apparent activation energies. These are functions of the activation energies and reaction enthalpies of many individual reaction steps. For the reaction between a silicide phase and hydrogen chloride, an apparent negative activation energy is a function of the exothermic adsorption enthalpy and the activation energy of precursor formation [20]. The Arrhenius-type temperature dependence of the adsorption equilibrium constant K_{ads} of hydrogen chloride adsorption (A_{ads} —pre-exponential factor of adsorption, ΔH_{ads} —adsorption enthalpy) and of a rate constant k_1 of precursor formation ($k_{1,0}$ —pre-exponential factor, E_A —activa-

tion energy) gives Eq. (10):

$$\frac{d[\text{precursor}]}{dt} = k_{1,0} A_{\text{ads}} p_{\text{eq}} e^{-(\Delta H_{\text{ads}} + E_A)/RT} \quad (10)$$

If $|\Delta H_{\text{ads}}| > E_A$ then a negative apparent activation energy for $T < T_{\text{start}}$ results. This model is consistent with other models to explain negative activation energies [24–30]. In case of complex reaction mechanisms, an equilibrium reaction followed by the rate-determining step seems to be a general pattern to cause apparent negative activation energies [20,31].

The apparent negative activation energies below T_{start} depend linearly on the silicon content of the silicide phase. In general, an increase of activation barrier with decreasing metal content indicates that solely the composition of the silicide phase, namely the metal constituent, controls this step (in similarity to geometric effect in bimetallic heterogeneous catalysis [32]). An exothermic chemisorption of hydrogen chloride on the silicide surface and exothermic formation of a chlorine-containing surface reaction layer, i.e. precursor formation, without liberation of gaseous products were identified as reactions that cause apparent negative activation energies [20].

Apparent positive activation energies are high for silicides with high silicon content (MSi_2 -type) or high metal content (M_3Si -type), but low for the phases in between. This led to a model that the silicide surface can be divided into hydrogen chloride adsorption sites (metal atoms) and reaction sites (silicon atoms), in which the crucial step is thought as the spillover from one site to another yielding to the formation of silylene precursors [20].

4.2. The compensation effect

Fig. 2 shows a linear relationship between pre-exponential factors and apparent positive and apparent negative activation energies for all studied silicide phases. An isokinetic temperature of $T_{\text{iso}} = 696.9 \pm 22.1$ K is obtained (cf. the arithmetic mean over all T_{start} is 648.1 K), which is ca. 100 K higher than for direct synthesis in case of Lieske's data. As in Ref. [12], T_{iso} is located within the range of the reaction temperatures.

Applying Larsson's model to our data in Fig. 2, we obtain a characteristic frequency of $969 \pm 46 \text{ cm}^{-1}$. The region between 1000 and 850 cm^{-1} is known for Si–H₂ scissor bend modes for molecules of SiH₂ (999 cm^{-1}) and SiH₄ (914 and 975 cm^{-1}) [33], and for vibration modes of Si–H_x species bound to Si(1 0 0) surfaces (Table 3).

The coincidence between the characteristic frequency and the region of Si–H_x species vibration modes does not necessarily imply that the compensation effect in trichlorosilane synthesis is exclusively linked to Si–H

Table 3
Si–H_x vibration modes on Si(1 0 0) in the range between 900 and 800 cm^{-1}

Vibration mode	Si–H ₂ (cm^{-1})	Si–H ₃ (cm^{-1})
Scissor	905 [37]	–
	907 [38]	–
	910 [39]	–
Deformation	–	862 [38]
	–	923 [38]
Wag, bend	890 [40]	–

bonds in the crucial reaction step. It has to be considered that T_{start} describes the liberation of chlorosilanes originated from precursor states. Possible mechanisms like reactive desorption, silylene insertion (Fig. 3) or spillover processes require necessarily an involvement of Si–H and Si–Cl bonds, even if their vibrations, like that from Si–Cl_x surface species on silicon (between 650 and 200 cm^{-1}) [34–36], are not active in the region between 900 and 800 cm^{-1} .

Finally, there is no reasonable explanation yet, why the order of silicide phases along the compensation line varies from negative to positive apparent activation energies. Lieske et al. [11,12] observed the same phenomena for various contact masses.

Based on the presented results we conclude that compensatory behavior in direct reactions is related to the preceding chemical reactions instead to the element silicon or to a certain group of transition metals. It seems that an involvement of two chemically different surface sites (metal and silicon) and a spillover process between them are essential. This is basically the same as pointed out by Poco et al. [14].

As mentioned above and in Section 4.1, the complex reaction mechanism of the hydrochlorination reaction may account for a validity of Rooney's model as well as for an explanation of the compensation effect in terms of adsorption of gases on solids. In fact, the derivation of the model of the apparent negative activation energy in Eq. (10) follows the same basic principles as Rooney's model. Unfortunately, without detailed knowledge of all reaction steps, their kinetics, and thermodynamics such a discussion remains qualitatively.

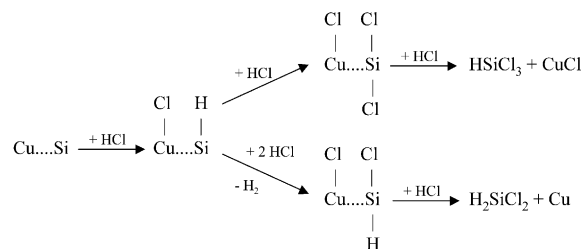


Fig. 3. Adapted reaction mechanism of dichlorosilane and trichlorosilane formation via silylene intermediates according to Lewis et al. [45].

4.3. One aspect on the role of the solid phase

In direct reactions, the metal is seen as catalyst or its precursor. But, the details of the mechanism are still unclear. It had been shown by Ertl and coworkers [41] that catalytic activity of RuO_2 origins from exchanging and restoring of lattice oxygen atoms. Iron as catalyst in ammonia synthesis becomes active by incorporation of nitrogen that leads to a metastable strained lattice structure at the iron surface [42]. For silicide-catalyzed hydrodechlorination of silicon tetrachloride it had been shown that the catalytic activity of the metal arises from thermodynamically stable transition metal silicide phases, which are continuously depleted and restored with silicon while the reaction runs [43,44]. Hence, the silicide catalyst is a reactant in silicide-catalyzed hydrodechlorination and a similar mechanism is thought for hydrochlorination of silicon in presence of a metal [20].

In direct synthesis, the situation becomes more complex by the use of silicon–copper mixtures. The state of a metal in a metal–silicon mixture is thermodynamically undefined and reactions in the solid phase (e.g. silicide formation) superimpose silane formation. If a pure silicide phase is used for reaction, then the solid phase entering the hydrochlorination is thermodynamically defined. And, if silicon depletion in the reaction is negligible, then a correlation of the physical and thermodynamic properties of the silicide phases to their reaction properties is justified [20]. Therefore, transport properties of the solid phase (as well as electronic properties) should play a role for such type of reaction.

In search for frequencies of silicide lattice vibrations related to T_{iso} , we have found a correlation between reaction rate and lattice dynamics. A parameter to describe the phonon vibration of a solid is the Debye temperature T_{Debye} . Due to the lack of data for all studied silicide phases we refer to an equation given in Ref. [46] to calculate this parameter (T_{m} —melting point, M —molar mass, V_{m} —molar volume).

$$T_{\text{Debye}} = \text{const} \sqrt{\frac{T_{\text{m}}}{MV_{\text{m}}^{2/3}}} \quad (11)$$

Eq. (11) is based on the equilibrium between lattice vibration and the kinetic energy of the atoms at T_{m} .

If one calculates the value of the constant in Eq. (11) for silicide phases with a known Debye temperature (NiSi: 497 K [47], 506 K [48]; FeSi: 745 K [49], 694 K [50], 596 K [51]; FeSi₂: 610 K [42]), the individual constants scatter around the suggested value of $200 \text{ K}^{1/2} \text{ g}^{1/2} \text{ cm mol}^{-5/6}$ [46]. To avoid any confusion about the value of the constant, in Fig. 4 the value of the expression in the root of Eq. (11) is plotted vs. the rate constant at T_{start} . The obtained dependence, which is not fully understood, implies an increasing reaction rate at T_{start} with increasing “hardness” of the silicide lattice.

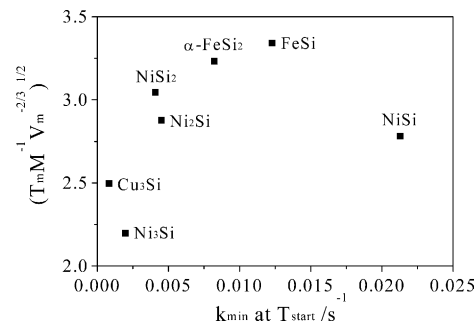


Fig. 4. Relationship between the “hardness” (as $(T_{\text{m}} M^{-1} V_{\text{m}}^{-2/3})^{1/2}$) of the silicide phases and their reaction kinetics (as minimum rate constant at T_{start}) in trichlorosilane synthesis.

We suggest the following interpretation. A high hardness results from strong bonds between the lattice constituents. Therefore, the unsaturated bonds at the surface of the solid should result in a strong attraction for gaseous molecules and lead to a high coverage of adsorbed molecules. A high reaction rate follows, if the reaction rate is proportional to the coverage with hydrogen chloride.

5. Conclusion

- 1) Positive and negative apparent activation energies and pre-exponential factors for reactions of silicide phases with hydrogen chloride were obtained from calorimetric measurements.
- 2) Due to the experimental procedure, the obtained kinetic parameters represent mainly processes at the very early stage of reaction, like chemisorption, surface reactions, and processes related to an initial depletion of silicon from the bulk silicide phase.
- 3) Although they reflect different stages of reaction, apparent positive and apparent negative activation energies show clearly a compensatory behavior. The isokinetic temperature was determined as $696.9 \pm 22.1 \text{ K}$, which lies within the range of the reaction temperatures.
- 4) The application of Larsson’s model of selective energy transfer gives a characteristic frequency of $969.3 \pm 46.5 \text{ cm}^{-1}$. This frequency might be attributed to Si–H_x vibrations and their involvement in the crucial step of reaction. This is in similarity to result of direct synthesis, in which the characteristic frequency was related to Si–CH₃ vibrations.

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