Compensation effect with Rochow synthesis

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The apparent activation energies and pre-exponential factors for the Rochow reaction, determined from reaction rate measurements at 280–360°C, strongly change, if contact masses are varied with respect to promoters, to the copper component's nature and percentage as well as to the silicon type. With each variation, the activation parameters consequently follow the same Cremer–Constable relation. The isokinetic temperature is in the range 330 ± 20°C, i.e., within the region of the reaction temperatures. This implies that the sequence of activities of compared contact masses can be reversed by a mere temperature variation. This may be a reason of contradictions in the literature on Rochow synthesis.

Keywords: methylchlorosilanes; Rochow synthesis; apparent activation energy; apparent pre-exponential factor; compensation effect

1. Introduction

The "direct synthesis" of methylchlorosilanes (MCS), the Rochow reaction,

$$\mathrm{Si}_{\mathrm{powder}} + \mathrm{CH_3Cl}_{\mathrm{gas}} \xrightarrow{\text{copper catalyst}} (\mathrm{CH_3})_x\mathrm{H}_y\mathrm{SiCl}_z; \quad x + y + z = 4,$$

is the basis of the whole of silicone industry, with dimethyldichlorosilane (DDS) being the desired main product. The reacting mixture of silicon, copper catalyst and promoters is called the "contact mass" (in units of measure: c.m.). Many papers deal with this reaction, reviewed e.g. in refs. [1–3], but, because of its high complexity, its scientific background is still poorly understood. The nature of the catalyst is still unclear. The catalyst is formed on the silicon surface from an added copper component (copper metal, oxides, salts) within the very first reaction period, the "induction period", during which activity and selectivity develop. The nature of the catalytically active sites and their number, the reaction mechanism, the nature of the induction period as well as the mode of action of the promoters are

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unsolved basic problems, despite recent efforts, which have brought some progress, e.g. [3–11].

We investigated the temperature dependence of the reaction on various types of contact masses in order to determine apparent activation parameters. We hoped that their possible changes might give some information, e.g. on changes of the reaction mechanism or of the number of active sites. The contact masses were varied with respect to promoters, to the copper component's nature and percentage as well as to the silicon type.

Activation energies for the Rochow reaction have been published, e.g. [1,3,4,9, 12,13]. In our paper, also corresponding pre-exponential factors will be reported for the first time.

The compensation effect ("isokinetic effect", "Cremer–Constable relation") has often been found in heterogeneous catalysis, but has no satisfactory explanation up to now. The inherent problems have been discussed for decades, e.g. [14]. Our paper cannot contribute to the solution of this theoretical problem. But we would like to show that just the phenomenology of the effect is worth knowing, because of its consistency in case of very different variations of the system and because of its consequences for the evaluation of experiments as well as for establishing scientific hypotheses.

2. Experimental

Materials. Two copper compounds were applied as copper components ("catalysts"): anhydrous copper(II) chloride $CuCl_2$ and copper(II) oxide CuO, pro analysi (Merck AG, Germany). As silicon, we used a highly pure semiconductor silicon, Si_{pure}, (Wacker-Chemie, Germany) and a technical-grade silicon, Si_{tech}, (Silgrain, Elkem, Norway). The particle size distribution of the two products was equal. The following well-known promoters were applied, single or in combination, each as pure metallic dust, as is usual, and mostly with standardized percentages: zinc, 0.25 wt%, antimony, 30 ppm; and tin, 30 ppm. From the above components, the contact masses as given in fig. 1 were prepared by thorough mechanical mixing, as is usual. The methyl chloride (in units of measure: mc) used was a product with a CH_3Cl content of $>99.6\%$. It was dried by means of zeolite 4-A.

Catalytic reactor. Catalytic measurements at normal pressure were carried out in a vibrating glass microreactor [15]. The reactor vibrated (rotating vibration) at 25 s^{-1}, causing an intensive whirling of the contact mass particles. Above 25 s^{-1}, the reaction rate did not change any more. The reactor charge amounted to $W = 10$ g contact mass. A methyl chloride flow of 2.7 ℓ/h was chosen. The reaction products were analyzed by on-line gas chromatography.

Procedure of catalytic measurements. The contact masses were dried in situ and afterwards heated to the reaction temperature of 340°C in flowing methyl chloride. The steady state of the reaction was reached at the latest after 1 h with copper chlor-

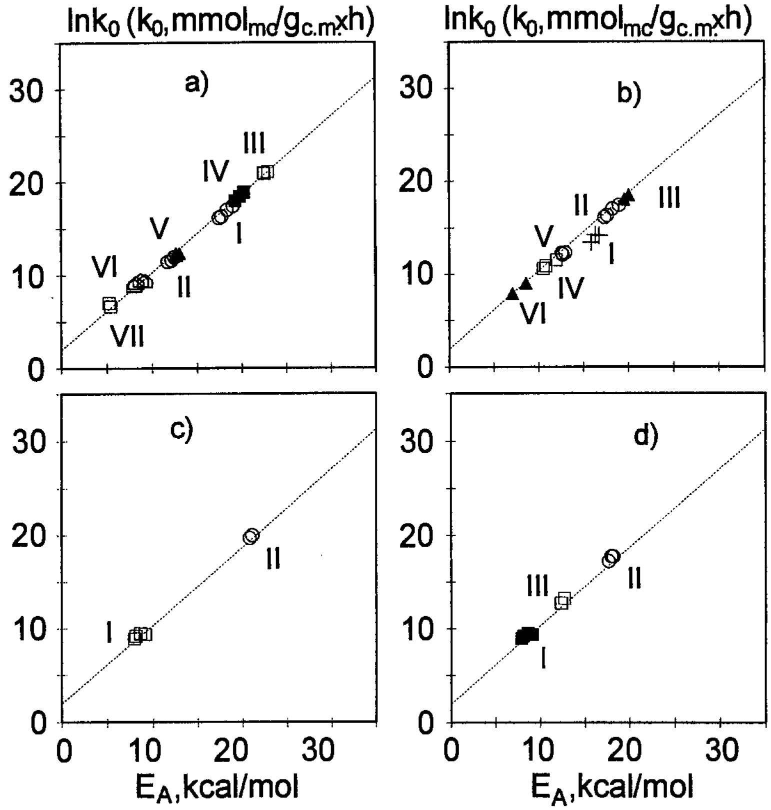

Fig. 1. Apparent activation parameters (individual, not averaged, measurements) on various contact masses as Constable–Cremer diagrams. (a) $CuCl_2/Si_{pure}$, 5 wt% Cu, with varied promoters; I: without promoters, II: 0.25 wt% Zn, III: 30 ppm Sb, IV: 30 ppm Sn, V: 0.25 wt% Zn + 30 ppm Sb, VI: 0.25 wt% Zn + 30 ppm Sn, VII: 0.5 wt% Zn + 0.015 wt% Sn; (b) $CuCl_2/Si_{pure}$ with varied copper content; I: 2.5 wt% Cu, without promoter, II: 5.0 wt% Cu, without promoter, III: 7.5 wt% Cu, without promoter, IV: I + 0.25 wt% Zn + 30 ppm Sb, V: II + 0.25 wt% Zn + 30 ppm Sb, VI: III + 0.25 wt% Zn + 30 ppm Sb; (c) Si_{pure} + 0.25 wt% Zn + 30 ppm Sn, with varied copper component; I: 5 wt% Cu as $CuCl_2$, II: 5 wt% Cu as CuO; (d) 5 wt% Cu as $CuCl_2$ + 0.25 wt% Zn + 30 ppm Sn; I: Si_{pure}, II: Si_{tech}, III: 50/50 mixture of Si_{pure} + Si_{tech}.

ide and after 3 h with copper oxide. In the steady state, the reaction temperature was varied in the range 280–360°C. This variation was realized within one single experimental run, i.e. with only one contact mass sample. Generally, the silicon conversion in our experiments was less than 15%. The methyl chloride conversion was calculated according to the method given in ref. [9]. Its values mostly amounted to $<15\%$. Under the precondition of a differential behaviour of the reactor, initial reaction rates were calculated as $r = Fx/W$ (F: methyl chloride flow rate, x: methyl chloride conversion). For the purpose of this paper, the errors connected with this simplification are negligible [8]. The error in the reaction rates was $< \pm 15\%$.

3. Results

With the experiments described in this paper, the selectivity of the reaction for the main product DDS amounted almost exclusively to values higher than 80%, i.e. the reaction proceeded rather uniformly. Therefore, for the conclusions to be drawn in this paper, it was sufficient to operate with the activation parameters of the total rate, i.e. of the methyl chloride consumption rate.

In fig. 1, the apparent activation energies E_A and pre-exponential factors k_0 are plotted in the coordinates of the Cremer–Constable relation $\ln k_0 = \ln k_i + E_A/RT_i$ (k_i: isokinetic rate constant, T_i: isokinetic temperature). The figure shows results of individual experimental runs and can give a visual impression of the reproducibility of E_A and k_0, therefore. The four parts of the figure represent four types of variation of the contact mass composition: variation of the promoters (a), of the copper content (b), of the copper component (c) and of the silicon quality (d). The straight line in the four partial figures is identical and is the result of an optimization including all results. The optimum line is defined by the abscissa segment $\ln k_i = 1.96$, corresponding to an isokinetic rate constant of 7.1 $\mathrm{mmol_{mc}/g_{c.m.}\,h}$, and by an isokinetic temperature T_i in the range 330 ± 20°C.

It can be seen that the activation parameters strongly vary and follow the compensation effect rather precisely. Even the scattering of the individual measurements is subject to the compensation effect. This means, the corresponding points scatter *only weakly around*, but *predominantly along* the compensation line. This appearance might be caused by accidental losses of varying amounts of copper or promoters, caused by the gas flow throughout the intensively whirling material. Figs. 1a and 1b show that varying promoter and copper contents also result in the isokinetic effect.

4. Discussion

Consistency of the compensation effect. The results show that E_A and k_0 strongly vary with changing contact mass composition and generally exhibit compensation behaviour. They follow the same compensation line. Two conclusions can be drawn:

– The compensation effect always occurs, if the contact mass composition is changed. Hence, it is not due to one special kind of contact mass variation. In so far, the compensation effect seems to be a general phenomenon in this system.

– The practical identity of the optimum line with all kinds of contact mass variation demonstrates the *consistency* of the effect, i.e. it is only one single effect.

Genuineness of the effect. With the detection of compensation effects, one must be careful [16]. For example, random errors in E_A correspond to random errors in $\ln k_0$ and can produce a picture similar to an isokinetic effect. But, there are strong arguments that the isokinetic effect reported in this paper is genuine, e.g.:

– The values of E_A and k_0 cover a wide range. The ratio of the highest and the lowest value of E_A is $22.7/5.4 = 4.2$. In ref. [17], a ratio of >2 was demanded.

– The practical identity of the compensation line in case of different kinds of contact mass variation can by no means be explained by statistical errors.

– The reproducibility of E_A and k_0 proves the clearness of the effect: The points of the individual measurements in fig. 1 form distinct clusters along the optimum line. The width of these clusters is about one order of magnitude below the total range of variation of E_A (5.4–22.7 kcal/mol). The logical consequence is that, with the next repetition of some experiment, the position of a new point along the optimum line can be *predicted* with sufficient accurateness. A prediction can by no means be based on statistical errors.

Some consequences for R&D work in this field of Rochow synthesis shall be discussed:

Interpretability of correlations. The most important implication of the compensation effect observed might be the following. As mentioned, the isokinetic temperature is positioned in a range 330 ± 20°C. Hence, if one compares two contact masses, their Arrhenius lines will intersect just within the range of typical reaction temperatures. The consequence is that the order of the reaction rate constants of compared contact masses can be reversed by a mere variation of the reaction temperature, if the isokinetic temperature is passed. The example in fig. 2 shows the Arrhenius plots of an unpromoted and of a zinc-promoted sample. The unpromoted sample is more active at high temperature, the zinc-promoted one is more active at low temperature. Thus, confusion must occur, if experiments below and above the isokinetic temperature are compared accidentally, without being aware of the compensation effect. The validity e.g. of the statement "Composition A is better than composition B", which is based on an empirically found correlation between contact mass composition and catalytic properties, is restricted to a certain

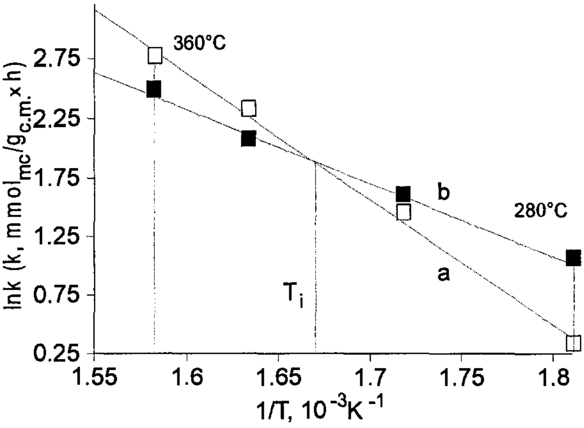

Fig. 2. Comparison of Arrhenius plots of contact masses with 5 wt% Cu in $CuCl_2/Si_{pure}$: unpromoted (a) and promoted with 0.25 wt% Zn (b).

temperature range, if the activation parameters on the contact masses A and B are subject to the compensation effect, If, in such a case, one ignores the effect and tries to explain the correlation in terms of science, one can easily come to a wrong hypothesis. Probably, this is one of the reasons of contradictions in the literature on Rochow synthesis.

Interpretability of the activation parameters. We showed that E_A and k_0 are interdependent by the isokinetic effect. But the physical background of this interdependence is not yet understood. Therefore, for the time being, it seems risky to interpret the activation parameters more in detail, as we intended originally. One should avoid to interpret changes in the activation energy as changes of the reaction mechanism, as has sometimes been tried, or, e.g., to explain changes in the pre-exponential factor as changes in the number of active sites.

Description of the Rochow system. The description of a catalytic system by the isokinetic equation and its parameters is a more complete and, therefore, useful description than only by reaction rates, selectivities and activation energies [14].

The question of interpretation. A generally accepted explanation of the frequently observed compensation effects in heterogeneous catalysis, first reported by Constable [18], is still missing. Compensation behaviour is found not only in heterogeneous catalysis, but also in case of homogeneous reactions [19]. This general occurrence should favour the assumption that the phenomenon "compensation effect" is best understood as only one single effect with a general mechanistic background, which applies to the whole of chemistry and not only to heterogeneous catalysis. Such general explanations have been given a basis of linear enthalpy–entropy relationships in the framework of the transition state theory, e.g. [20,21]. Recently, Patterson and Rooney [21] succeeded in an extension of Conner's [20] treatment, which could perhaps lead to a general solution of the problem.

On the other hand, it seems not yet possible to definitively assess those interpretations of the effect, which are based on assumptions specific for heterogeneous catalysis. One can, for example, at present certainly not exclude that the compensation effect is not a unique phenomenon, i.e. that compensation behaviour can be brought about by more than one mechanism. Among those specific explanations, some have frequently been discussed: an energetically heterogeneous catalyst surface [22], more than one type of catalytically active surface [23], linear relations between adsorption enthalpy and adsorption entropy [24], or surface concentrations of active sites, which differently depend on the reaction temperature on the related catalysts [17]. The compensation effect has also been explained in terms of selective energy transfer from the catalyst to the relevant vibration mode ("resonance hypothesis") of the reacting molecule [25].

Interpretations of compensation effects observed should be based on information on catalytically active sites. For example, following the concept of surface heterogeneity [22], the authors of [26] interpreted compensation effects in zeolite-catalyzed reactions essentially as a consequence of the heterogeneity of the acidic or basic sites, which had been characterized by appropriate methods. In the case of the Rochow reaction, our knowledge is still too poor by far for such an attempt. It is not even possible, at present, to relate the reaction rate to a number of active sites or to an active surface area, respectively, as is usual for other catalytic reactions. Provided such information, we feel that the compensation effect could be observed with even higher preciseness. But, there are no results from chemisorption / thermodesorption methods or from modern surface spectroscopic methods, which selectively characterize nature, number and energetic distribution of the active sites. Hence, reflections on the origin of the compensation effect with Rochow synthesis cannot be based on experiments, up to now.

5. Conclusions

– The apparent activation energy E_A and the apparent pre-exponential factor k_0 of the Rochow reaction on various contact masses strongly change when varying the promoters, the copper component's nature and percentage as well as the purity of the silicon.

– With all types of contact mass variation, the activation parameters exhibited a consequent isokinetic effect. The effect proved to be consistent, i.e. a single phenomenon. Because of the not yet understood interdependence of E_A and k_0, their interpretation in terms of reaction mechanism or catalyst structure is uncertain.

– The isokinetic temperature of 330 ± 20°C is positioned in the range of usual reaction temperatures of the Rochow reaction. That means that the sequence of the reaction rate constants of compared contact masses can be reversed already by a mere variation of the temperature. This implies an aggravation of the interpretation of experiments. The validity of comparing statements about the activity of contact masses is always restricted to a certain temperature range. It can be risky to derive scientific hypotheses from such statements, as long as the theoretical explanation of the compensation effect is pending. This might be one of the reasons of contradictions in the literature on Rochow synthesis.

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