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The Critical Transition between Phase Formation Modes in the Pyrolysis of Silane

Sergei V. Maklakov,* Rafik G. Aivazyan, Vylen V. Azatyan, Pavel V. Zhirkov and Lyudmila F. Satunkina

Institute for Structural Macrokinetics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 201 7357 "Vneshtekhnika"

A jump-wise transition between two different kinetic modes of phase formation in the course of silane pyrolysis has been found experimentally. In one mode the solid phase is formed as an aerosol, in the other as a film; the phenomenon can be reproduced by mathematical analysis of a model mechanism.

In spite of the importance of silane (SiH_4) pyrolysis in various branches of engineering, data on its kinetic regularities and mechanism are scarce and in many aspects inconsistent. The reaction exhibits a number of special features inherent to non-branching chain processes.[1,2] A number of particularly carefully accomplished investigations[1,3,4] enable an explanation of the very first stage of the process in the gaseous phase to be given. However, the suggested models do not explain the subsequent course of the pyrolysis, especially those features caused by heterogeneous reactions, such as the dependence of the rate of the process on the surface to volume ratio of the reactor (S/V), *etc*. This is also recognized in, *e.g*., refs. 3 and 4. Pyrolysis of monogermane (an analogue of SiH_4) proceeds by a non-branching chain mechanism[5] accompanied by the following critical phenomenon: a change in temperature and/or pressure in a certain very narrow region results in a change in the solid phase formation mode: instead of an aerosol a film is formed on the reactor surface.[6] An aerosol is also formed during pyrolysis of silane.[7,8]

This paper is focused on searching and explaining this critical transition in silane pyrolysis. In the majority of models and simulations the only solid phase formation taken into consideration is the formation of silicon film on the reactor walls. In the present paper the formation of aerosol is studied as well.

Experiments were carried out using a static vacuum set-up combined with an IKSS-2 spectrometer (for details, see refs. 5 and 6). A vacuumed and thermostated spectrometer cell with optical quartz or CaF_2 windows was used as a reactor. The reactor was 20 cm long and 4.0 cm in diameter. The temperature and pressure were varied within 723–833 K and 66–1335 Pa, respectively. During the course of the reaction, the pressure growth and the intensity of light transmitted by the cell were monitored with an S9-16 oscillograph. A glowbar and a KGM-100 tungsten-halogen lamp were used as light sources. The silane concentration was determined from the light absorption at 2189 cm^{-1} with an accuracy of ±5%. Mechanotrons allowed pressure measurement to an accuracy of ±1%. The relative concentration of aerosol (*i.e.*, phase formation course) was monitored by light extinction at 517 and 755 nm.

At constant temperature the formation of aerosol was found to be replaced by the formation of a film at nearly the same rate of thermal decay of SiH_4 and within a certain narrow pressure range. This is exemplified by the data presented in Figs. 1 and 2. As this phenomenon (a critical transition) has not been known before the reaction schemes proposed by different authors do not take this into account and accordingly do not explain it.

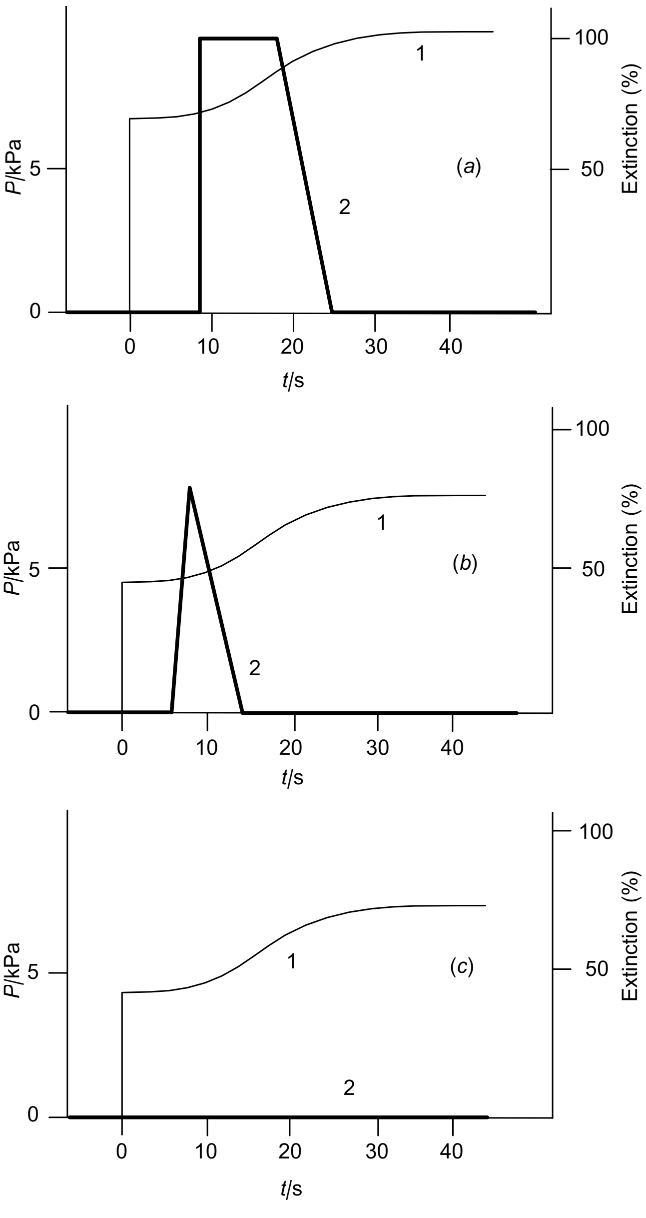

Fig. 1 Development of the current pressure P (1) and the light extinction (2) in the experiment. $T_0 = 753$ K. (*a*) $P_0 = 6.65$ KPa; (*b*) $P_0 = 4.4$ KPa; (*c*) $P_0 = 4.26$ KPa.

To reveal the main factors responsible for this critical nature, the reaction kinetics were studied as a function of the initial values of the pressure and the temperature. The initial state of the reactor surface was also varied using pre-treatment with the reaction itself and molecular oxygen.

The critical pressure P_* decreases from 4.4 to 0.45 kPa, the temperature being increased from 753 to 840 K. The decrease in P_* is also observed after pre-treatment with oxygen. Hysteresis is observed when the initial pressure is varied. Below P_* the symbatic dependence of the reaction rate on S/V with temperature increase changes to a weak antibatic one. The data obtained and available[1,3,4,9–11] allowed us to suggest the following simplified reaction mechanism (Scheme 1) which is compatible with the results, though not necessarily exclusively so. The distinctive feature of the scheme is that it accounts for homogeneous nucleation.

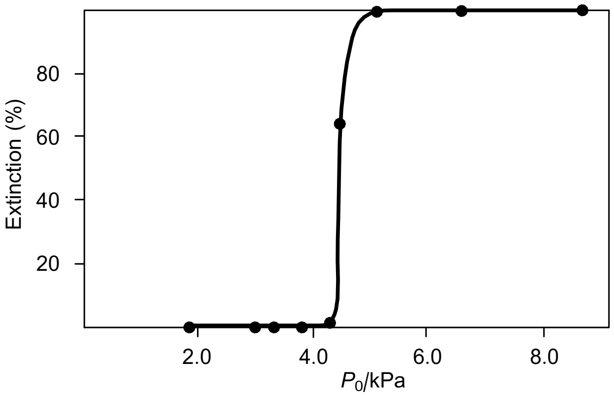

Fig. 2 Dependence of the light extinction *vs.* the initial pressure P_0.

0. SiH_4 + surface → $(SiH_2)_s + H_2$
1. *a* $(SiH_2)_s + SiH_4 \rightarrow (Si_2H_6)_s$
   b $(Si_2H_6)_s \rightarrow (Si_2H_4)_s + H_2$
   c $(Si_2H_4)_s \rightarrow (Si_2H_2)_s + H_2$
   d $(Si_2H_2)_s \rightarrow (SiH_2)_s + (Si)_s$

$(SiH_2)_s + SiH_4 \rightarrow (SiH_2)_s + (Si)_s + 2H_2$

2. $(SiH_2)_s + SiH_4 \rightarrow SiH_2 + (SiH_4)_s$
3. $SiH_4 + M \rightarrow SiH_2 + H_2 + M$
4. *a* $SiH_2 + SiH_4 \rightarrow Si_2H_6$
   b $Si_2H_6 + M \rightarrow Si_2H_4 + H_2 + M$
   c $Si_2H_4 + M \rightarrow Si_2H_2 + H_2 + M$
   d $Si_2H_2 + M \rightarrow SiH_2 + Si + M$

$SiH_2 + SiH_4 \rightarrow SiH_2 + Si + 2H_2$

5. SiH_2 + surface → termination
6. $SiH_2 + SiH_2$ → termination
7. Si + surface → $(Si)_s$
8. Nucleation process.

Scheme 1

The reactions (1) and (4) are presented as the result of corresponding links in the reaction chain (steps *a*–*d*). An analogous overall equation for the reaction chain link with the same stoichiometry is obtained when Si_3H_8 is taken into consideration. The reactions of Si_2H_6 and higher silanes do not limit the process due to their much higher reactivity.[3,4,12–14]

Solid silicon is produced by a heterogeneous reaction on the silicon surface and by deposition of gaseous silicon. The formation rate for aerosol particles is then proportional to the gaseous silicon concentration.

$$V_n = k_8[Si]$$

$$V_r = k_{71}[Si] + k_{11}[SiH_4][SiH_2]_s$$

Let us denote: $Y_1 = [Si]$ as the silicon aerosol volume; S as the aerosol surface; $Y_2 = [Si]$ as the volume of the silicon film on the reactor wall; $V_0 = 251$ cm^3 as the reactor volume; and

$S_0 = 264\ \mathrm{cm}^2$ as the reactor wall surface. The initial silane concentration was within $0.13–13 \times 10^{17}$ molecules cm^{-3}.

The Kolmogorov (Avrami) equation[15,16] for the aerosol volume (assuming that $Y_1 \ll V_0$) and the equation for aerosol surface can be written:

$$Y_1 = \frac{4\pi}{3}\int_0^t V_n\Big(\int_{t^*}^t V_\mathrm{r}\mathrm{d}\tau\Big)^3 \mathrm{d}t^* \tag{1}$$

$$S = 4\pi\int_0^t V_n\Big(\int_{t^*}^t V_\mathrm{r}\mathrm{d}\tau\Big)^2 \mathrm{d}t^* \tag{2}$$

Regarding t in equation (1) as a parameter, differentiating equation (1) with respect to t four times, taking into account equation (2) and introducing variables R and N, the integral equations (1) and (2) can be transformed into the differential equations (3)–(6).

$$\frac{\mathrm{d}N}{\mathrm{d}t} = V_n \tag{3}$$

$$\frac{\mathrm{d}R}{\mathrm{d}t} = NV_\mathrm{r} \tag{4}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 8\pi RV_\mathrm{r} \tag{5}$$

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = SV_\mathrm{r} \tag{6}$$

Variables N and R have a clear physical meaning: N is the number of aerosol particles and R is the sum of the radii of the aerosol particles.

The main kinetic equations have the form:

$$-\frac{\mathrm{d}[\mathrm{SiH_4}]}{\mathrm{d}t} = \frac{S+S_0}{S_0}[\mathrm{SiH_4}]\{k_0 + (k_1+k_2)[\mathrm{SiH_2}]_\mathrm{s}\} + [\mathrm{SiH_4}]\{k_3 + k_4[\mathrm{SiH_2}]\} \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{SiH_2}]_\mathrm{s}}{\mathrm{d}t} = \frac{S+S_0}{S_0}[\mathrm{SiH_4}]\{k_0 - k_2[\mathrm{SiH_2}]_\mathrm{s}\} \tag{8}$$

$$\frac{\mathrm{d}[\mathrm{SiH_2}]}{\mathrm{d}t} = \frac{S+S_0}{S_0}\{k_2[\mathrm{SiH_4}][\mathrm{SiH_2}]_\mathrm{s} - k_5[\mathrm{SiH_2}]\} + k_3[\mathrm{SiH_4}] - k_6[\mathrm{SiH_2}]^2 \tag{9}$$

$$\frac{\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = \frac{S+S_0}{S_0}[\mathrm{SiH_4}]\{k_0 + 2(k_1+k_2)[\mathrm{SiH_2}]_\mathrm{s}\} + k_3[\mathrm{SiH_4}] \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{Si}]}{\mathrm{d}t} = k_4[\mathrm{SiH_4}][\mathrm{SiH_2}] - k_7[\mathrm{Si}](S+S_0) \tag{11}$$

$$\frac{\mathrm{d}Y_2}{\mathrm{d}t} = S_0V_\mathrm{r} \tag{12}$$

Phase formation proceeds differently above and below the critical pressure from the very beginning of the process after the induction period. Thus, to elucidate the features of the critical transition, let us consider the initial stage when the silane concentration is close to the initial one (as in the blow-up theory[17]), *i.e.*, $[\mathrm{SiH_4}] \approx X_0$. It is taken into consideration that during this stage the quasi-stationary concentrations of intermediate products $[\mathrm{SiH_2}]_\mathrm{s}$, $[\mathrm{SiH_2}]$ and $[\mathrm{Si}]$ take place. From equation (8) it therefore follows that $[\mathrm{SiH_2}]_\mathrm{s} = k_2/k_0$. Neglecting the quadratic (non-linear) chain termination in equation (9), we obtain $[\mathrm{SiH_2}] = X_0/k_5[k_0 + k_3S_0/(S_0+S)]$. The estimated rate constants are $k_0 = 1.7 \times 10^{-3}\ \mathrm{s}^{-1}$ and $k_3 = 1.66 \times 10^{-5}\ \mathrm{s}^{-1}$, *i.e.*, $k_0 \gg k_3S_0/(S_0+S)$. Thus, we obtain $[\mathrm{SiH_2}] = X_0k_0/k_5$. Taking [Si] from equation (11), the nucleation rate and normal growth rate for a film can be written as follows:

$$V_\mathrm{n} = \frac{k_8X_0^2k_0k_4}{k_5k_7(S_0+S)};\ V_\mathrm{r} = F_7 + F_1$$

$$F_7 = \frac{k_{71}X_0^2k_0k_4}{k_5k_7(S_0+S)};\ F_1 = k_{11}k_2/k_0X_0$$

Let us consider two limiting cases:

1. The normal growth of solid silicon occurs mainly by heterogeneous reaction on the silicon surface ($F_7 \ll F_1$). From equations (6) and (12), it follows that $\mathrm{d}Y_1/\mathrm{d}t = X_0^5F_4(t)$; $\mathrm{d}Y_2/\mathrm{d}t = X_0F_5(t)$ and consequently $\mathrm{d}Y_1/\mathrm{d}Y_2 = X_0^4F_3(t)$.
2. Normal growth of solid silicon proceeds mainly by gaseous silicon deposition ($F_7 \gg F_1$). From equations (6) and (12) it follows that $\mathrm{d}Y_1/\mathrm{d}t = X_0^8F_1(t)$; $\mathrm{d}Y_2/\mathrm{d}t = X_0^2F_2(t)$; $\mathrm{d}Y_1/\mathrm{d}Y_2 = X_0^6F_3(t)$.

Let us consider the initial concentration of silane to be a parameter. In any case the relative rate of aerosol formation $\mathrm{d}Y_1/\mathrm{d}Y_2$ depends on X_0 at least as a polynomial of the fourth degree. At small values of X_0, aerosol is hardly formed and silicon deposits totally on the reactor wall. With increasing X_0, the relative rate of aerosol formation increases drastically and at $X_0 > X_{0*} = 1/F_3(t)^n$, $n < 1/4$, silicon precipitates mainly as an aerosol (Fig. 3). Thus, there exists a value $X_0 = X_*$ that separates two markedly different modes: aerosol formation and silicon film growth on the reactor walls.

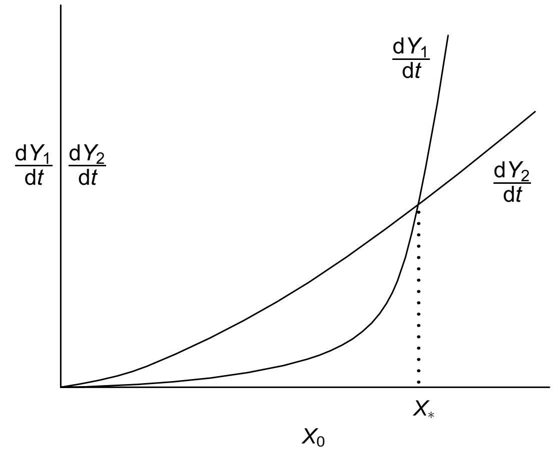

Fig. 3 Schematic dependence of the silicon growth rate: as a film, $\mathrm{d}Y_2/\mathrm{d}t$; as an aerosol, $\mathrm{d}Y_1/\mathrm{d}t$ *vs.* the initial silane concentration X_0.

Our approach makes it possible to demonstrate that the critical transition from one mode to another has a topological nature. The film growth is a one-dimensional process, whereas aerosol particle growth is a three-dimensional one [see equations (6) and (12)]. If the normal rate $\mathrm{v_r}$ increases monotonically with a parameter (X_0 in our case), then an increase in this parameter will result in a transition from the film growth mode to an aerosol formation mode. Because of the steep dependence of the relative rate of aerosol formation ($\mathrm{d}Y_1/\mathrm{d}Y_2 \sim X_0^4$), this abrupt change of mode is observed in our experiments.

The above kinetic scheme is chosen only because we need to be specific, and the details are not crucial to the argument: the important feature is that it does demonstrate a mathematically monotonic increasing dependence of the normal rate of solid phase growth on the initial concentration. It must be emphasized that if the process under consideration were not a chain and the scheme were different, the main conclusion would be the same: the critical transition is caused by the topological nature of the solid phase growth.

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