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Model for the Formation of Silicon Carbide from the Pyrolysis of Dichlorodimethylsilane in Hydrogen: II, Silicon Carbide Formation from Silicon and Methane

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A model is developed for the deposition of silicon carbide from the pyrolysis of dichlorodimethylsilane in hydrogen, in a tubular reactor at temperatures from 700° to 1100°C and 1.013 × 10^5 Pa (1 atm) pressure. Concentration of dichlorodimethylsilane varied from 2 to 8 vol%. Gas chromatography was used to determine the volatile products of reaction, and gravimetric analysis was used to determine the total silicon and silicon carbide deposition on the tube. The model developed based on the experimental data that assumes the following chemical reactions:

$$(CH_3)_2SiCl_2 + 2H_2 \rightarrow 2CH_4 + H_2SiCl_2$$

$$HSiCl_3 + H_2 \Leftrightarrow H_2SiCl_2 + HCl$$

$$H_2SiCl_2 \Leftrightarrow 2HCl + Si$$

$$HSiCl_3 + HCl \Leftrightarrow SiCl_4 + H_2$$

$$Si + CH_4 \rightarrow SiC + 2H_2$$

The rate constants derived from a nonlinear regression analysis are reported.

I. Introduction

The manufacture of silicon carbide (SiC) ceramic composites, by chemical vapor infiltration (CVI), can use methylchlorosilanes as starting compounds. These compounds pyrolyze to form SiC matrix material in the piles of woven fabric. Background information describing the process may be found in over 70 citations which are included in Refs. 1 to 3.

In designing reactors for the infiltration process and in understanding the deposition process, it would be beneficial to develop an engineering model for the pyrolysis chemistry. A model, based on previous work, has been suggested for this process.[1–3] For the reaction of the particular methylchlorosilane of interest, dichlorodimethylsilane (DMS) pyroysis in hydrogen (H_2), the following simple reaction scheme was assumed:

$$DMS + 2H_2 \xrightarrow{k_1} H_2SiCl_2 + 2CH_4 \tag{1}$$

(assumed 1st order in DMS and H_2)

$$H_2SiCl_2 \xrightarrow{k_2} Si + 2HCl \tag{2}$$

(assumed 1st order in H_2SiCl_2)

$$Si + 2HCl \xrightarrow{k_3} H_2SiCl_2 \tag{3}$$

(assumed 2nd order of HCl; 0 order in Si)

$$H_2SiCl_2 + HCl \xrightarrow{k_4} HSiCl_3 + H_2 \tag{4}$$

(assumed 1st order in H_2SiCl_2 and HCl)

$$HSiCl_3 + H_2 \xrightarrow{k_5} H_2SiCl_2 + HCl \tag{5}$$

(assumed 1st order in $HSiCl_3$; 0 order in H_2)

$$HSiCl_3 + HCl \xrightarrow{k_6} SiCl_4 + H_2 \tag{6}$$

(assumed 1st order in $HSiCl_3$ and HCl)

$$SiCl_4 + H_2 \xrightarrow{k_7} HSiCl_3 + HCl \tag{7}$$

(assumed 1st order in $SiCl_4$; 1/2 order in H_2)

$$Si + CH_4 \xrightarrow{k_8} SiC + 2H_2 \tag{8}$$

(assumed 1st order in CH_4; 0 order in Si)

The rate equations for this scheme are as follows:

$$\frac{d(DMS)}{dt} = -k_1(DMS)(H_2) \tag{I}$$

$$\frac{d(SiCl_4)}{dt} = -k_7(SiCl_4)(H_2)^{1/2} + k_6(HSiCl_3)(HCl) \tag{II}$$

$$\begin{aligned}\frac{d(HSiCl_3)}{dt} &= k_7(SiCl_4)(H_2)^{1/2} - k_6(HSiCl_3)(HCl) \\ &\quad - k_5(HSiCl_3) + k_4(H_2SiCl_2)(HCl)\end{aligned} \tag{III}$$

$$\begin{aligned}\frac{d(H_2SiCl_2)}{dt} &= k_5(HSiCl_3) - k_4(H_2SiCl_2)(HCl) \\ &\quad - k_2(H_2SiCl_2) + k_3(HCl)^2 \\ &\quad + k_1(DMS)(H_2)\end{aligned} \tag{IV}$$

$$\frac{d(Si)}{dt} = k_2(H_2SiCl_2) - k_3(HCl)^2 - k_8(CH_4) \tag{V}$$

$$\begin{aligned}\frac{d(HCl)}{dt} &= k_7(SiCl_4)(H_2)^{1/2} - k_6(HSiCl_3)(HCl) \\ &\quad + k_5(HSiCl_3) - k_4(H_2SiCl_2)(HCl) \\ &\quad + 2k_2(H_2SiCl_2) - 2k_2(HCl)^2\end{aligned} \tag{VI}$$

$$\frac{d(CH_4)}{dt} = 2k_1(DMS)(H_2) - k_8(CH_4) \tag{VII}$$

$$\begin{aligned}\frac{d(H_2)}{dt} &= -2k_1(DMS)(H_2) + k_4(H_2SiCl_2)(HCl) \\ &\quad - k_5(HSiCl_3) + k_6(HSiCl_3)(HCl) \\ &\quad - k_7(SiCl_4)(H_2)^{1/2} + 2k_8(CH_3)\end{aligned} \tag{VIII}$$

where *t* is time.

In this sequence, DMS forms methane (CH_4) and chlorosilanes first. The chlorosilanes are reduced to Si, which can be etched by hydrogen chloride (HCl) (reaction (3)) or react with

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CH_4 to form SiC (reaction (8)). Reference 3 presents the model development and the rate coefficients derived from experimental data for a subset of this sequence, the formation of Si from chlorosilanes (reactions (2) to (7)). The model assumed plug flow and no mass transfer effects. For operation at steady state, reactor length was substituted for time as the independent variable.[3] Using this model, an analogous mathematical treatment, and experimental data obtained in a similar tubular reactor, the reaction coefficients are derived for reactions (1) and (8) (i.e., for SiC formed from the pyrolysis of DMS in H_2).

II. Experimental Apparatus and Procedure

The experimental hardware and procedure were similar to those already described in detail in Refs. 1 and 2. The reactor was an integral reactor; therefore, the data obtained were integral, not differential, rate data. The experimental setup is shown in Fig. 1. The DMS, used as the feed compound, was vaporized from a bubbler immersed in a constant-temperature bath. Hydrogen was used as the carrier gas. The DMS was diluted or mixed with other gases in a manifold, and this mixture was fed into a heated quartz reactor. The reactor consisted of a removable quartz tube within an outer quartz jacket; the reaction took place in the inner tube. The heated zone was 38.1 cm long, the inside diameter was 2.1 cm, and the nominal total flow rate was 150 cm^3/min. At the nominal flow rate, the Reynolds number was estimated to be 20 or laminar flow. Temperatures in the reactor were measured with a thermocouple along the center of the reaction tube and at five locations around the outer walls along the axis of the tube. No significant radial temperature gradients were found at reaction temperatures. Typical axial temperature profiles along the center of the reactor tube are shown in Fig. 2. Volatile products were analyzed with a Varian Model 3300 chromatograph, fitted with corrosion-resistant nickel tubes and a thermoconductivity cell.

The standard procedure for a run was, first, to evacuate the system and refill it with H_2. The flow of DMS was then started, after the reactor was heated to reaction temperature. The reaction tube was weighed before and after the run to obtain the total weight of solid deposited as a function of reactor condition. The deposit was stripped from the walls and analyzed for the total amount of elemental Si, free C, Cl, O, H, and for SiO_2 and SiC. The SiO_2, Si, and SiC were analyzed using a technique developed by the French Association for Standardization (AFNOR).[1]

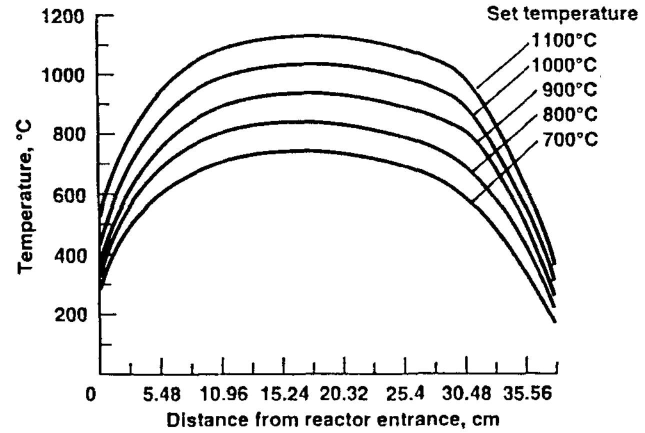

Fig. 2. Typical temperature profiles.

III. Results and Discussion

Figures 3 to 6 present experimental data for products issuing from the reactor as a function of reactor temperature. The nominal feed concentration was 4 vol% DMS and the flow rate was 150 cm^3/min. In Figs. 3 and 4, both $HSiCl_3$ and $SiCl_4$ reach maximum concentrations of about 1% each at 800° to 900°C. This accounts for about half of the original atomic Si present in the DMS feed. At 1100°C these volatile chlorosilanes are negligible. Thus at lower temperatures, a major portion of the DMS which reacts remains as volatile products in the gas stream, which can vent from the reactor. At higher temperatures, most of the DMS has reacted to a solid product, which remains as a deposit in the reactor. Figure 5 shows the concentration of CH_4 produced as a function of temperature. Between 800° and 900°C, the yield of CH_4 produced reaches a maximum and is

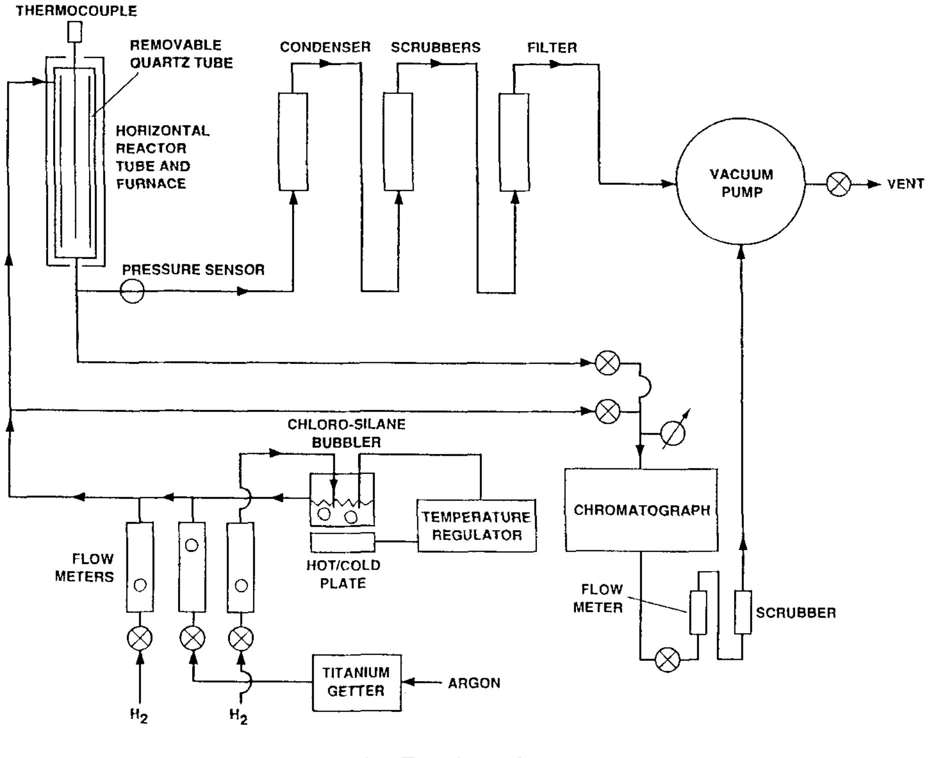

Fig. 1. Experimental apparatus.

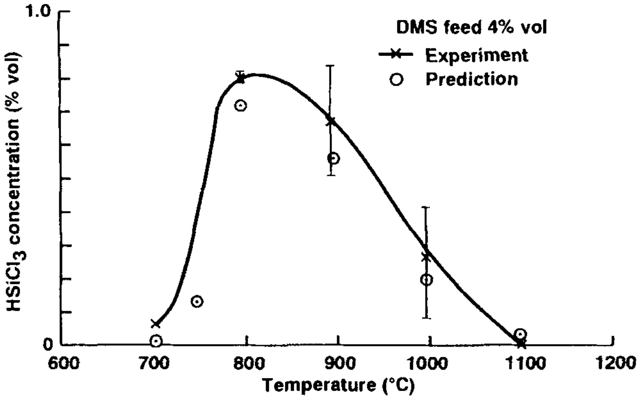

Fig. 3. Product $HSiCl_3$ concentration vs temperature; 4% DMS feed.

almost the stoichiometric equivalent of the two methyl groups in the DMS in the feed. At higher temperatures, the CH_4 decreases, and at 1100°C, where most of the Si is now present as a solid, the remaining CH_4 in the gas is almost equivalent to one methyl group in the DMS in the feed. Therefore, based on a carbon (C) and Si balance, the solid must contain a ratio of atomic Si to C of about 1 at high temperature, but greater than 1 at lower temperatures. Figure 6 shows the experimental analysis of the SiC deposited on the walls of the reactor; the rest of the solid was Si. The amount of SiC present in the total deposit increases with temperature. At temperatures greater than 1000°C, the solid contains about 90% by weight SiC (i.e., very little free Si). At 800°C, it contains about 35% SiC, or a major quantity remains as free Si. By independent elemental analyses, no major quantities of chlorine, oxygen, free carbon, or hydrogen were found in the deposit on the wall. Volatile trichloromethylsilane (TMS), H_2SiCl_2, and a solid aerosol were also products. The maximum amount of TMS detected experimentally was about 0.2% by volume and the H_2SiCl_2 nearly zero. The aerosol trapped on the filter at the exit of the reactor was generally less than 10% by weight of the total deposit in the tube. It was probably due to condensation reactions which produce silanes or to the etching of Si by $SiCl_4$ to produce polymers such as Si_nCl_{2n+2}.[1,2] The small quantities of TMS detected in the product stream or the small quantities of solid aerosol trapped at the exit of the reactor were not included in the development of the model. Figures 7 and 8 show the total rate of solid deposited in the reactor tube as a function of temperature and concentration of DMS in the feed. The total rate increases nearly linearly with an increase in temperature or concentration. Figure 9 shows the total rate of deposition as a function of temperature for flow rates from 150 to 1200 cm^3/min. At higher temperatures where the reaction nears completion, the deposition rate is nearly proportional to the throughput.

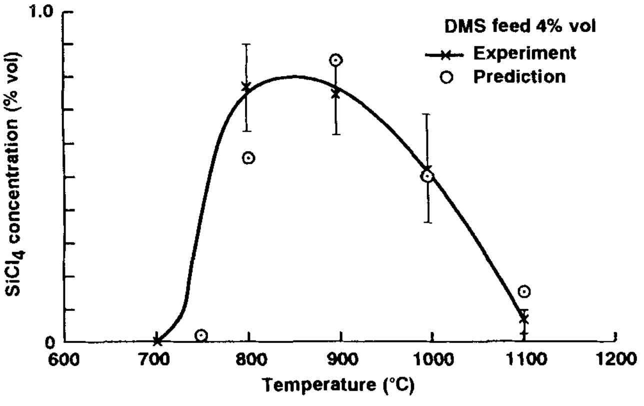

Fig. 4. Product $SiCl_4$ concentration vs temperature; 4% DMS feed.

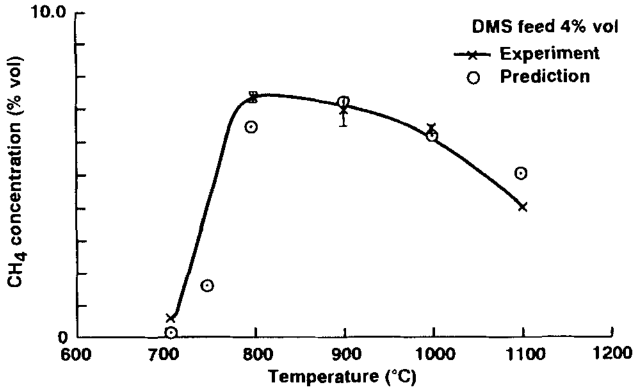

Fig. 5. Product CH_4 concentration vs temperature; 4% DMS feed.

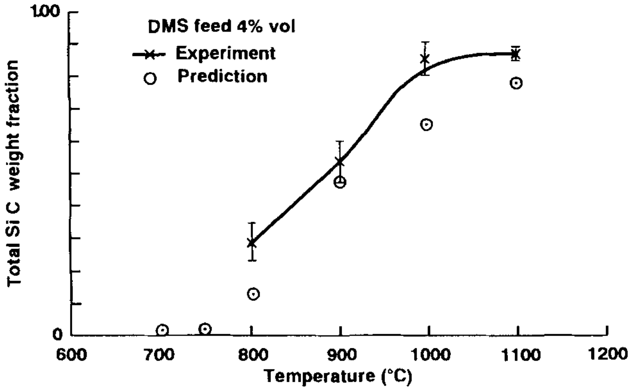

Fig. 6. Total weight fraction of SiC in solid deposit vs temperature; 4% DMS feed.

The data in Figs. 5 and 6 were used to predict the kinetic coefficients for reactions (6) and (8) (Eqs. (I) and (VII)), using a nonlinear regression analysis similar to that described previously.[3] Other coefficients were obtained from independent analyses for Si deposition from $SiCl_4$.[3] All of the coefficients are summarized in Table I. The activation energy found for the initial pyrolysis of DMS (77.5 kcal/mol) is close to the dissociation energy of the Si–C bond (77.0 kcal/mol); the activation energy found for the reaction of Si with CH_4 to form SiC (99.1 kcal/mol) is close to the dissociation energy reported for the C–H bond in CH_4 (102 kcal/mol).[4] These activation energies are the result of just mathematical analysis, and should be verified by experimental tests to determine whether dissociation is truly the rate-determining step. Figures 3 and 4 also show the predicted $HSiCl_3$ and $SiCl_4$ concentrations compared to the experimental values measured at the exit of the reactor. There is good

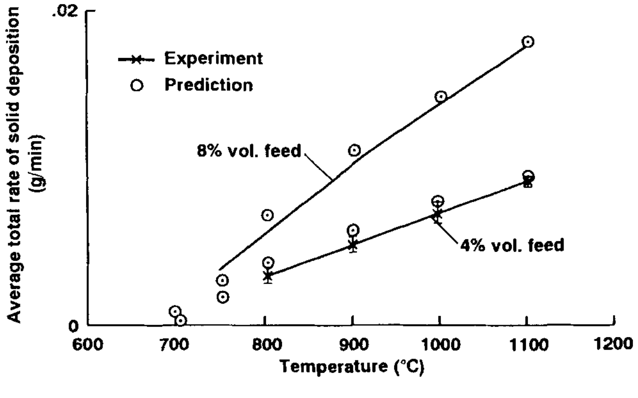

Fig. 7. Rate of solid deposition vs temperature; 4 and 8% DMS in feed.

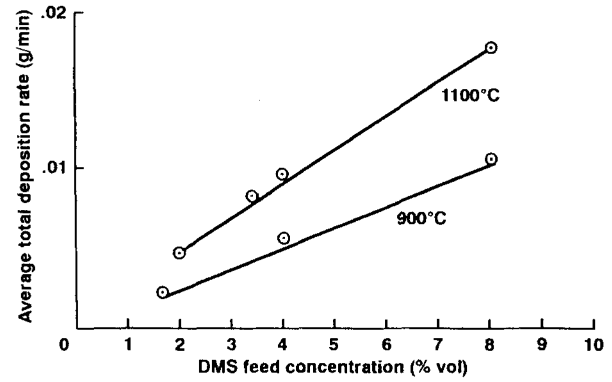

Fig. 8. Rate of solid deposition vs concentration of DMS in feed; 900° and 1100°C.

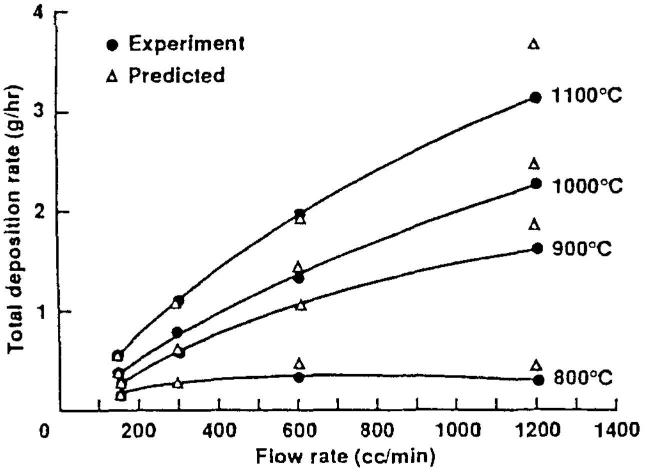

Fig. 9. Total deposition rate vs temperature at different flow rates, 4% DMS feed.

agreement between the predicted quantities for $HSiCl_3$ and $SiCl_4$ compared to experiment; however, these are generally lower than those measured experimentally at temperatures between 700° and 1000°C. Figures 5 and 6 show the predicted values of CH_4 and SiC compared to those measured experimentally. There is good agreement with the experimental results for CH_4 over most of the entire temperature range studied. The predicted weight fraction of SiC in the product is about 10% to 20% below that measured experimentally. Figures 7 and 8 show the predicted total rate of solid deposited as a function of temperature and DMS feed concentration. The model overpredicts the rate at lower temperatures by about 20%, but is in good agreement at higher temperatures. These errors may be due in part to the lower chlorosilane concentrations predicted as well as the presence of the aerosol and the TMS byproduct (e.g., the model does not account for the reduction in weight or gas concentrations due to the loss in these products). Figure 9 shows the predicted total rate of deposition at various flow rates. The results compare favorably.

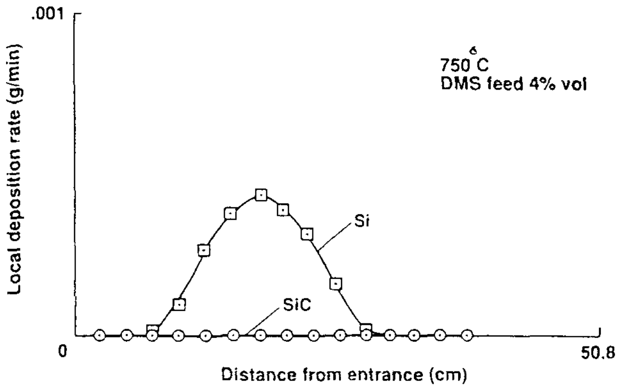

Fig. 10. Local rate of deposition vs reactor length; 750°C, 4% DMS feed.

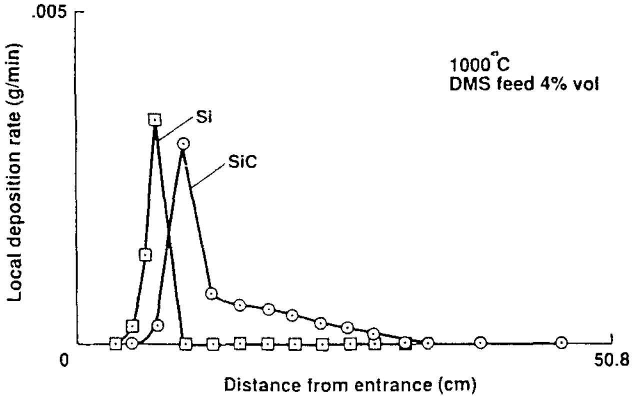

Fig. 11. Local rate of deposition vs reactor length; 1000°C, 4% DMS feed.

Figures 10 and 11 show the plots of predicted local rate of deposition of Si and SiC as a function of the distance from the front of the furnace. It should be recognized that these are also a function of the temperature profile that exists in the reactor, but are shown as a function of the setpoint temperature of the temperature controller. At low temperatures, for example 750°C, the prevalent product is predicted to be Si. Above 900°C, there is a substantial amount of SiC deposited. The plots for the higher temperatures indicate that the disappearance of Si may be due to Si being etched by HCl or its rapid and irreversible reaction with CH_4 to form SiC.

Examining the experimental data for the integral reactor and the reaction model, one observes that at temperatures over 1000°C, the only major products are a solid deposit of SiC and the gaseous products HCl and CH_4. Here, the reaction scheme would appear to "collapse." In an excess of H_2, which is generally the case, the formation of SiC would appear to be a first-order reaction in DMS. However, a profile as a function of reactor length may still confirm the presence of a complex reaction scheme and intermediate compounds along the reactor length.

Table I. Reaction Rate Constants

Reaction	Constants	Preexponent	Activation energy	
			This work	Lit.
$2H_2 + DMS \rightarrow 2CH_4 + H_2SiCl_2$	k_1	0.405×10^{22} $cm^6/(mol \cdot min)$	324252 J (77498 cal)	
$H_2SiCl_2 \rightarrow Si + 2HCl$	k_2	4.187×10^4 $cm^3/(cm^2 \cdot min)$	469700 J (12261 cal)	24267–62760 J (5800–15000 cal)[5,6]
$Si + 2HCl \rightarrow H_2SiCl_2$	k_3	4.41×10^8 $cm^6/(mol \cdot cm^2 \cdot min)$	30405 J (7267 cal)	0–90918 J (0–21730 cal)[7,8]
$H_2SiCl_2 + HCl \rightarrow HSiCl_3 + H_2$	k_4	5.815×10^{15} $cm^6/(mol \cdot min)$	147775 J (49582 cal)	
$HSiCl_3 + H_2 \rightarrow H_2SiCl_2 + HCl$	k_5	2.49×10^{10} cm^3/min	207451 J (49582 cal)	213384 J (51000 cal)[9]
$HSiCl_3 + HCl \rightarrow SiCl_4 + H_2$	k_6	2.002×10^5 $cm^6/(mol \cdot min)$	156952 J (37506 cal)	
$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl$	k_7	4.51×10^{14} $cm^3 \cdot cm^{1.5}/(mol^{0.5} \cdot min)$	231651 J (55366 cal)	230120 J (55000 cal)[9]
$Si + CH_4 \rightarrow SiC + 2H_2$	k_8	1.226×10^{19} $cm^3/(mol \cdot cm^2 \cdot min)$	414509 J (99070 cal)	

Besides predicting the yield and rate of formation of products in the tabular reactor, the model can also be used to study the effect of changing a reactor design. Two designs of interest will be studied and presented in future papers. In one design, a preheated, but nonreacting, jet enters a chamber held at a higher reaction temperature. In the other, the reactor is a completely stirred tank.

IV. Conclusion

Experimental data are presented for the deposition of Si and SiC from DMS in H_2 in a tubular reactor in laminar flow at 1.013×10^5 Pa (1 atm) and temperatures from 700° to 1100°C. At low temperatures, the DMS pyrolysis forms chlorosilanes, Si solid, and almost a stoichiometric equivalent of CH_4 based on the methyl groups in the DMS feed. At higher temperatures, CH_4 decreases, the SiC content increases, and the Si content decreases. An engineering rate model, for the formation of SiC from DMS in H_2, is developed based on the experimental data and independent data for the formation of Si from the reduction of chlorosilanes. The model assumes plug flow. Rate coefficients based on these data for each kinetic step in the reaction sequence are reported. Predictions are in general agreement with the experimental data. The model, however, underpredicts the amount of $HSiCl_3$ and $SiCl_4$ present and overpredicts the solid deposition rate at lower temperatures. The model also underpredicts the SiC content of the solid by about 10% to 20%.

References

[1] D. E. Cagliostro, S. R. Riccitiello, and M. G. Carswell, "Analysis of the Pyrolysis of Dichlorodimethylsilane in the Chemical Vapor Deposition of SiC in Argon," *J. Am. Ceram. Soc.*, **73** [3] 607–14 (1990).

[2] D. E. Cagliostro, S. R. Riccitiello, J. Ren, and Z. Farshad, "A Comparison of the Pyrolysis Products of Dichlorodimethylsilane in the Chemical Vapor Deposition of SiC in Hydrogen and Argon," submitted to *J. Am. Ceram. Soc.*

[3] D. E. Cagliostro and S. R. Riccitiello, "Model for the Formation of Silicon Carbide from the Pyrolysis of Dichlorodimethylsilane in Hydrogen: I, Silicon Formation from Chlorosilanes," *J. Am. Ceram. Soc.*, **75** [12] 39–48 (1992).

[4] C. T. Mortimer, Reaction Heats and Bond Strengths; pp. 127 and 148. Pergamon Press, New York, 1962.

[5] A. Lekholm, "Epitaxial Growth of Silicon from Dichlorosilane," *J. Electrochem. Soc.*, **119** [8] 1122–23 (1972).

[6] W. A. P. Claassen and J. Bloem, "The Growth of Si from Silane in Cold Wall CVD Systems," *Philips J. Res.*, **36,** 124–39 (1981).

[7] W. H. Shepard, "Vapor Phase Deposition and Etching of Si," *J. Electrochem. Soc.*, **112** [10] 988–93 (1965).

[8] L. V. Gregor, P. Balk and F. J. Campagna, "Vapor-Phase Polishing of Si with H_2–HBr Gas Mixtures," *IBM J. Res. Dev.*, **9** [4] 327–32 (1965).

[9] D. J. Ashen, G. C. Bromberger and T. J. Lewis, "Kinetics of Reduction of $SiCl_4$ and $HSiCl_3$ by H_2," *J. Appl. Chem.*, **18** [12] 348–52 (1968). □