

Preparation of vinylsilane from monosilane and vinyl chloride

Masayoshi Itoh *, Kenji Iwata, Mineo Kobayashi

Material Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura-city, Chiba 299-0265, Japan

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Abstract

Vinylsilane ($\text{CH}_2=\text{CH}-\text{SiH}_3$) was prepared by the dehydrochlorination reaction between SiH_4 and vinyl chloride. The reactions were carried out in the gas phase at 450–500°C using a tube reactor, and the maximum yield of vinylsilane was 21% when the conversion of SiH_4 was 32%. A small amount of CCl_4 and CH_3NO_2 accelerated the reaction. A reaction mechanism involving $:\text{SiH}_2$, which was generated by the thermal decomposition of SiH_4 , was proposed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vinylsilane; Dehydrochlorination; Monosilane; Vinyl chloride; Thermal reaction

1. Introduction

Regarding organic silicon compounds, the chemical industry has been making amazing strides, as typified by silicones (polyorganosiloxanes). In most cases, the starting materials of the organic silicon compounds are alkylchlorosilanes obtained by Rochow's direct process, which can be exhibited by the following formula:



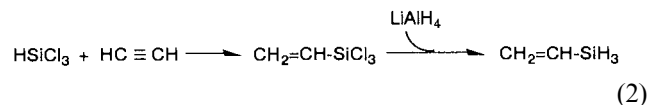
wherein R^1 is industrially limited to a methyl group or a phenyl group.

On the other hand, the current mass production of monosilane (SiH_4) and disilane (Si_2H_6) (hereinafter referred to simply as 'silanes') has become possible along with the development of the semiconductor industry, and so these silanes are inexpensive and easily available. In connection with techniques for manufacturing organic silicon compounds by the use of these silanes, research has scarcely been conducted. Pyrolytic reactions and photochemical reactions have been carried out between SiH_4 or Si_2H_6 and ethylene or acetylene

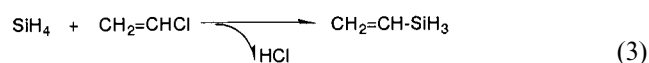
at elevated temperature in the gas phase with very low yields and selectivities [1].

We have recently reported the hydrosilylation reactions of olefins with SiH_4 and Si_2H_6 in the presence of transition metal complexes [2,3], metal hydrides [3,4], and radical initiators [3] to give the hydrosilylated compounds with high yields. Moreover, we have found that the dehydrogenative coupling reactions between SiH_4 and monosubstituted alkynes under metal hydride give the alkynylsilanes with high yield and selectivity [5].

Vinylsilane ($\text{CH}_2=\text{CH}-\text{SiH}_3$, b.p. -22.8°C , abbreviated VS) is an interesting and useful compound as a monomer for the polymerization reaction to yield poly(vinylsilane), which is a ceramic precursor [6–8], and as a monomer for the copolymerization reaction with propylene [9]. VS has usually been prepared by reaction (2).



This report concerns a new preparation method of VS using a dehydrochlorination reaction between SiH_4 and vinyl chloride to give vinylsilane (reaction (3)).



* Corresponding author.

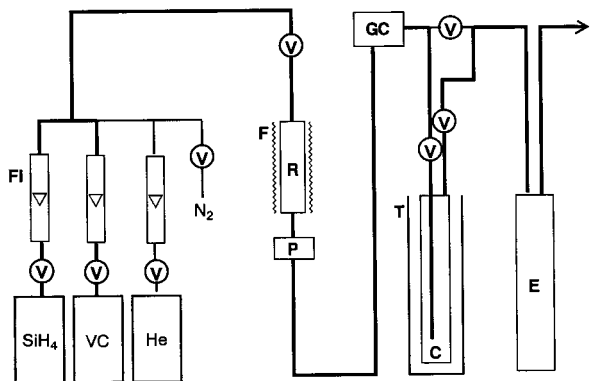


Fig. 1. Reaction equipment: FI, gas flow meter; V, valve; R, reactor; F, electric furnace; P, gas filter; C, condenser; T, trap containing ethanol solution of LiOEt, or condenser; E, exclusion apparatus of VC.

2. Experimental

2.1. Reaction procedures

The reaction equipment is shown in Fig. 1. SiH₄ of 99.999% purity and vinyl chloride (VC) of 99.5% purity were fed at constant flow rates (30–170 N ml min⁻¹) to a reaction tube having an inner diameter of 16 mm and a height of 90 mm (Table 1) or 60 mm (Tables 2 and 3, Figs. 2–4) that had been set to reaction temperatures (350–500°C), and the reaction was then carried out for 5 h under atmospheric pressure. The gaseous products were analyzed by GC and then poured into an ethanol solution of LiOEt (Li 0.5 wt.%). In some experiments, the reactants were accompanied by a small amount of CCl₄, CH₃NO₂, CBrCl₃ or CCl₂BrCH₂Br. BCl₃, AlCl₃, CuCl, CoCl₂ or NiCl₂ were packed in the reaction tube

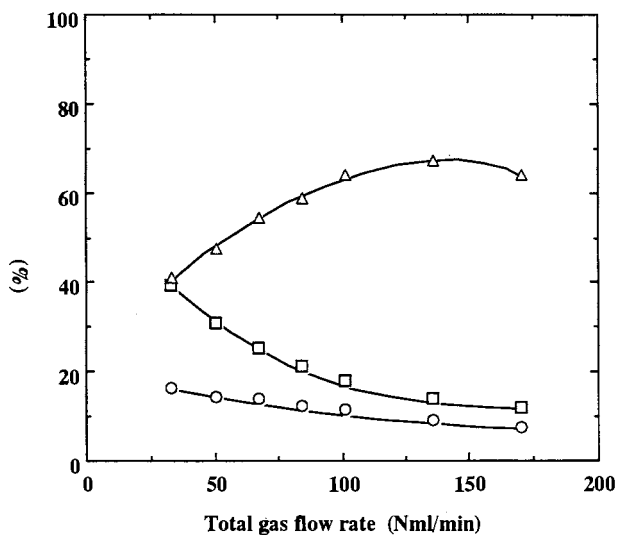


Fig. 2. Changes in the reaction results vs. the total gas flow rate of SiH₄ and VC. Reaction conditions: reactor, inner diameter of 16 mm and height of 60 mm; reaction temperature, 475°C; mole ratio of VC/SiH₄ (1.1/1), 100 N ml min⁻¹ corresponds to a residence time of 4.0 min. (□) Conversion of SiH₄, (○) yield of VS, (△) selectivity for VS.

Table 1
Dehydrochlorination reactions of SiH₄ with vinyl chloride (VC)^a

Run no.	Mole ratio of VC/SiH ₄	Conversion (%)		Yield of silicon-containing product (%) ^b						Mole ratio of ethylene to VS ^h		Selectivity for VS (%) ⁱ	
		SiH ₄	VC	SiH ₄	VC	VS	Si ₂ H ₆	DVS ^c	BS ^d	UK-1 ^e	UK-2 ^f	Polymer (I) ^g	
1	1.1/1	28.0	26.7	12.5	0.4	1.2	1.3	UK-10.9	0.8	0.29	7.4	44.6	
2	3.8/1	32.2	11.1	19.6	0.1	2.4	1.6	0.8	0.8	0.30	9.2	60.9	
3	8.8/1	32.2	3.9	21.1	Trace	2.5	1.5	1.0	1.0	0.31	6.6	65.5	

^a Reactor was a tube having an inner diameter of 16 mm and a height of 90 mm. The total amount of SiH₄ and VC was 100 N ml min⁻¹ (residence time 4.1 s), and all reactions were carried out at 475°C for 5 h. Small amounts of HCl, CH₄, H₂ and EtSiH₃ were also produced.

^b Based on the charged SiH₄ (Si atom base).

^c Divinylsilane.

^d CH₂CHCHSiH₃.

^e Calculated as H₃SiCl.

^f Calculated as vinylchlorosilane.

^g Calculated as poly(vinylsilane).

^h Ethylene/VS.

ⁱ % ratio of VS versus the reacted SiH₄.

Table 2
Thermal reaction of several compounds ^a

Run no.	Reactant ^b (volume %)	Conversion (%)	Main product	
1	SiH ₄	(57)	8.9	H ₂ , Si ₂ H ₆
2	VC	(67)	0.2	CH ₂ =CH ₂ , CH=CH
3	VS	(10)	8.9	poly(vinylsilane) > SiH ₄ , DVS
4	SiH ₄ VS	(54) (10)	4.3 21.0	H ₂ , Si ₂ H ₆ > EtSiH ₃ , DVS
5	SiH ₄ HCl	(49) (15)	8.2 15.1	H ₂ , Si ₂ H ₆ > chlorosilanes
6	VC VS	(54) (10)	2.6 8.2	CH ₂ =CH ₂ > SiH ₄ , DVS
7	VC HCl	(56) (13)	0.1 0	
8	VS HCl	(10) (16)	17.7 13.0	SiH ₄ > CH ₂ =CH ₂ , DVS

^a Reactor was a tube having an inner diameter of 16 mm and a height of 60 mm. The total amount of the charged gases is 100 N ml (residence time, 2.7 s), and the reactions were carried out at 475°C.

^b Accompanied by argon. The volume % of the reactants and products in the reaction of SiH₄ with VC.

and used as catalysts. CH₂=CHCH₂Cl, CH₃CH₂Cl, C₆H₅Cl, CH₂=CHBr and CH₂=CHF were also used instead of VC.

The reaction results were obtained using the following data. (1) The composition of gaseous products

Table 3
Dehydrochlorination reactions between SiH₄ and vinyl compounds ^a

Run no.	Charged gas (N ml min ⁻¹)	Reaction temperature (°C)	Conversion of SiH ₄ (%)	Yield of RSiH ₃ (%) ^b	Selectivity for RSiH ₃ (%) ^c		
1	CH ₂ =CHCl 48	SiH ₄ 52	450	6.5	5.0	77.4	
			475	18.2	11.7	64.1	
2	CH ₂ =CHCH ₂ Cl ^d 54	SiH ₄ 54	He 8	450	12.5	5.7	45.5
			475	28.6	11.8	41.3	
3	CH ₃ CH ₂ Cl 58	SiH ₄ 58	450	8.0	0	0	
			475	32.7	0	0	
4	C ₆ H ₅ Cl ^d 58	SiH ₄ 47	500	20.0	0.2	1.0	
5	CH ₂ =CHBr ^e 41	SiH ₄ 41	He 33	425	21.1	7.6	36.1
			450	41.6	10.4	25.1	
			475	50.3	6.0	11.9	
6	CH ₂ =CHF 58	SiH ₄ 58	450	3.7	0.1	2.5	
			475	9.2	0.1	1.0	
			500	28.6	0.3	0.9	

^a Reactor was a tube having an inner diameter of 16 mm and a height of 60 mm. Residence time is 2.7 s at 475°C when the total amount of the charged gases is 100 N ml.

^b Based on the charged SiH₄.

^c % ratio of RSiH₃ versus the reacted SiH₄.

^d Charged using a liquid feed pump.

^e Accompanied by helium.

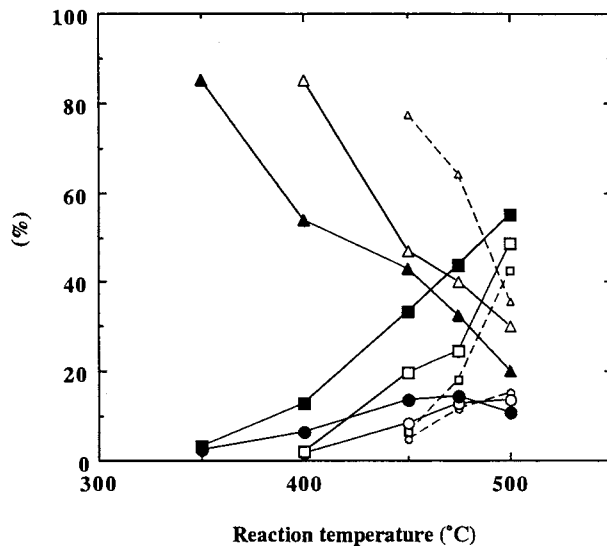


Fig. 3. Effects of additions of CCl₄ and CH₃NO₂. Reaction conditions: reactor, inner diameter of 16 mm and height of 60 mm; total gas flow rate of SiH₄ and VC, 100 N ml min⁻¹; mole ratio of CCl₄ or CH₃NO₂/VC/SiH₄ (0.02/1.1/1), (□,○,△) VC/SiH₄ (1.1/1.0), (□,○,△) VC/SiH₄/CCl₄ (1.1/1.0/0.02), (■,●,▲) VC/SiH₄/CH₃NO₂ (1.1/1.0/0.02). (□,□) Conversion, (○,○) yield of VS, (△,△) selectivity for VS.

determined by GC measurement, the amounts of Si(OEt)₄ (calculated as SiH₄ and chlorosilane) and CH₂=CHSi(OEt)₃ (calculated as VS and vinylchlorosilane) in the ethanol solution of LiOEt, which were obtained by chemical analysis and GC, and the weight of the liquid polymer in the reactor and the gas filter. The results in Table 1 were obtained using these

data. (2) The amounts of gaseous products determined by GC using a small amount of argon as an internal standard. The results in Table 3 and Figs. 2–4 were obtained by using these data.

2.2. Product assignment

The gaseous and liquid products were collected in a trap cooled to -100°C or less, and after completion of the reaction, the products were identified by means of mass spectroscopy, IR and GC.

VS; IR (gas): $\nu(\text{CH}_2)$ 3050, 2951, $\nu(\text{Si-H})$ 2154, $\nu(\text{C=C})$ 1598, $\delta(\text{CH}_2)$ 1398, $\delta(\text{SiH}_3)$ ca. 910, $\nu(\text{SiC})$ ca. 700 cm^{-1} . MS (m/z): (EI mode) 58 (M^+), 57, 56, 55, 43 (base peak). Si_2H_6 ; MS (m/z): (EI mode) 62 (M^+), 61, 60 (base peak), 58, 57. $\text{CH}_2=\text{CH}_2$; MS (m/z): (EI mode) 28 (M^+ , base peak), 27, 26, 25. EtSiH_3 ; MS (m/z): (EI mode) 60 (M^+), 59, 58 (base peak), 43, 31. $(\text{CH}_2=\text{CH})_2\text{SiH}_2$; MS (m/z): (EI mode) 84 (M^+), 83 (base peak), 58, 56, 55. $\text{CH}_2=\text{CHCH}=\text{CHSiH}_3$; MS (m/z): (EI mode) 84 (M^+), 83, 57, 56 (base peak), 55, 53. Polymer (I); IR (neat): $\nu(\text{CH}_2)$ 2930 cm^{-1} , $\nu(\text{Si-H})$ 2160, $\delta(\text{CH}_2)$ 1450, 1410, $\delta(\text{C-H in CHCl})$ 1260, $\nu(\text{SiHn})$ 920, $\delta(\text{C-Cl})$ 715 cm^{-1} .

The spectral data for VS [10], Si_2H_6 [11], $\text{CH}_2=\text{CH}_2$ [12] and EtSiH_3 [12] coincided with those in the literature. Polymer (I) was assigned to be poly(vinylsilane) [6] $[-\text{CH}_2\text{CH}(\text{SiH}_3)-]_x[-\text{CH}_2\text{CH}_2\text{SiH}_2-]_y$, IR adsorption bands 2930, 2160, 1450, 920 cm^{-1} , which included some poly(vinylchloride) (very weak adsorption bands 1410, 1260, 715 cm^{-1}).

3. Results

The reaction of SiH_4 with VC proceeded above 420°C in the reaction equipment shown in Fig. 1 to yield VS and a small amount of other silicon-containing compounds such as Si_2H_6 , divinylsilane, vinylchlorosilane, 1,3-butadienyl silane and some chlorosilanes, as shown in Table 1. Considerable amounts of ethylene and polymer (I), which is almost poly(vinylsilane), were also produced. The results indicate that the dehydrochlorination reaction occurred between SiH_4 and VC.

The mole ratio of VC/ SiH_4 , the gas flow rate and the reaction temperature affected the reaction results greatly as shown in Table 1 and Figs. 2 and 3, respectively. The correlations between the yield of VS, the selectivity for VS and the conversion of SiH_4 are plotted in Fig. 4 using the data obtained from the experiments at various reaction temperatures, mole ratios of VC/ SiH_4 , and gas flow rates. The high conversion produced a high yield of VS but low selectivity for VS except for one experimental result, in which much SiH_4

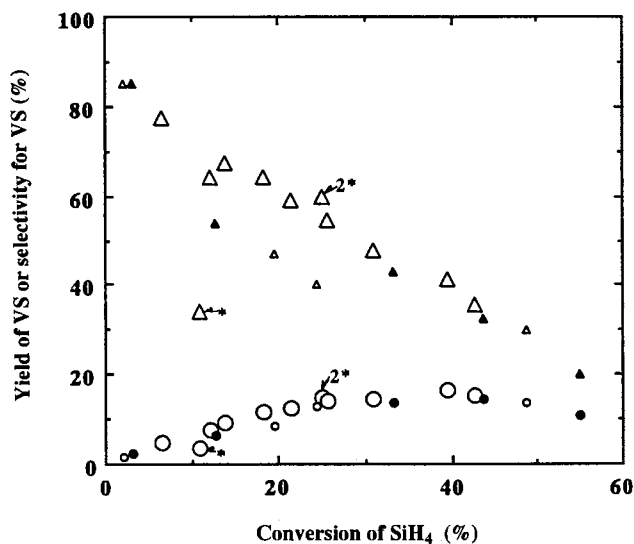


Fig. 4. Correlations of the yield of VS and the selectivity for VS with the conversions of SiH_4 . All the data in Figs. 2 and 3, and two data (*, 2*) are plotted. *, 2*: total gas flow rate of SiH_4 and VC, 100 N ml min^{-1} ; reaction temperature, 475°C ; mole ratio of VC/ SiH_4 , 18/82 (*) and 86/16 (2*). (○) Yield of VS, (△) selectivity for VS, yield of VS and selectivity for VS when (○, △) CCl_4 and (●, ▲) CH_3NO_2 were added.

(VC/ $\text{SiH}_4 = 18/82$) was used. From these results, the best reaction condition to obtain VS using the reaction apparatus in Fig. 1 would be as follows: gas flow rate, $100\text{--}170\text{ N ml min}^{-1}$; reaction temperature, 475°C ; and the mole ratio of VC/ $\text{SiH}_4 = 4/1$. A small volume reaction tube having an inner diameter of 2 or 10 mm and that having a diameter of 16 mm which was packed with glassy or stainless steel wool were used. All of the yields, conversions and selectivities are on the curves in Fig. 4.

Halogenated hydrocarbons and metal chlorides (Lewis acid) that catalyze the dehydrochlorinative coupling reaction between HSiCl_3 and $\text{C}_6\text{H}_5\text{Cl}$ to give $\text{C}_6\text{H}_5\text{SiCl}_3$ [13,14] were used in order to accelerate the reaction. Only CCl_4 and CH_3NO_2 had effects on the reaction as shown in Figs. 3 and 4, that is, the reaction occurred at lower temperature when CCl_4 or CH_3NO_2 was present.

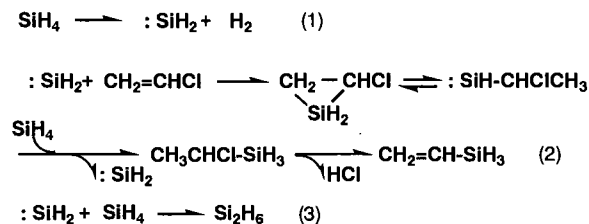


Fig. 5. Postulated mechanism of the reaction of SiH_4 with VC.

The thermal reactions of SiH_4 , VC, VS, SiH_4 -VS, SiH_4 -HCl, VC-VS, VC-HCl and VS-HCl were carried out in order to investigate the reaction mechanism using the same reaction apparatus. The conversions and the main products are shown in Table 2.

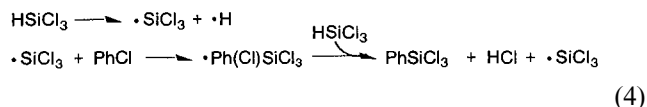
Several kinds of halogenated hydrocarbons were reacted with SiH_4 (Table 3). $\text{CH}_2=\text{CHCH}_2\text{Cl}$ and $\text{CH}_2=\text{CHBr}$ reacted like VC and gave the silyl compounds (RSiH_3). In the case of $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{Cl}$ and $\text{CH}_2=\text{CHF}$, the silyl compounds were not obtained.

4. Discussion

There have been many reports about the dehydrohalogenation reaction between hydrosilanes ($\text{H}_n\text{SiY}_{4-n}$, wherein $\text{Y} = \text{Cl}$, phenyl or alkyl) and halogenated hydrocarbons (RX , wherein $\text{X} = \text{Cl}$ [13], Br [14,15] or I [16]). With regard to the reaction between SiH_4 and halogenated hydrocarbons concerning the present report, only a thermal reaction between SiH_4 and VC has been reported [17], but the production of organic silicon compounds (in this case, VS, divinylsilane and similar compounds), which the present report discusses, is not found at all in the above-mentioned report. Perhaps, the results would be caused by failure in trapping the compounds of low boiling point. In our experiment, VS which was identified by IR and GC-MS was the main product.

4.1. Mechanism of the dehydrochlorination reaction

$\text{CH}_2=\text{CHSiCl}_3$ and PhSiCl_3 were synthesized by the dehydrochlorination reactions at high temperature (500–720°C) through a hot tube between HSiCl_3 and $\text{CH}_2=\text{CHCl}$ or $\text{C}_6\text{H}_5\text{Cl}$, respectively. The workers concluded that the initial step is homolytic dissociation of the Si-H bond of HSiCl_3 to produce the $\cdot\text{SiCl}_3$ radical and that this is followed by the attack of the radical on the halogenated hydrocarbon [13] (reaction (4)).



Claassen, Bloem and Kuiper et al. reported that the $\cdot\text{SiH}_2$ radical is generated by the thermal decomposition of SiH_4 in the gas phase based on kinetic studies of the thermal reaction [18]. As shown in Table 2 (run nos. 1 and 2), SiH_4 reacted at 475°C, but VC did not react. Therefore, SiH_4 would decompose thermally and would generate a reactive species of $\cdot\text{SiH}_2$, and then it would induce the next reactions as shown in Fig. 5. From Table 2, the order of the reaction rates is roughly $\text{VS-HCl} > \text{SiH}_4\text{-VS}$, SiH_4 , VS, $\text{SiH}_4\text{-HCl}$, $\text{VC-VS} > \text{VC-HCl}$, VC. The side reactions involving SiH_4 or VS were fast. At a high ratio of VC/ SiH_4 , the chance of the

reaction between $\cdot\text{SiH}_2$ and VC would be high, which would result in a high selectivity for VS. On the other hand, a low ratio of VC/ SiH_4 causes low selectivity and yield even at low conversion, because the side reactions involving SiH_4 would proceed considerably (see Fig. 4). A part of the produced VS was converted to poly(vinylsilane) ($[-\text{CH}_2\text{CH}(\text{SiH}_3)-]_x[-\text{CH}_2\text{CH}_2\text{SiH}_2-]_y$) in the reactor by radical polymerization reaction [6]. Ethylene would be produced by the reactions of VS with HCl and VC (see run nos. 6 and 8 in Table 2).

When CCl_4 or CH_3NO_2 was poured with SiH_4 and VC, a radical ($\cdot\text{CCl}_3$ or $\cdot\text{CH}_3$) would be produced at a temperature lower than 450°C, and a silyl radical ($\cdot\text{SiH}_3$) would be produced by the reaction of $\cdot\text{CCl}_3$ or $\cdot\text{CH}_3$ with SiH_4 , followed by other reactions. The low yield of silyl compound in the reactions of SiH_4 with $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{Cl}$ and $\text{CH}_2=\text{CHF}$ suggests that the species ($\cdot\text{SiR}_2$) formed by the reaction between $\cdot\text{SiH}_2$ and hydrocarbon would not be obtained, but the exact reason for this result is not obvious. The correlation curves of yield, conversion and selectivity were quite the same in any reactor. The reaction results depended on the volume of the reactor, so most of the reaction would occur in the gas phase, not on the surface of the reactor.

4.2. Process of synthesis of vinylsilane

The following recycle process for synthesizing VS can be considered. VS (b.p. -22.8°C) would be separated by distillation. Unreacted VC (b.p. -13.9°C) and the products of higher boiling point than VS, such as Si_2H_6 (b.p. -14.3°C), $\text{CH}_3\text{CH}_2\text{SiH}_3$ (b.p. -14.0°C), $\text{CH}_2=\text{CHSiH}_2\text{Cl}$ and $(\text{CH}_2=\text{CH})_2\text{SiH}_2$, would be washed with alkaline water, which results in the hydration of the hydrosilanes to give the siloxane polymers, and then VC would be dried through zeolite and fed to the reactor again. Unreacted SiH_4 (b.p. -112°C), and the products of lower boiling point than VS, such as H_2 , CH_4 , $\text{CH}_2=\text{CH}_2$ (b.p. -103.9°C), HCl and H_3SiCl (b.p. -30°C), would be distilled, and SiH_4 would be recycled to the reactor. HCl and H_3SiCl would be removed by the washing with alkaline water, and H_2 and CH_4 of low boiling point would be disposed of as industrial waste. A considerable amount of $\text{CH}_2=\text{CH}_2$ is produced, but it could be removed by adsorption on 5 Å molecular sieves [19].

Alkynylsilanes having a reactive and useful silyl group ($-\text{SiH}_3$) are usually prepared by the reduction of the corresponding alkynylchlorosilane using an expensive metal hydride [20]. We offer a new process for synthesizing a silyl compound using SiH_4 . The selectivity for the silyl compound is not sufficient. Further study is needed for the development of a more effective process.

5. Conclusions

Vinylsilane ($\text{CH}_2=\text{CH}-\text{SiH}_3$) was prepared by the dehydrochlorination reaction between SiH_4 and vinyl chloride. The reactions were carried out in the gas phase at 450–500°C using a tube reactor, and the maximum yield of vinylsilane was 21% when the conversion of SiH_4 was 32%. Divinylsilane, 1,3-butenylsilane, disilane, chlorosilanes and poly(vinylsilane) were produced as by-products. A radical reaction mechanism involving $\cdot\text{SiH}_2$, which was generated by the thermal decomposition of SiH_4 , was proposed. A small amount of CCl_4 and CH_3NO_2 accelerated the reaction.

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