AN ABSTRACT OF THE THESIS OF

Panut Vongpayabal for the degree of Master of Science in Chemical Engineering

presented on July 28, 1997.   Title: Direct Synthesis of Tetramethoxysilane from

Silicon Fines.

Redacted for Privacy

Abstract approved: _____

Shoichi Kimura

It is an urgent need to find methods to utilize silicon fines, a waste material from

silicon wafer manufacturing processes, that have been disposed of in the landfill. It has

been know that tetramethoxysilane (TMOS), a raw material for a variety of organosilicon

compounds, is synthesized from Si via the reaction with methanol (CH_3OH) or from SiO_2

via the reaction with dimethyl carbonate (DMC). This study has focused on looking into

the possibility to use up the silicon fines, mixtures of Si, SiO_2, and inerts, in the production

of TMOS or other useful chemicals through either reaction of the two. Four samples of

silicon fines from different stages/locations of two silicon-wafer manufactures have been

tested for this purpose.

A differential flow reactor was set up to carry out the reactions. A sequence of

solid pretreatments, including catalyst impregnation and palletization, was developed to

make the silicon fines ready for reaction. An analytical method using a gas-

chromatograph was also developed to determine the composition of gas mixtures

containing DMC, CH_3OH, TMOS, and others. A number of reaction runs were made to measure the rate of silicon fines consumption as well as TMOS production at temperatures ranging from 250 to 325 °C.

It was found that KOH was useful for catalytically converting both Si and SiO_2 with DMC into TMOS while Cu(II)Cl_2 was useful for converting only Si with CH_3OH. In the reaction with DMC at temperature below 300 °C, TMOS was the only liquid product. A higher temperature than this led to the formation of carbonaceous materials and byproducts. On the other hand, the reaction with CH_3OH always produced a mixture of TMOS with byproducts at any temperatures investigated.

The reaction of silicon fines with DMC took place in two stages: the rapid initial stage and rather slow steady stage. The consumption of silicon fines in this reaction increased with an increase in the reaction temperature, yielding 6% at 300 °C in 5 hours. Based on these findings, a process to convert silicon fines into TMOS was proposed for discussion. Also, further study needed for realizing the process in the future was proposed.

Direct Synthesis of Tetramethoxysilane from Silicon Fines

by

Panut Vongpayabal

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented July 28, 1997

Commencement June, 1998

Master of Science thesis of Panut Vongpayabal presented on July 28, 1997

APPROVED:

Redacted for Privacy

Major Professor, representing Chemical Engineering

Redacted for Privacy

Head or Chair of Department of Chemical Engineering

Redacted for Privacy

Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorized release of my thesis to any reader upon request.

Redacted for Privacy

Panut Vongpayabal, Author

ACKNOWLEDGEMENTS

I would like to take this opportunities to express my sincere appreciation to the following people:

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

Page

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF APPENDICES

Page

LIST OF APPENDIX TABLES

Direct Synthesis of Tetramethoxysilane from Silicon Fines

Chapter 1

Introduction

Tetramethoxysilane (TMOS, $(CH_3O)_4Si$) is one of most important chemicals from which a variety of organosilicon compounds can be derived. Rochow [1948] reported that TMOS could be obtained when silicon fused with copper was brought into contact with methanol (CH_3OH) vapor at 553 °K in a fixed-bed reactor. In the last forty years, many efforts have been made to synthesize TMOS with high selectivity, because it is an important intermediate key step in the synthesis of silicone polymers, in the production of glasses and in the ceramics production by the sol-gel process. It is also used as a starting material for producing high purity silica.

Silicon-fines, which consists of mainly Si and SiO_2, are obtained as a waste from the process of silicon wafer production, in which silicon rods are sliced into pieces of wafer to be used further in computer processing. The silicon-fines have been disposed of in the landfill beside the plant. Owing to recent increase of environmental awareness, this research attempts to utilize silicon-fines as a starting material for the production of useful chemicals, including TMOS. Presently, there are two gas-solid reactions found to produce TMOS with high selectivities.

The first one is to use the reaction between silicon and CH_3OH with $Cu(II)Cl_2$ as a catalyst [Suzuki et. al., 1991]. Under the pretreatment at high temperature in a hydrogen stream, the reaction of silicon with CH_3OH yields trimethoxysilane $(TMS, (CH_3O)_3SiH)$ and TMOS with high selectivities. The second is a gas-solid reaction between SiO_2 and dimethyl carbonate (DMC) with an alkali metal as a catalyst [Ono et. al., 1993].

The purpose of this study is to find possibilities to economically convert the silicon-fines into useful materials. Since the silicon-fines are mainly composed of Si and SiO_2, an effort has been made to choose one of the two reactions mentioned above, that is more appropriate to the characteristics of silicon-fines.

Seven chapters present the overall investigation in this study. In chapter 2, a literature survey of various methods reviews all possible ways for the synthesis of organosilicon compounds. It will provide the background for this study. The dissociation of CH_3OH as well as DMC at high temperature is also discussed. In chapter 3, the experimental apparatus and procedure used in this study are briefly illustrated. In chapter 4, the experimental results are discussed. In chapter 5, the effect of mass transfer limitation will be tested. In chapter 6, the TMOS process is proposed. Finally, chapter 7 includes the summary and the recommendation for future work.

Chapter 2

Literature Review

In the past few years, the potential role of inorganic and organometallic silicon compounds in the development of new chemical reagents, polymers, glasses and ceramics is limited at present by the paucity of simple silicon-containing starting materials [Kluwer, 1991]. Therefore, many efforts were attempted to find new synthetic routes to produce these materials. Relying on low cost, the processing methods which avoid the energy-intensive and equipment-intensive carbothermal reduction step are highly desirable [Richard, 1991].

The synthesis of organosilicon compounds started via the carbothermal reduction of SiO_2 to Si reacting with HCl. This has been known for a long time as the way to produce methoxy-chlorosilanes due to the low-cost of SiO_2. Later, direct synthesis of methoxychlorosilanes was developed by means of reacting Si with methyl chloride at 200-300 °C over a copper catalyst. Because of the increasing demand in fields ranging from organic synthesis to ceramics to the electronics industry in the recent years, several new methods to synthesize those materials have been developed. As a result, many routes evolved later. Finally, TMOS was introduced and played a manifest role as one of the most important organosilicon compounds in the field of glasses and ceramics.

With regard to the composition of silicon-fines comprising mainly Si and SiO_2, this chapter is divided into two main parts related to the evolution of organosilicon compounds

from the past to present: the synthesis of organosilicon compounds from Si and that from SiO$_2$.

2.1 Synthesis of tri-/tetramethoxysilane from element Si

2.1.1 Production of organosilicon compounds from element Si.

The important innovation of organosilicon compounds was developed by Rochow et. al.[1945]. The reaction was carried out by using element Si with methyl chloride (CH$_3$Cl) in the presence of copper (Cu), as a catalyst which lowers the temperature of the reaction. The main product is dimethyldichlorosilane, (CH$_3$)$_2$SiCl$_2$, including a series of other substances; such as, CH$_3$SiCl$_3$, (CH$_3$)$_3$SiCl, CH$_3$SiHCl$_2$, carbon, hydrogen, methane, etc [Klebensky, 1955].

The main overall gas-solid reactions (between CH$_3$Cl and Si in a presence of Cu) are shown below.

$$\text{Si}_{(s)} + \text{CH}_3\text{Cl}_{(g)} \xrightarrow{\text{Cu}} \text{CH}_3\text{SiCl}_{(g)} \qquad (2.1.1.1)$$

$$\text{Si}_{(s)} + 2\text{CH}_3\text{Cl}_{(g)} \xrightarrow{\text{Cu}} \text{Si(CH}_3)_2\text{Cl}_{2(g)} \qquad (2.1.1.2)$$
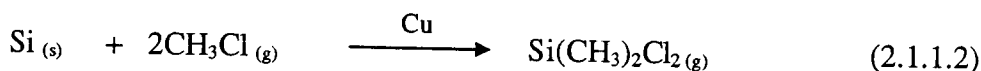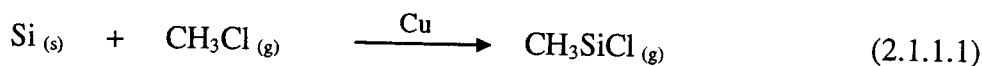
Both the reactions above can be divided into three elementary reaction steps [Rochow et. al., 1945].

$$\text{Step 1:} \quad 2\text{Cu}_{(s)} + \text{CH}_3\text{Cl}_{(g)} \xrightarrow{250\,°\text{C}} \text{CuCl}_{(s)} + \text{CuCH}_3{}_{(s)} \qquad (2.1.1.3)$$

$$\text{CuCH}_3{}_{(s)} \xrightarrow{\text{decompose}} \text{Cu}_{(s)} + \text{CH}_3 \bullet_{(g)} \qquad (2.1.1.4)$$

$$\text{Step 2:} \quad \text{CuCl}_{(s)} + \text{Si}_{(s)} \xrightarrow[\text{Exothermic rxn.}]{T \geq 265\,°\text{C}} \text{SiCl}_{(s)} + \text{Cu}_{(s)} \qquad (2.1.1.5)$$

Step 3: $SiCl_{(s)} + CH_3 \bullet_{(g)}$ ⟶ $CH_3SiCl_{(g)}$ (2.1.1.6)
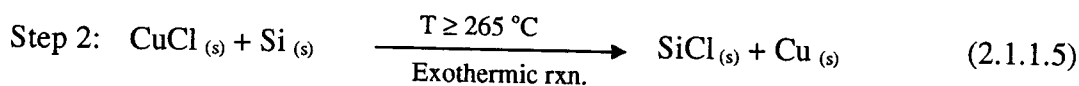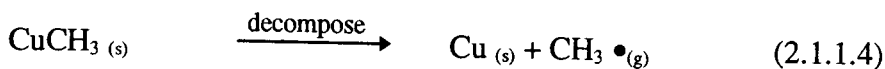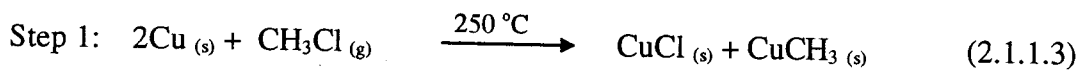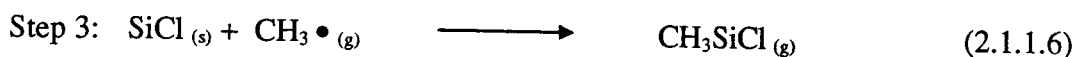
In the first step, Si and Cu contact-mass is exposed to $CH_3Cl_{(g)}$ at 250 °C in order to form cuprous chloride and an active free methyl group. $SiCl_{(s)}$, activated Si nuclei, are formed in the second mechanism. The last step is methylation or further chlorination of the activated silicon to form the volatile molecules of CH_3SiCl.

Many researchers have postulated that the reaction rate and selectivity of methylchloro-silanes depend on the first step: "contact mass preparation". Therefore, some attentions have already been devoted to figure out the role of Cu as the catalyst in the synthesis of organosilanes from Si and organohalides [Voorhoeve et. al., 1965].

Voorhoeve et. al.(1964) presented that free Cu is not effective as a catalyst since the organic radical can decompose into carbonaceous material and hydrogen in reaction 2.1.1.4. Consequently, instead of Cu, Cu(I)Cl reacted with Si was applied to produce an active Cu-Si complex instead, which easily gives rise to the formation of the η phase (a kind of copper presented in an alloyed state) as following

$4 CuCl_{(s)} + n Si_{(s)}$ ⟶ $(n-1)Si_{(s)} + 4Cu_{(s)} + SiCl_{4(g)}$

(2.1.1.7)

$3Cu_{(s)} + Si_{(s)}$ $\xrightarrow{\text{diffuse}}$ $Cu_3Si_{(\eta)}$ (2.1.1.8)
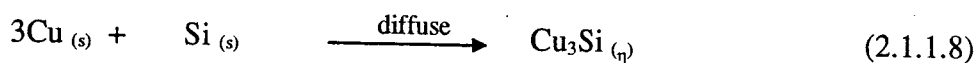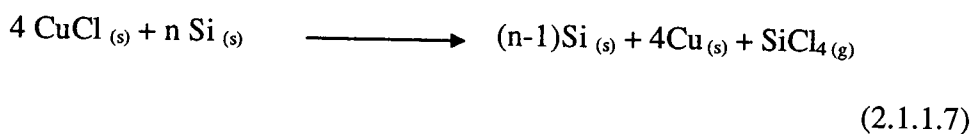
Side-reaction (free copper)

$CH_3Cl_{(g)} + Cu_{(s)}$ ⟶ $CuCl_{(s)} + CH_3\bullet_{(g)}$ (2.1.1.9)
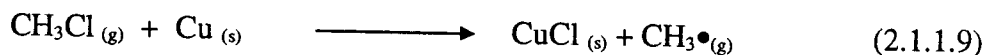
The η phase (Cu_3Si) compound yields a highly selective and rapid production of $(CH_3)_2SiCl_2$ from the beginning of the reaction with CH_3Cl. Owing to the side-reaction in equation 2.1.1.9, the heat treatment of contact-mass, prepared from Si and Cu(I)Cl, in the atmosphere of argon mixed with hydrogen sulfide was applied to reduce free Cu [Voorhoeve et. al., 1965].

However, the drawback of this reaction is the corrosive nature of the reactant (CH_3Cl) and the products which include HCl. Thus, the direct synthesis of organosilanes from metallic Si without the use of halides is highly desired [Ono and Suzuki, 1995].

2.1.2 Synthesis of methoxysilanes via the gas-solid reaction of Si with CH_3OH using Cu compounds as a catalyst.

For many years, the reaction of silicon with CH_3OH is known to give methoxysilanes. In 1948, Rochow reported that TMOS was obtained when silicon fused with copper was contacted with CH_3OH vapor at 250 °C in a fixed-bed reactor [Ono, 1990]. Also, both TMS and TMOS were produced when CH_3OH vapor was fed slowly at 250 °C into a reactor containing silicon fused with Cu in silicone oil [Rochow, 1970]. Thus,

$$Si_{(s)} + 3CH_3OH_{(g)} \xrightarrow{Cu} (CH_3O)_3SiH_{(g)} + H_{2\,(g)} \qquad (2.1.2.1)$$

$$(CH_3O)_3SiH_{(g)} + CH_3OH_{(g)} \xrightarrow{Cu} (CH_3O)_4Si_{(g)} + H_{2\,(g)} \qquad (2.1.2.2)$$
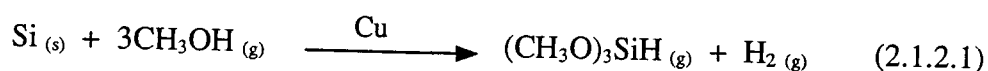
Many efforts have been made to investigate the most effective way to obtain high yield and selectivity of methoxysilanes from the Si-CH$_3$OH reaction. Ono et. al. (1990) found that the reactivity of Si with CH$_3$OH greatly depended on the kind of catalyst and the preheating temperature. The four types of reduced-copper compounds already studied are Cu(I)Cl, Cu(II)Cl$_2$, Cu(II)acetate and Cu(II)hydroxide, each of which was applied in the pretreatment stage involving the formation of active sites in the Si- CH$_3$OH reaction.

By using either Cu(I)Cl or Cu(II) Cl$_2$, Ono et. al. (1991) reported that Si grains, washed with an HF solution for Si-Cu contact-mass and pretreated at 260-450 °C for 1 hour in a hydrogen stream before the reaction, could remove the SiO$_2$ layer on the Si surface, which prevented the active-site formation. The optimal operating temperature for both the reactions is in the range of 240-280 °C at atmospheric pressure. Higher temperature will cause CH$_3$OH to decompose to other compounds as

$$CH_3OH_{(g)} \longrightarrow HCHO_{(g)} + H_{2(g)} \qquad (2.1.2.3)$$

$$2CH_3OH_{(g)} \longrightarrow CH_3CHO_{(g)} + H_2O_{(g)} + H_{2(g)} \qquad (2.1.2.4)$$
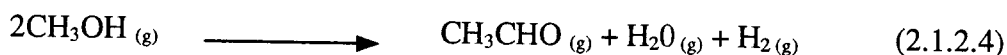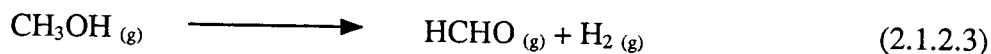
Therefore, the CH$_3$OH decomposition will be one of the essential steps in this process. By using Cu(I)Cl or Cu(II)Cl$_2$ as a catalyst in the Si-CH$_3$OH reaction, TMS is the primary product and TMOS is the secondary product derived from the reaction of TMS with CH$_3$OH over metallic Cu [Ono et. al., 1995]. By using the active catalyst containing halide ions, chlorine-containing compounds are formed, that can cause the

corrosive problem in the process. Alternatively, Cu(Π)acetate and Cu(Π)hydroxide were developed as new routes for preparing active catalysts for the Si-CH₃OH reaction.

2.2 Synthesis of TMOS from Silica (SiO₂)

2.2.1 Production of organosilicon compounds from SiO₂

For a long time, element Si was used as the starting material to produce organosilicon compounds. One way to obtain element Si inexpensively was the carbothermal reduction of SiO_2 to Si [Richard, 1991]. Thus, it is an interesting challenge to find a route to synthesize organosilicon compounds from silica without having to convert it into element Si [Boudin et. al., 1988]. The first investigation was made by Rosenheim who converted silica into hexacoordinated silicon complex 1 in water with catechol in 1931.

$$SiO_2 + 3 \left[\text{catechol-(OH)}_2\right] + 2KOH \xrightarrow{H_2O} Si\left(\text{O}_2\text{C}_6\text{H}_4\right)_3^{2-} \cdot 2K^+ \cdot 8H_2O \qquad (2.2.1.1)$$
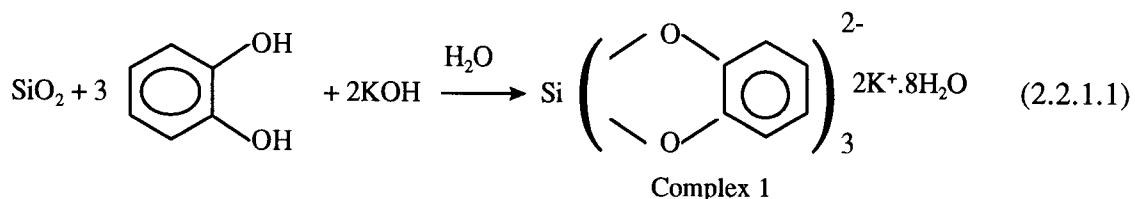
Complex 1

To transform hexacoordinated Si complex 1 into organosilanes (complex 2), Boudin (1986) reported the nucleophile attack of organometallic reagent (RMgX) on complex 1 leading to the formation of silicon-carbon bonds as shown below.

$$Si\left(\text{O}_2\text{C}_6\text{H}_4\right)_3^{2-} \cdot 2K^+ \cdot 8H_2O \xrightarrow[\text{Cp}_2\text{TiCl}_2]{\text{RMgBr (excess)}} \left(R_3Si-\text{O}-\text{C}_6\text{H}_4-\text{OMgX}\right) \qquad (2.2.1.2)$$
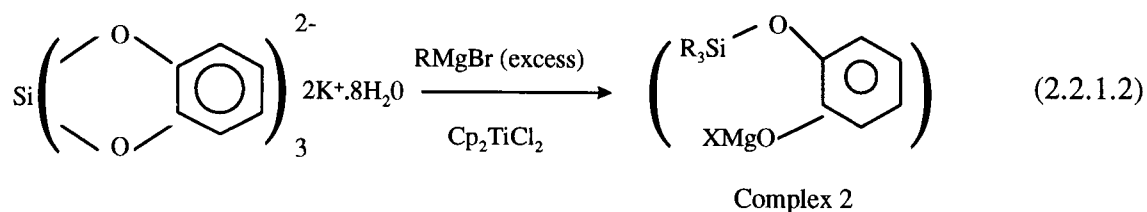
Complex 2

Moreover, various organosilanes can be obtained by reacting complex 2 with different nucleophiles, as illustrated in Figure 2.1.
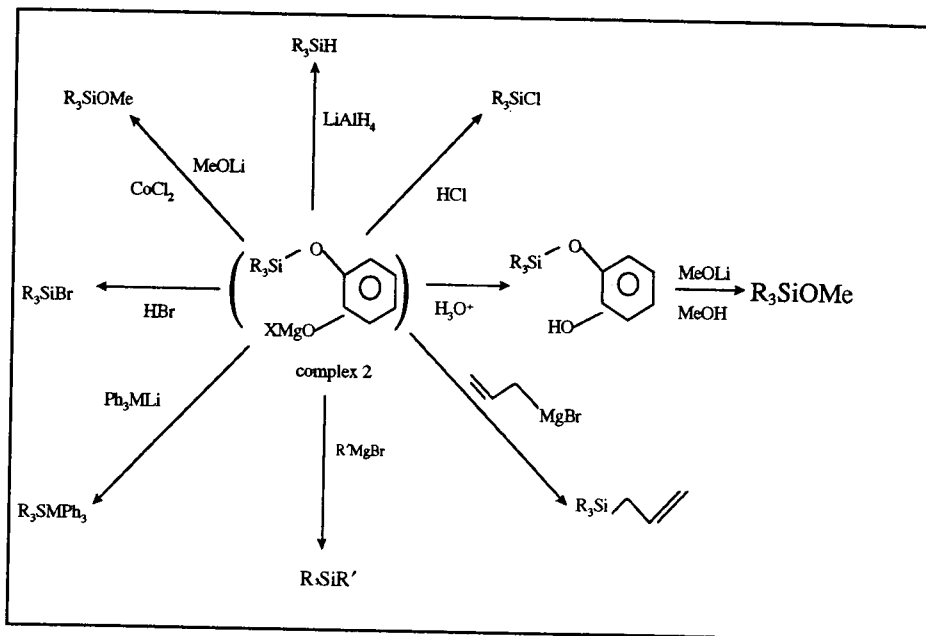
Figure 2.1 : Routes for transformation of complex 2 into organosilanes by different reageents.

Finally, there are two possible routes for the transformation of silica into organosilanes, known at that time, as shown in Figure 2.2.
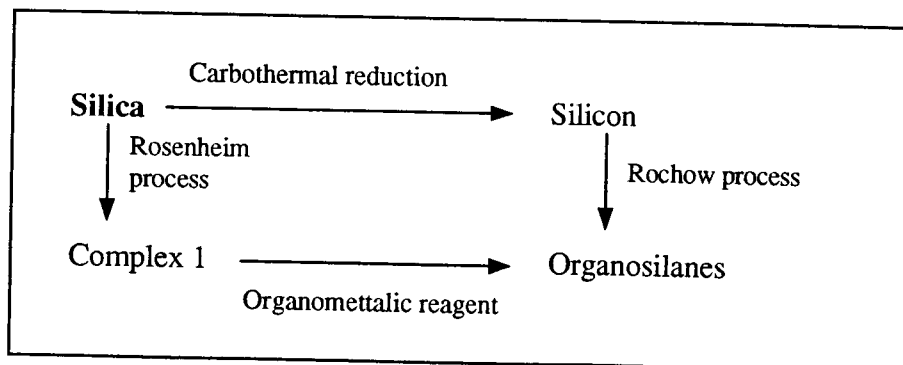
Figure 2.2 : Two routes for transforming silica into organosilanes.

2.2.2 Synthesis of tetramethoxysilane via the gas-solid reaction of SiO_2 with DMC with KOH as a catalyst

Recently, Ono et. al.[1992] presented a new route to produce alkoxysilanes through the gas-solid reaction of pure silica, loaded with 5 wt% of potassium hydroxide, with DMC at 227-327 °C. The order of the reaction rate with respect to DMC is 0.68, the activation energy being 89 KJ/mol [Ono et. al., 1992]. The reaction is shown below.

$$SiO_{2\,(s)} + CH_3O\overset{\overset{\displaystyle O}{\|}}{C}CH_3O_{\,(g)} \xrightarrow{\text{KOH}} Si(OCH_3)_{4\,(g)} + 2CO_{2\,(g)} \qquad (2.2.2.1)$$
$$\text{(DMC)}$$
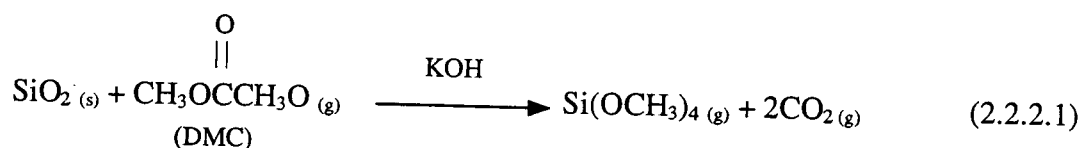
Furthermore, to increase the rate of reaction especially in the early stage, the high-temperature treatment over 250 °C in a helium stream for one hour is necessary. Besides the reaction with SiO_2, DMC was consumed in its thermal decomposition into dimethyl ether and carbon dioxide by about 4% at 327 °C and 25% at 352 °C, respectively [Ono, 1993].

$$CH_3O\overset{\overset{\displaystyle O}{\|}}{C}CH_3O_{\,(g)} \longrightarrow CH_3OCH_{3\,(g)} + CO_{2\,(g)} \qquad (2.2.2.2)$$
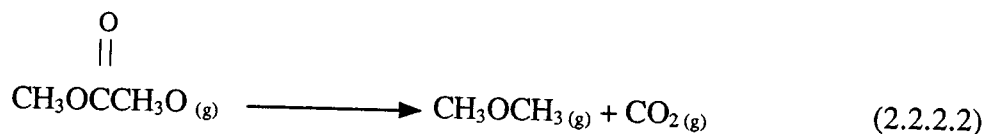
Consequently, the DMC decomposition is another significant step to be considered.

2.3 Synthesis of tetramethoxysilane from silicon-fines

It has been mentioned so far that TMOS can be synthesized by the reaction of Si or SiO_2 with CH_3OH or DMC. However, silicon-fines are mixtures of Si, SiO_2, and some inerts, and it has not been known if TMOS or some other useful chemicals can be synthesized from this waste material using the catalysts developed for pure materials. One of the two objectives of this research is to measure the rate of TMOS production via the silicon-fines-CH_3OH reaction and silicon-fines-DMC reaction to evaluate the reactivity of silicon-fines. There are four possible ways:

$$Si_{(s)} + 4CH_3OH_{(g)} \xrightarrow{CuCl_2} (CH_3O)_4Si_{(g)} + 2H_{2(g)} \; ; \Delta G^\circ = 107.4 \text{ Kcal/mol} \qquad (2.3.1)$$

$$SiO_{2(s)} + 4CH_3OH_{(g)} \xrightarrow{CuCl_2} (CH_3O)_4Si_{(g)} + 2H_2O_{(g)} \; ; \Delta G^\circ = 228.5 \text{ Kcal/mol} \qquad (2.3.2)$$

$$SiO_{2(s)} + 2(CH_3O)_2CO_{(g)} \xrightarrow{KOH} (CH_3O)_4Si_{(g)} + 2CO_{2(g)} \; ; \Delta G^\circ = 145.5 \text{ Kcal/mol} \qquad (2.3.3)$$

$$Si_{(s)} + 2(CH_3O)_2CO_{(g)} \xrightarrow{KOH} (CH_3O)_4Si_{(g)} + 2CO_{(g)} \; ; \Delta G^\circ = 33.3 \text{ Kcal/mol} \qquad (2.3.4)$$
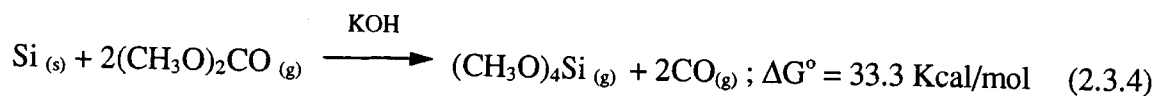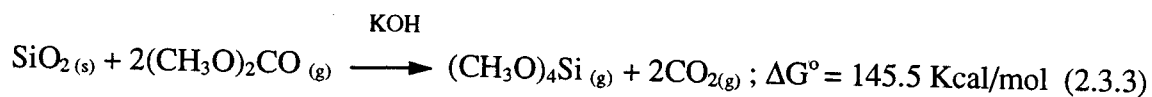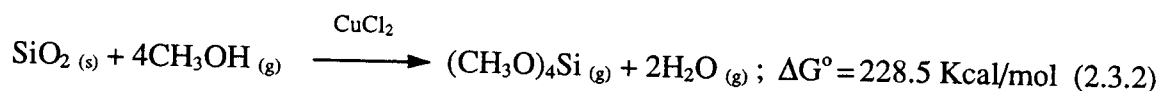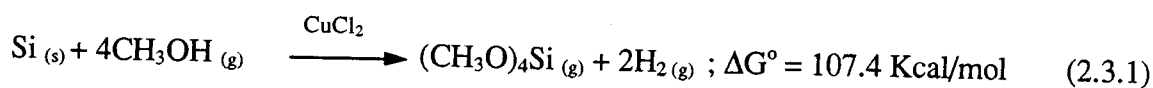
The Gibbs free energy change in each reaction is estimated at 573 °K (300 °C).

Since the Gibbs free energy change of the reaction 2.3.2 has a big positive value, it may be most unfavorable. The other objective is to determine most appropriate operating conditions for the reaction selected, which produce TMOS efficiently as well as economically.

Chapter 3

Experimental Apparatus and Procedures

3.1 Characteristics of silicon samples

3.1.1 Silicon-fines

3.1.1.1 Chemical analysis

Silicon fines are obtained from landfill at four different places, denoted BG, TS, NS, and SR. They were dried in an oven at 100 °C for 24 hr; then, were sent to LECO for O/N/C analysis which has been known as the LECO method. Solid samples are heated to 1800 °C or higher to liberate nitrogen and oxygen in helium. Also, solids are heated in air to liberate carbon as CO. With the use of a thermal conduction detector (TCD), O_2, N_2 and CO are detected to predict chemical composition. The major components of silicon-fines are believed to be Si, SiO_2, and SiC. The element analyses of the four different sources of silicon fines, obtained from the LECO lab, are shown in Table 3.1. Based on the mass fractions of carbon and oxygen determined by the analysis, the chemical compositions (% in mass) of silicon fines are estimated and summarized in Table 3.2.

For example, analytical contents of BG are: 10.97 %wt C, 5.82 %wt O. Thus, assuming O is from SiO_2 gives

$$\text{wt\% of } SiO_2 = \frac{MW. \ SiO_2}{MW. \ O_2} \times \text{wt\% } O_2 = \frac{60.09}{32.0} \times 5.82 = 10.92$$

Also, assuming that all carbon is in SiC.

$$\text{wt\% of SiC} = \frac{\text{MW. SiC}}{\text{MW. C}} \times \text{wt\% C} = \frac{40.1}{12.0} \times 10.97 = 36.66$$

$$\text{wt\% of SiO}_2 = 100 - \text{wt\% SiO}_2 - \text{wt\% SiC}$$

$$= 52.42$$

where MW. is the molecular weight.

The composition of BG is hence 52.42% Si, 10.92% SiO_2, and 36.66% SiC.

Table 3.1 : The chemical compositions of silicon fines from LECO

Type	C (wt%)	O (wt%)
BG	10.97	5.82
NS	3.68	34.03
TS	0.93	39.08
SR	8.56	22.80

Table 3.2 : The chemical properties of silicon fines (% in mass)

Type	Si	SiO₂	SiC
BG	52.42	10.92	36.66
NS	23.80	63.90	12.30
TS	23.59	73.30	3.11
SR	28.60	42.80	28.60

Since it is known that neither CH_3OH nor DMC can react with SiC at low temperatures considered in this study, only Si and SiO_2 are possibly converted to useful materials; TMS and TMOS. According to the reactions and their Gibbs free energy changes presented in section 2.3, Si may react with both CH_3OH and DMC to produce TMOS while SiO_2 may not react with CH_3OH. Consequently, Si seems to be a higher reactive material than SiO_2. Among the four types of silicon fines, BG and TS were selected because the former contains Si at a highest fraction and in the latter SiO_2 is the major component. Tests using SR were also made, which has intermediate composition.

3.1.1.2 Particle-size distribution analysis

BG, TS, and SR as received were dried in an oven at 100 °C for 24 hr. Then, a sample was dispersed by deionized water in a glass cell and immersed in an ultrasonic water-bath. The cell was put into a centrifugal particle size distribution analyzer (HORIBA CAPA 7000), which is capable of measuring particle sizes in the range from 0.001 μm to 700 μm. An average particle size of about 5.71 μm was obtained for BG, 15.5 μm for TS, and 4.46 μm for SR. The size distributions are shown in Figure 3.1.1, 3.1.2, and 3.1.3. The densities of the three were also measured with a picnometer, which are shown in Table 3.3.

Table 3.3 : The physical properties of silicon fines

Specification	BG	TS	SR
Density (g/cm^3)	2.60	2.24	1.32
Average particle size (μm.)	5.71	15.5	4.46

3.1.2 Pure silicon powder and SiO_2

Since Si and SiO_2 are the major component in silicon fines, it is important to know which of the CH_3OH or DMC reaction can highly convert Si to TMOS. To test this, pure Si powder and SiO_2 beads were used in the respective reactions. The physical and chemical properties of the pure silicon powder and SiO_2 beads are shown in Table 3.4 and 3.5.

Table 3.4 : Physical properties of pure silicon powder and SiO_2

Symbol	Material	d_p (μm)	ρ_p (g/cm^3)	BET surface (m^2/g)	Pore Size ($^\circ$A)
*Si-F	Silicon	2.0	2.4	N/A	N/A
#SiO$_2$	Silicon dioxide	1700-4000	0.415	193	154

Table 3.5 : Element analysis of pure silicon powder and SiO_2 (% mass)

Symbol	Si	Fe	Al	Ca	C	O	H
*Si-F	99.27	0.08	0.10	0.02	0.02	0.51	-
#SiO$_2$	46.05	-	-	-	-	53.80	0.15

* Shin-Etsu Chemical Company Ltd.

Fuji Silysia Chemical Ltd.
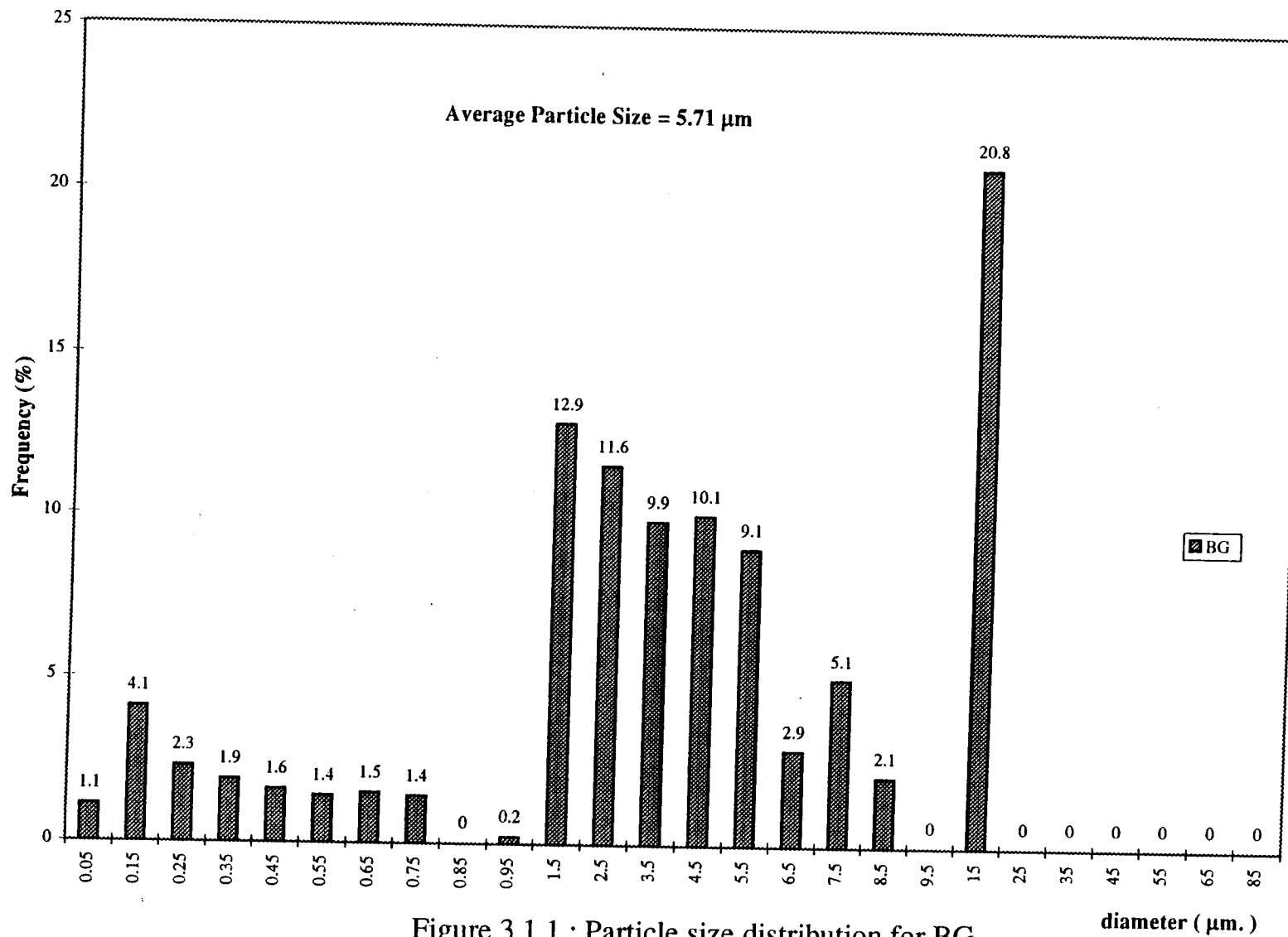
Figure 3.1.1 : Particle size distribution for BG
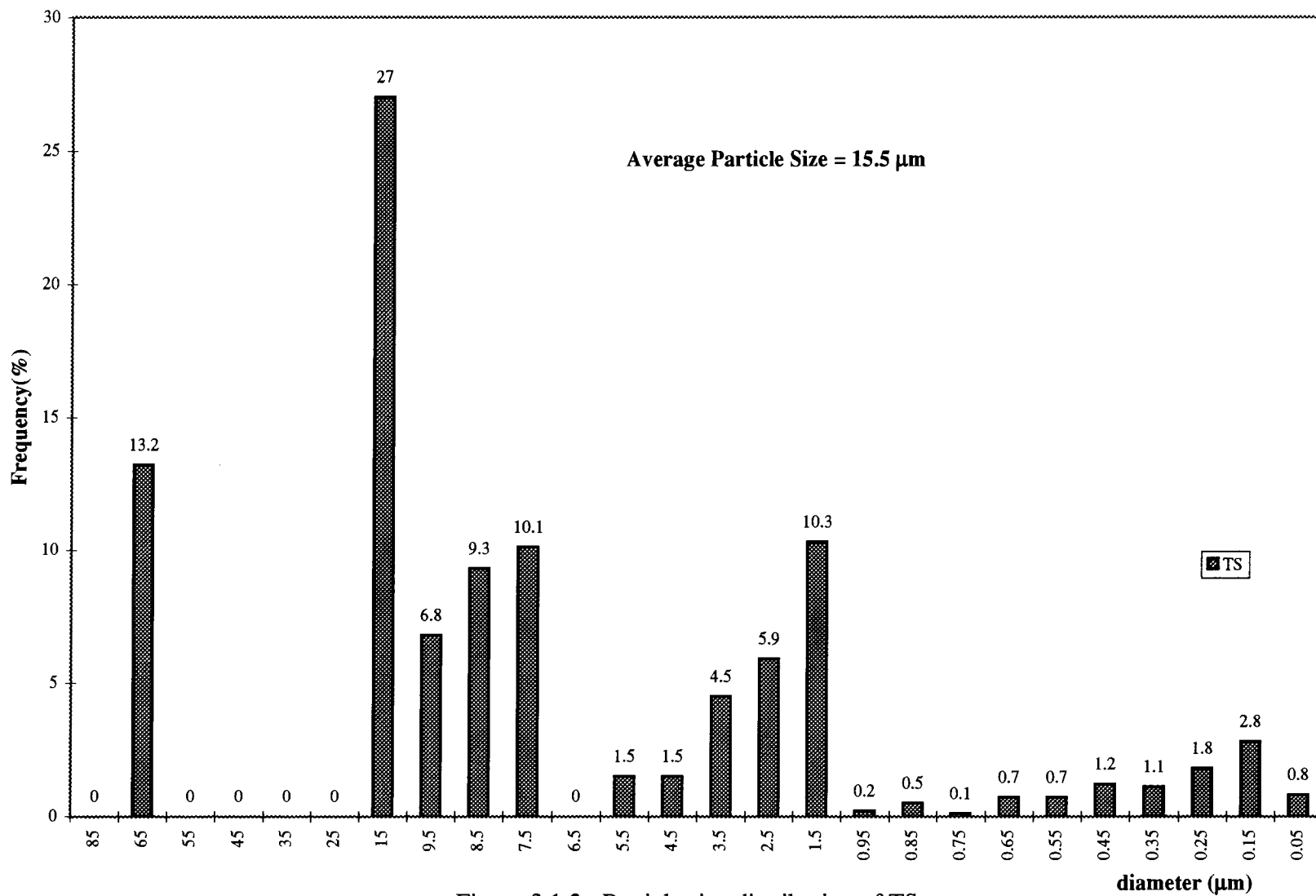
Figure 3.1.2 : Particle size distribution of TS
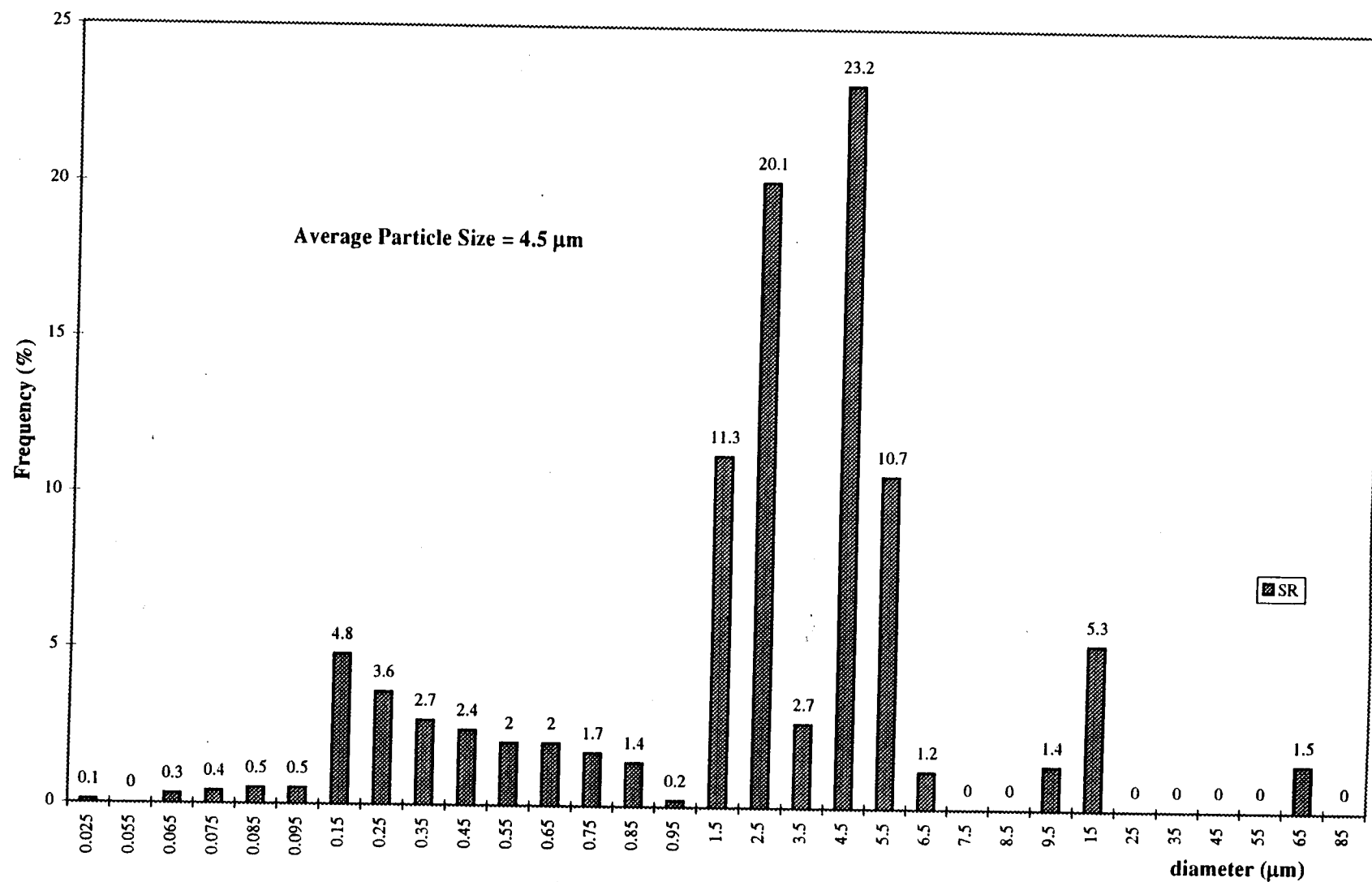
Figure 3.1.3 : Particle size distribution of SR

3.2 Sample preparation

3.2.1 For CH₃OH reaction

Sample solid materials obtained from landfill were first dispersed in deionized water in individual beakers, filtered and then dried at 100 °C for 24 hr. 0.5 g of Cu(II)Cl₂ was dissolved in 5 cm³ of CH₃OH in a beaker. 9.5 g of cleaned and dried solids were immersed in the CH₃OH/Cu(II)Cl₂ solution, and dispersed in it by using an ultrasonic water-bath. The mixture in the beaker was left in a well ventilated hood until all CH₃OH had evaporated. Solids impregnated with Cu(II)Cl₂ were then brought into an oven to be dried at 100 °C for 12 hr. Next, the cake of solids was broken into small pieces and palletized by compressing 0.3 g of the mixture in a die of 0.5 inch diameter at a pressure of 15,000 lb$_f$. The pallets ,0.5 inch diameter and 1.10 mm thick, were cut into small particles of about 2 mm in size.

Later, the particles were sieved by a mesh with 1.168 mm. openings. Particles larger than 1.168 mm but smaller than 2 mm were selected to be dried at 100 °C for 3 hr. in the oven and immediately weighed before packing them to the tubular reactor for the reaction experiment.

3.2.2 For DMC reaction

The preparation of solids for the DMC reaction is almost identical to that for the CH$_3$OH reaction mentioned above. 0.5 g of KOH was used instead of Cu(II)Cl$_2$. The steps of preparation for both the CH$_3$OH and DMC reactions are summarized in Table 3.6.

3.2.3 Pure silicon powder for CH$_3$OH reaction

The steps of sample preparation for pure silicon powder obtained from Shin-Etsu Chemical company Ltd. are similar to those described in section 3.2.1, except some specifications, as illustrated in Table 3.7.

Table 3.6 : Preparations of BG for CH$_3$OH and DMC reactions

Specifications	CH$_3$OH reaction	DMC reaction
Catalyst	Cu(II)Cl$_2$	KOH
Palletization	0.3 g/15,000 lb$_f$	0.3 g/9,000 lb$_f$
Pallet thickness	1.10 mm	1.05 mm
Mesh	1.168 mm opening	1.168 mm opening

3.2.4 Pure silicon powder for DMC reaction

The steps are almost identical to those for the BG/TS preparation except for a few operating conditions, as shown in Table 3.7.

3.2.5 SiO₂ beads for CH₃OH reaction

9.5 g of SiO₂ beads were immersed in a solution of 0.5-g $Cu(II)Cl_2$ dissolved in 5 cm³ of CH₃OH in a beaker. Then, the mixture in the beaker was left in a well-ventilated hood until all CH₃OH had evaporated. SiO₂ beads impregnated with $Cu(II)Cl_2$ were then brought into an oven to be dried at 100 °C for 12 hr and immediately weighed before packing them in the tubular reactor for the reaction experiment.

Table 3.7 : Preparations of pure silicon powder for CH₃OH and DMC reactions.

Specifications	CH₃OH reaction	DMC reaction
Catalyst	$Cu(II)Cl_2$ (5 wt%)	KOH (5 wt%)
Palletization	0.3 g/3,000 lb$_f$	0.3 g/3,000 lb$_f$
Pallet diameter	0.5 inch	0.5 inch
Pallet thickness	1.70 mm	1.75 mm
Solvent for contact mass	methanol	methanol
Sieve opening	1.168 mm	1.168 mm
Dry before reaction	100 °C for 3 hr	100 °C for 3 hr

3.3 Experimental Apparatus

3.3.1 Synthesis of TMOS from CH₃OH/DMC reaction.

The experimental apparatus designed for the synthesis of TMOS is shown in Figure 3.2. Samples from BG, TS, SR or pure Si powder were inserted in an 1.5 m. long

1. 3-way valve   2. Control valves   3. Rotameters   4. 3-way valve   5. Bubbler   6. Water bath
7. 3-way valve   8. Silicon fines   9. Furnace   10. By-pass line 11. Reactor tube 12. 3-way valve
13. Back-pressure regulator   14. Valve   15. Sample trap   16. Ice-bath   17. Valve
18. Gas Sampling Loop   19. Thermocouple   20. Gas Chromatograph   21. Computer Acquisition
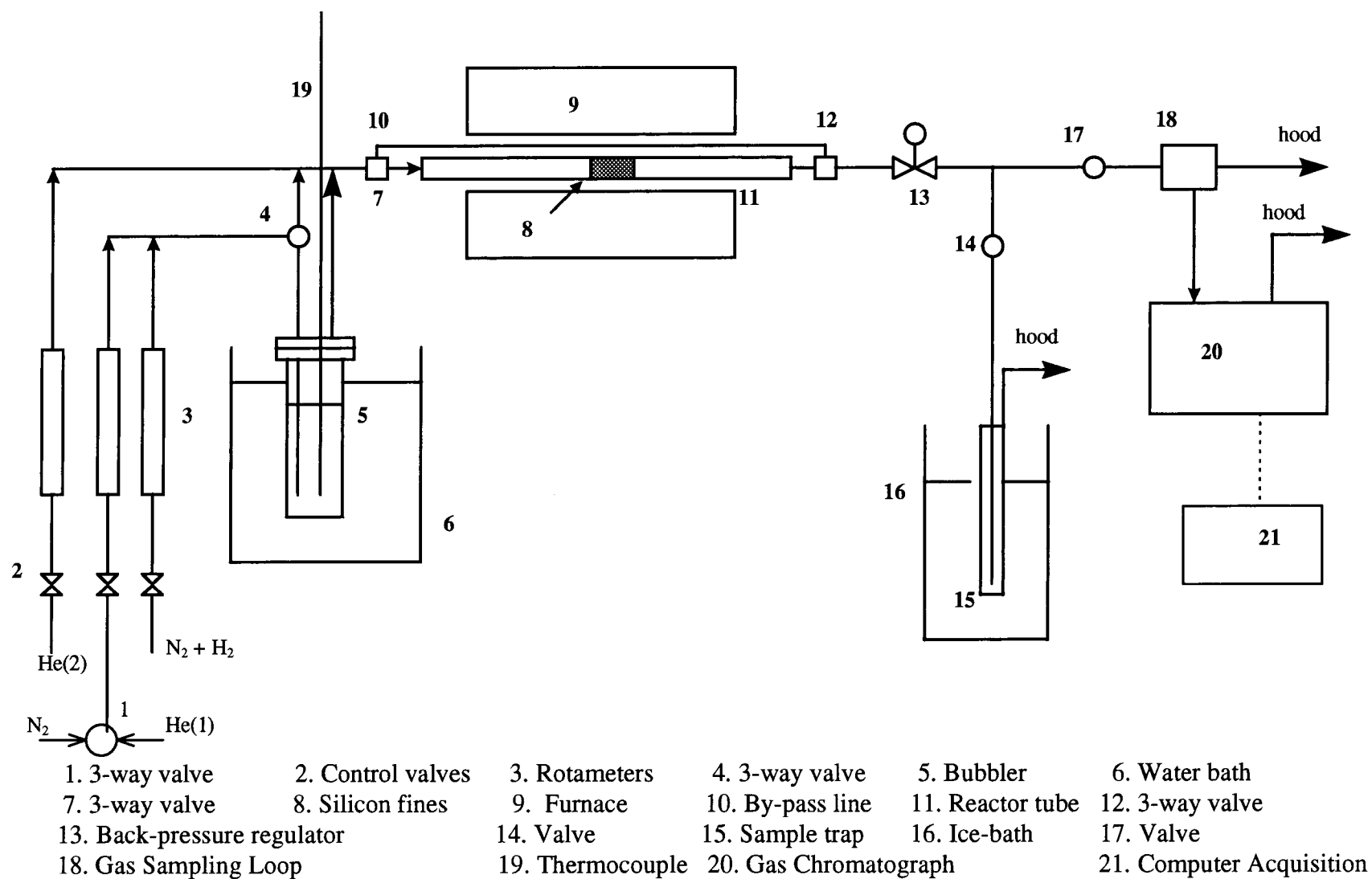
Figure 3.2: Experimental set-up for TMOS synthesis from silicon fines

tubular reactor, which is made of a 0.5 inch ID stainless steel tube. They were sandwiched with stainless steel filaments and placed in the center of a 3-foot long electric furnace. The temperature of the furnace was controlled by a programmable controller. To obtain temperature measurements, a thermocouple was inserted inside the tubular reactor close to the samples.

The water bath, item 6, in Figure 3.2 was used to heat the reactant, either CH_3OH or DMC, kept inside a stainless steel bubbler, item 5. In order to obtain the steady flow rate of the reactant, operating conditions were investigated. It was found that the effective operating pressures are 144.7 KPa for the CH_3OH reaction and 101.3 KPa for the DMC reaction, respectively. Before the reaction was initiated, CH_3OH and DMC were heated to 76 and 91°C, respectively. These temperatures are the boiling points at the mentioned operating pressures. Then, reactant vapor was carried by a helium stream through the reactor where it reacted with sample particles impregnated with KOH or $Cu(II)Cl_2$ (see section 3.4 for more details). In Figure 3.2, He(1) is helium gas directly used to carry the reactant vapor out of the bubbler. He(2) goes through the side stream to be used for adjusting the molar concentration of the reactants.

The effluent gas from the reactor was splitted into 2 parts for analysis. The first part of the outlet gas was introduced into a gas sampling loop (EV-91 Model) periodically in order to analyze the composition of products. The sampling loop was connected to a gas chromatograph (Shimadzu, Model 14-A) equipped with a 3-m column of 10% SE-30 chromosorb, operating at 35-55 °C, and a TCD. The other part was

introduced into the ice trap where vapor was condensed into liquid. Later, the composition of the condensate was determined by gas chromatography. The gas chromatograph was connected to a computer equipped with the EZChrom data acquisition program (Shimadzu).

3.3.2 CH₃OH and DMC decomposition

According to the thermal decomposition analysis reported by Ono [1993], DMC decomposes to dimethyl ether and carbon dioxide by about 4% at 327 °C and 25% at 352 °C. Also, CH_3OH decomposse to aldehyde, formaldehyde, water and hydrogen at high temperature[Frank D. M., 1988].

Therefore, it is necessary to know how much DMC or CH_3OH remains for the desired reaction after the thermal decomposition. The tubular stainless steel reactor inserted into the same furnace operated under the same operating conditions was applied, as shown in Figure 3.2. In addition, the reactant, either CH_3OH or DMC, was heated inside the bubbler in the water bath at the same conditions as described in section 3.3.1 and carried by helium gas through the reactor. All effluent gas products from the reactor were introduced into the gas sampling loop for gas chromatograph analysis with a TCD and a 3 m. column of 10% SE-30 chromosorb operating at 35°C. The gas chromatograph (Shimadzu, Model 14-A) was connected to a computer which analyzes the data via the EZChrom data acquisition program (Shimadzu).

3.4 Experimental Conditions and Procedures

To synthesize TMOS via the SiO_2-DMC reaction, Ono [1993] reported that the effective operating temperature was between 227-327 °C, at a pressure close to atmospheric pressure. The partial pressure of DMC, evaporated by heating it, was controlled by adjusting the flow rate of cofeeding helium. Ono et. al. [1993] also presented the synthesis of TMOS via the Si-CH_3OH reaction operated in the range of 260-280 °C. CH_3OH was fed by a motor-driven syringe at a rate of 87 mmol/hr with helium as cofeeding gas.

Since silicon fines contain both Si and SiO_2, this study attempted to synthesize TMOS via both the CH_3OH and DMC reactions. The direct and side streams of He gas were adjusted to control the flow rate as well as concentration of reactant, either CH_3OH or DMC. The effective operating pressure for the CH_3OH reaction was found to be slightly higher than the atmospheric pressure(144.7 KPa) while for the DMC reaction the pressure was close to the atmospheric pressure(101.3 KPa).

3.4.1 Experimental procedure to produce TMOS from CH_3OH reaction

Approximately 3.0 g of sample particles impregnated with $Cu(II)Cl_2$ were packed into the tubular flow reactor. All the apparatus connections were set as shown in Figure 3.2 and inspected one by one to prevent the gas for leaking before starting the operation. Then, N_2 was fed to purge all the lines in the reactor system. Next, the reactor was heated

at a heating rate of 10 °C/min. To obtain highly selective active sites (Cu_3Si), the sample particles were to be pretreated by introducing nitrogen and hydrogen (5 mol%) to the system [Weber, 1987]. After the pretreatment at 500 °C for 3 hr, the reactor temperature was dropped to 300 °C at a cooling rate of 10 °C/min. During this cooling down period, all the reactor inlet and outlet lines were heated in order to prevent any possible gas condensation.

CH_3OH in the water bath was heated to a temperature slightly above the normal boiling point. When the CH_3OH temperature reached 76 °C, helium gas was supplied into the bubbler at a rate of 10 ml/min in order to carry out CH_3OH vapor. In addition, helium gas from the side stream was supplied and mixed with the CH_3OH /helium vapor before entering the reactor to adjust the molar concentration of CH_3OH. To prevent the sample from reacting with CH_3OH vapor while waiting for the reactant flow to get steady, the CH_3OH /helium stream was sent to the by-pass line going out of the system. Once desired operating conditions were reached, the mixture of CH_3OH /helium was introduced into the reactor to initiate the reaction with sample. Immediately, the effluent gas product was analyzed automatically every 15 minutes with a gas chromatograph (Shimadzu, Model 14-A). The operating conditions of the gas chromatograph are shown in Table 3.8.

In addition, the product was condensed in an ice trap, collected for every 10 minutes, and analyzed by the gas chromatograph (Shimadzu, Model 14-A). The analysis of condensed liquid was carried out after the automatic gas analysis was over. More details of the operating conditions are shown in Table 3.9. After the reaction was ceased,

the sample solids were weighed as soon as possible to measure the mass lost due to the reaction.

Table 3.8 : The operating conditions of the gas chromatograph

Column temperature	35 °C for 5 minutes and 55 °C for 4 minutes
Injection temperature	130 °C
Detector temperature	130 °C
TCD temperature	130 °C
TCD current	100 mA

3.4.2 Experimental procedure to produce TMOS from DMC reaction

Silicon samples of about 3.0 g impregnated with KOH were placed at the center of the tubular flow reactor. Prior to starting the reaction, all apparatus connections were inspected and the system was purged by N_2 gas. To increase the rate of reaction, especially in the early stage of the reaction [Ono and Suzuki, 1993], the samples were heat-treated in N_2 stream at 400 °C for 3 hr. The reactor was heated at a heating rate of 10 °C/min. Also, all the inlet and outlet lines of the reactor system were heated for preventing gas condensation. The operating conditions are presented in Table 3.9.

After the pretreatment period, the reactor was cooled down to a subscribed reaction temperature at a cooling rate of 10 °C/10 min. During the heat treatment period, DMC was heated inside the bubbler immersed in the water bath. Helium gas was charged

directly into DMC when its temperature reached its boiling point. DMC vapor was carried out by helium gas through the by-pass line connected to the hood until the flow of reactant became stabilized. As soon as all desired operating conditions were attained, the DMC/helium mixture was fed into the reactor to start the reaction with sample solids. The effluent gas and condensate products from the reactor were analyzed in the same way as for the CH_3OH reaction. Finally, the sample was weighed to determine the mass lost in the reaction.

Table 3.9 : The operating conditions of CH_3OH and DMC reaction

Conditions	CH_3OH Reaction	DMC Reaction
Pretreatment temperature	500 °C	400 °C
Pretreated gas	$N_2 + H_2$ (5 mol%)	N_2
Water bath temperature	76 °C	93 °C
Reactant temperature	74 °C	91 °C
Direct stream of He flow	10 ml/min	26.1 ml/min
Side-stream of He flow	36.5 ml/min	-
Reaction temperature	300 °C	300 °C
Operating pressure	144.7 KPa	101.3 KPa
Inlet temperature to reactor	80 °C	95 °C
Outlet temperature from reactor	130 °C	130 °C
Inlet temperature to EV-91	140 °C	140 °C

3.4.3 CH₃OH and DMC decomposition analysis

It is believed that DMC and CH_3OH decompose at high temperature. The thermal decomposition is suspected to have important effects in this study. Imperatively, the amount of reactant remaining undissociated needs to be determined so that the reactant molar concentration can be estimated.

Using the empty tubular reactor, all the operating conditions and procedures for the CH_3OH decomposition study were maintained identical to those described in section 3.4.1. Also, the DMC decomposition study was analyzed using the same procedures described in section 3.4.2. While CH_3OH decomposition was investigated at 300 °C, the DMC decomposition was measured at 300 °C and 325 °C. Table 3.10 summarizes operating conditions used for the decomposition study.

Table 3.10 : The operating conditions for CH₃OH/DMC decomposition

Conditions	DMC reaction	CH₃OH reaction
Reactor temperature	300 °C and 325 °C	300 °C
Operating pressure	101.3 KPa	144.7 KPa
Direct He flow rate	26.1 ml/min	10 ml/min
Side-stream He flow rate	-	36.5 ml/min
Average flow of reactant/He	226 mmol/hr	240 mmol/hr
Average molar concentration of reactant	3×10^{-2} mol/L	2.14×10^{-2} mol/L
Inlet temperature to reactor	95 °C	80 °C
Outlet temperature from reactor	130 °C	130 °C
Inlet temperature to EV-91	140 °C	140 °C

Without programming the column temperature, the outlet gas from the reactor was analyzed every 5 minute by a gas chromatograph (Shimadzu, Model 14-A) with a 3-m column of 10%SE-30 chromosorb operated at 35 °C. All operating conditions, except the column temperature of the gas chromatograph, are the same as those in Table 3.8.

Chapter 4

Results and Discussion

This chapter is divided into six sections: the decomposition of DMC, the decomposition of CH_3OH, the formation of TMOS from BG, the formation of TMOS from pure silicon powder, effects of operating conditions on the synthesis of TMOS from BG via the DMC reaction, and the formation of TMOS from TS and SR.

As mentioned earlier, CH_3OH and DMC decompose at high temperature. It is necessary to predict their amount remaining undissociated, which determines the reactant concentration. The decomposition of the two is discussed in the first two sections.

Because silicon-fines contain mainly Si, SiO_2, and SiC, it is needed to find the better process, either the CH_3OH or DMC reaction, that has higher selectivity of product and a higher conversion rate of solids. This selection study will be discussed in the last four sections.

4.1 DMC decomposition

The DMC decomposition was investigated at 300 °C and 325 °C because of the following two reasons. First, the effective temperature for the gas-solid reaction of silica with DMC is about 227-327 °C, as reported by Ono et. al.(1992). Second, the thermal decomposition of DMC is about 4% at 327 °C and 25% at 352 °C [Ono et. al., 1993], which proceeds as

$$(CH_3O)_2CO_{(g)} \longrightarrow (CH_3)_2O_{(g)} + CO_{2\,(g)} \qquad (4.1.1)$$
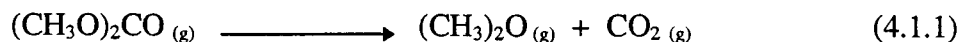
Based on their work, the experiment for TMOS synthesis in this study was performed in the range of 250-325 °C. Two temperatures were hence selected for the DMC decomposition experiment; 300 °C and 325 °C. Helium gas was introduced into DMC in the bubbler to carry its vapor out at an average DMC/He molar ratio of 3.8 for 300 °C and 3.2 for 325 °C.

The effluent gas from the reactor was directly analyzed by gas chromatography (Shimadzu, Model 14-A). The analysis of outlet gas obtained from the EZChrom data acquisition program (Shimadzu) is shown in Figure 4.1. According to the gas chromatography data, the molar flow rates of DMC and CO_2 (one of the two products in the DMC decomposition), see equation 4.1.1, at 300 °C were determined as shown in Figure 4.2. The DMC decomposition proceeds at an almost constant level.

The fraction of DMC decomposition at 300 °C was then calculated to be 0.34%. The DMC decomposition at 325 °C was 0.48%. These results are summarized in Table 4.1.

Table 4.1 Experimental results of DMC dissociation at 300 °C and 325 °C

Conditions	300 °C	325 °C
*Volumetric flow of He	25 ml/min	25 ml/min
*Average volumetric flow of DMC	92.3 ml/min	77.8 ml/min
Average molar ratio of DMC/He	3.8	3.2
% dissociation by mole	0.34	0.48

*Referred to room temperature.
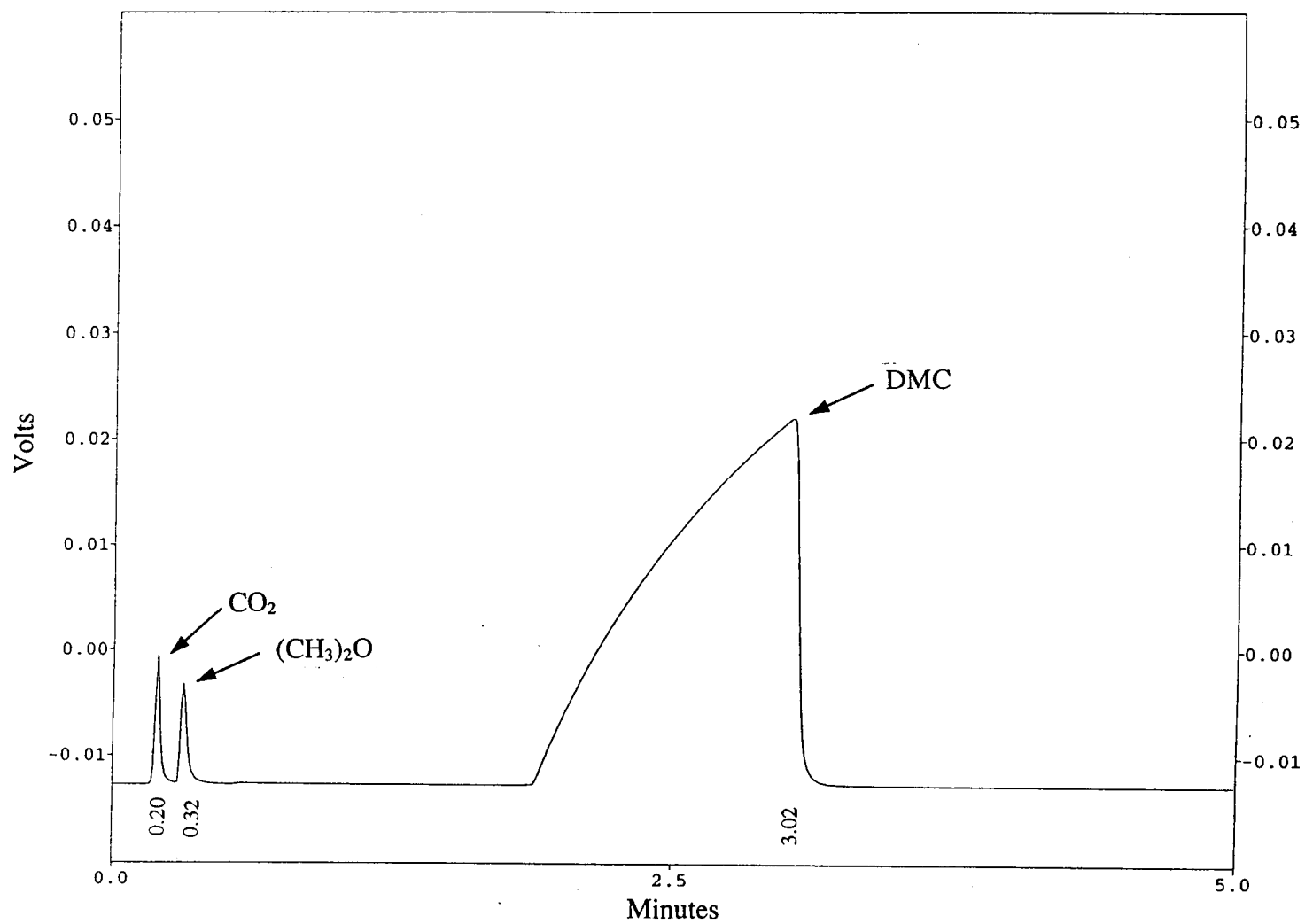
Figure 4.1 : The composition of reactor outlet gas in DMC decomposition at 300 °C
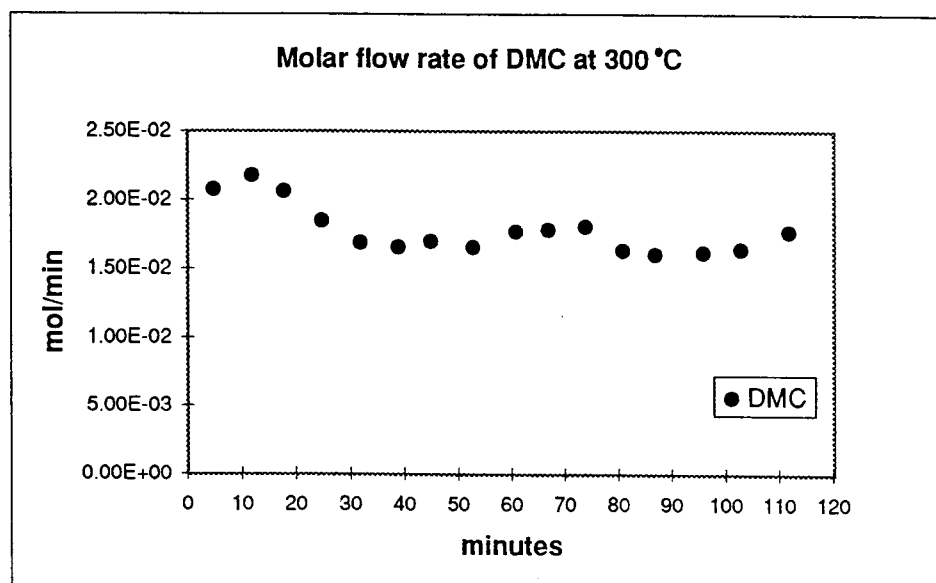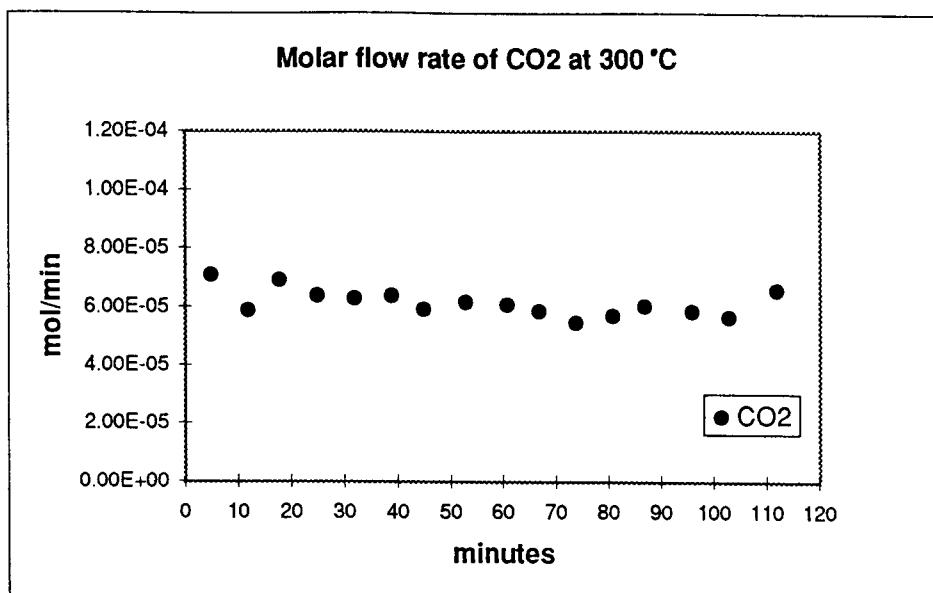
Figure 4.2 : Molar flow rates of DMC and CO_2 produced in DMC decomposition at 300 $^\circ$C

Compared to Ono's data at 327 °C, the current result at 325 °C is significantly lower because of a shorter residence time applied in this study. Based on the small percentage of DMC decomposition at 300°C and 325 °C, the thermal decomposition of DMC at temperatures used in this study can be neglected. Because all the conditions (pressures, temperatures, apparatus materials) employed in the DMC decomposition study are identical to those in the experiment for the TMOS synthesis, the amount of DMC that contacts sample solids is roughly the same as fed into the reactor at any temperature lower than 325 °C.

4.2 CH₃OH decomposition

Since the effective temperature for the Si-CH_3OH reaction with $Cu(II)Cl_2$ as a catalyst is about 200 °C or higher [Ono et. al., 1991], the CH_3OH reaction with silicon fines and pure Si powder was operated at 300 °C. Consequently, the thermal decomposition of CH_3OH was also studied at 300 °C. CH_3OH decomposes as

$$CH_3OH_{(g)} \longrightarrow HCHO_{(g)} + H_{2\,(g)} \qquad (4.2.1)$$

$$2CH_3OH_{(g)} \longrightarrow CH_3CHO_{(g)} + H_2O_{(g)} + H_{2\,(g)} \qquad (4.2.2)$$
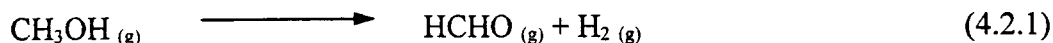
He(1) was introduced into the bubbler to carry CH_3OH vapor. Then, He (2) was added to the CH_3OH/He(1) mixture. The average CH_3OH/He molar ratio of the gas entering the reactor was 1.1. In this experiment, the composition of outlet gas was also
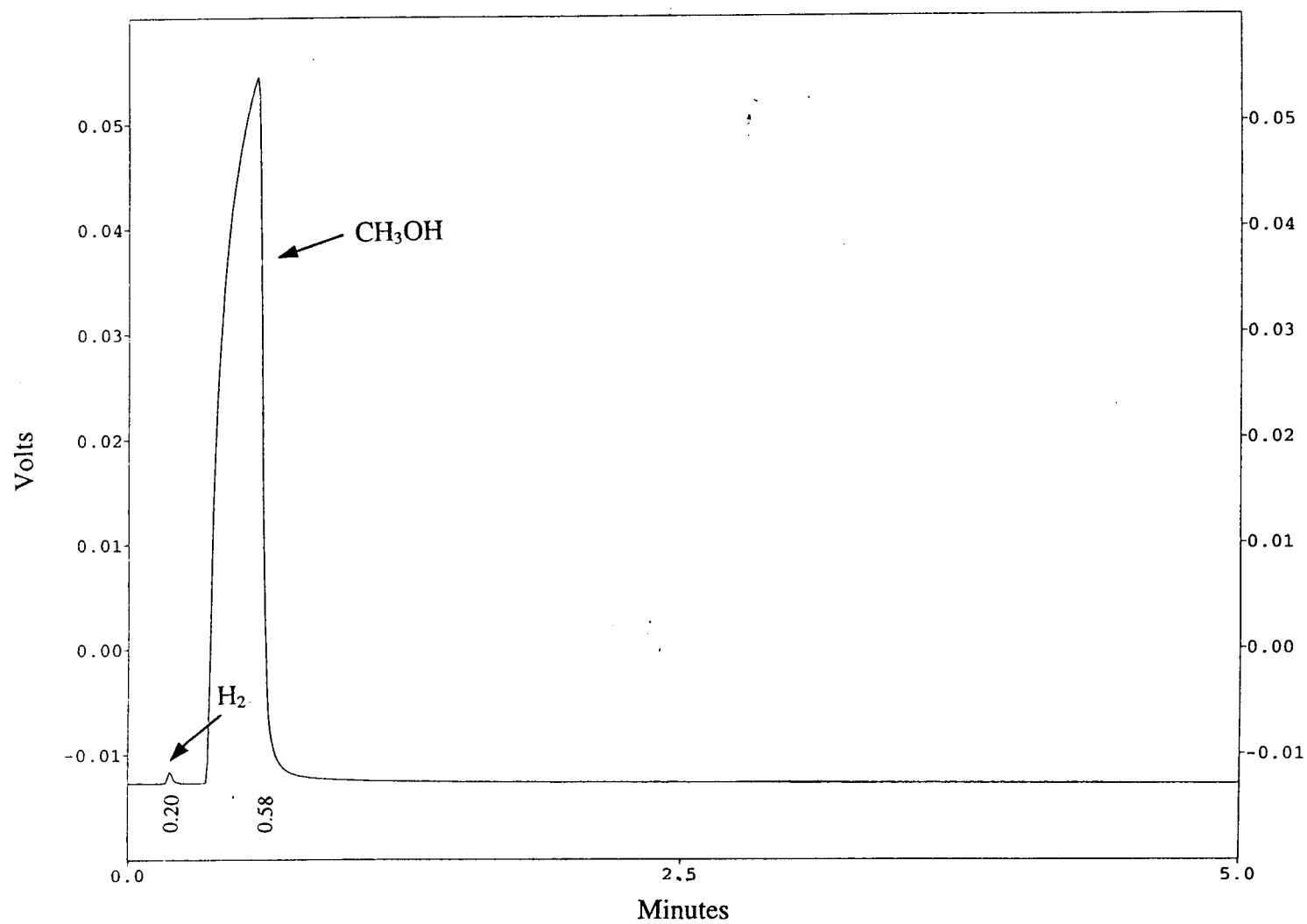
Figure 4.3 : The composition of reactor outlet gas in CH₃OH decomposition at 300 °C
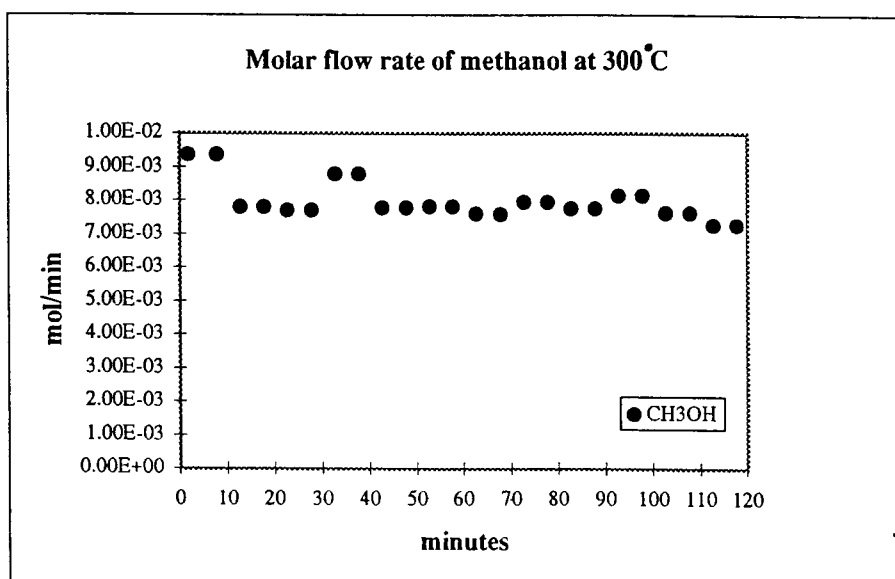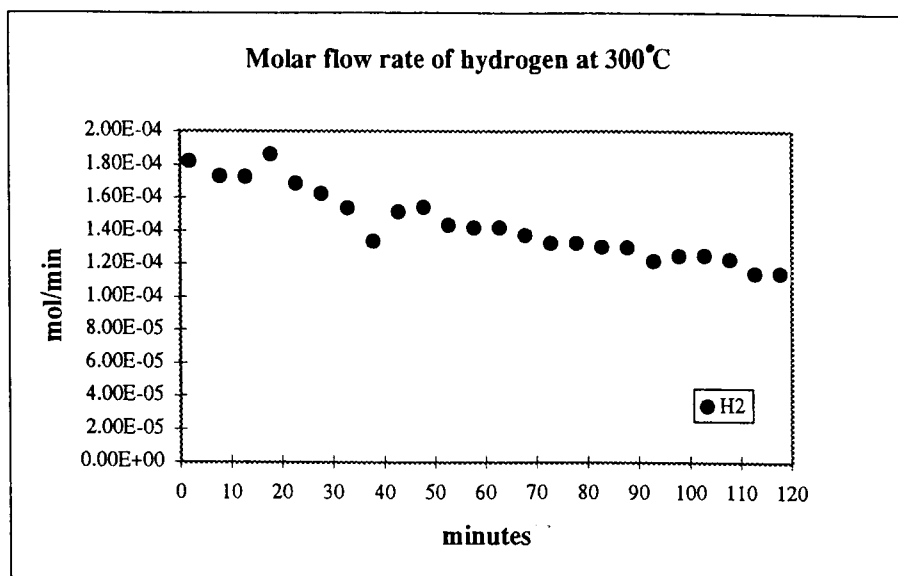
Figure 4.4 : Molar flow rates of CH_3OH and H_2 produced in
CH_3OH decomposition at 300 °C

obtained by the gas chromatograph with the EZChrom data acquisition. The gas sampling loop in the gas analyzer collected the outlet gas every five minutes. Figure 4.3 shows two peaks of CH_3OH and H_2 produced in the CH_3OH decomposition. Any peaks corresponding to the other products were not detected, probably because of overlapping with the CH_3OH peak. The molar flow rates of H_2 and CH_3OH calculated are shown in Figure 4.4.

The experimental CH_3OH decomposition at 300 °C yielded 2.6% (by mole), a rather small fraction of decomposition due to the short residence time applied. Since all the conditions (pressures, temperatures, apparatus materials) employed were identical to those in the synthesis of TMOS from the CH_3OH reaction, the CH_3OH decomposition in the CH_3OH reaction was neglected in this study as long as the molar concentration of CH_3OH available for the TMOS formation reaction was concerned.

4.3 TMOS formation study from BG

4.3.1 CH₃OH reaction

Over the period of 5-hr, the outlet gas from the reactor was analyzed by gas chromatography every fifteen minutes. Figure 4.5 shows one of GC charts obtained when BG was used for the TMOS formation from CH_3OH. There are nine peaks corresponding to H_2, CH_3OH, TMS, TMOS, and five unknowns. The TMOS peak is located at 7.3 minute. More details about the unknown peaks will be discussed in section 4.4.
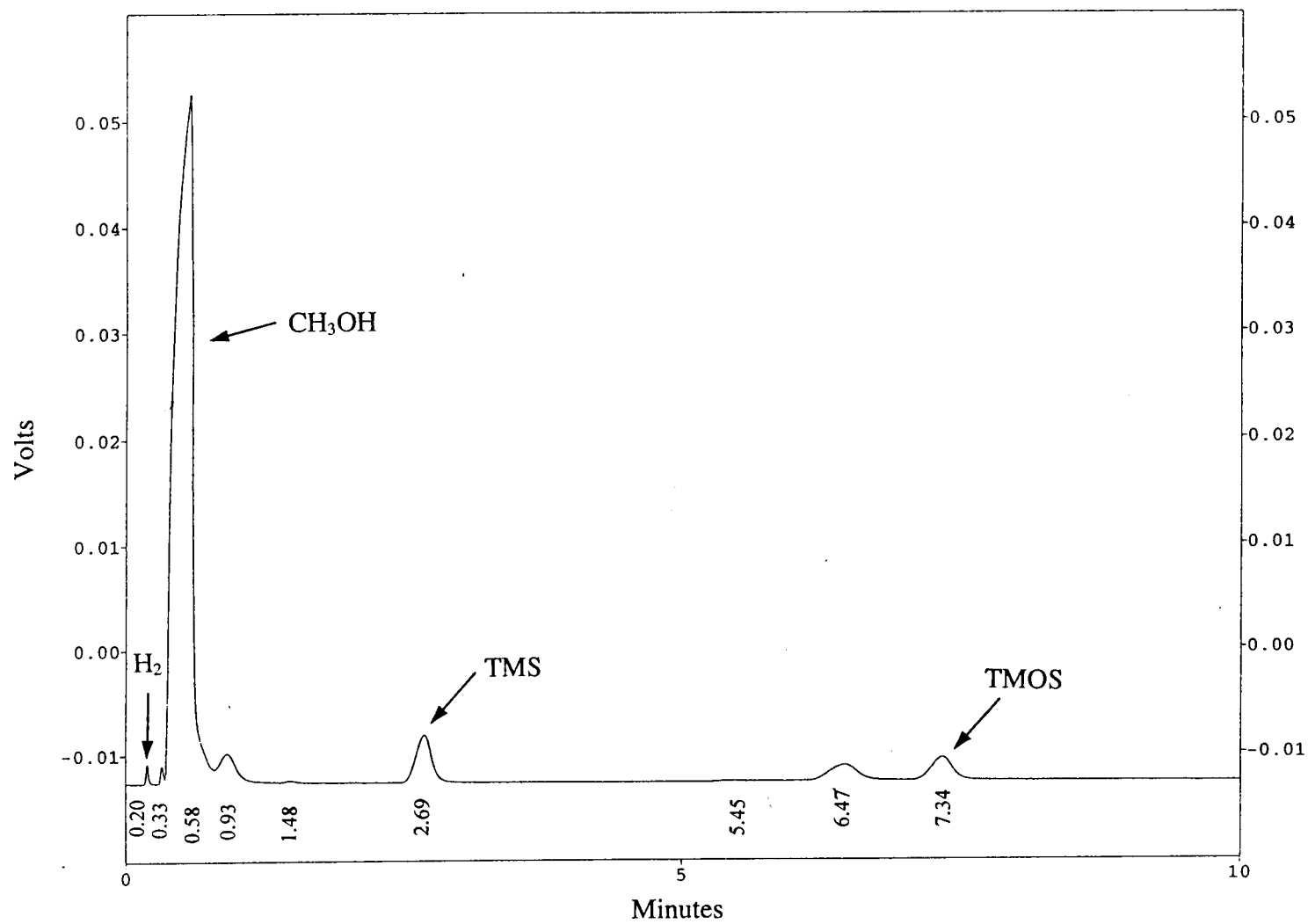
Figure 4.5 : The composition of reactor outlet gas in the BG-CH₃OH reaction at 300 °C

The color of the condensate collected in the ice trap was light-yellow. It is suggested that there are some side reactions involved in the CH_3OH reaction.

An effort was made to find from which TMOS was obtained, either Si or SiO_2, in the CH_3OH reaction. 3 g of SiO_2 beads of about 2 mm diameter, impregnated with $Cu(II)Cl_2$, were packed in the reactor. All conditions (pretreatment, reaction temperature, material) are identical to those of the BG-CH_3OH reaction. By analyzing the effluent gas from the reactor and the condensate in the ice trap, there were no obvious TMOS peak observed in the GC chart. In addition, there was no change in the mass of SiO_2 beads between before and after the reaction. It is hence suggested that only Si in BG was converted to TMOS and TMS in the reaction with CH_3OH. TMOS is the major product produced from TMS as its intermediate product (see section 4.4 for more details). The operating conditions and obtained results are summarized in Table 4.2.

4.3.2 DMC reaction

All the operating conditions used for the BG-DMC reaction are also shown in Table 4.2. Figure 4.6 shows one of GC charts of the effluent gas analysis. The four peaks correspond to CO/CO_2, dimethyl ether, DMC and TMOS. TMOS is the major product whose peak appears at 7.4 minute. No side reaction occurred in this process except the formation of a negligibly small amount of by-product $(CH_3)_2O$ from the DMC decomposition. Because the peaks of CO_2 and CO overlapped and could not be separated, it is difficult to tell which of Si or SiO_2 reacted to produce TMOS.
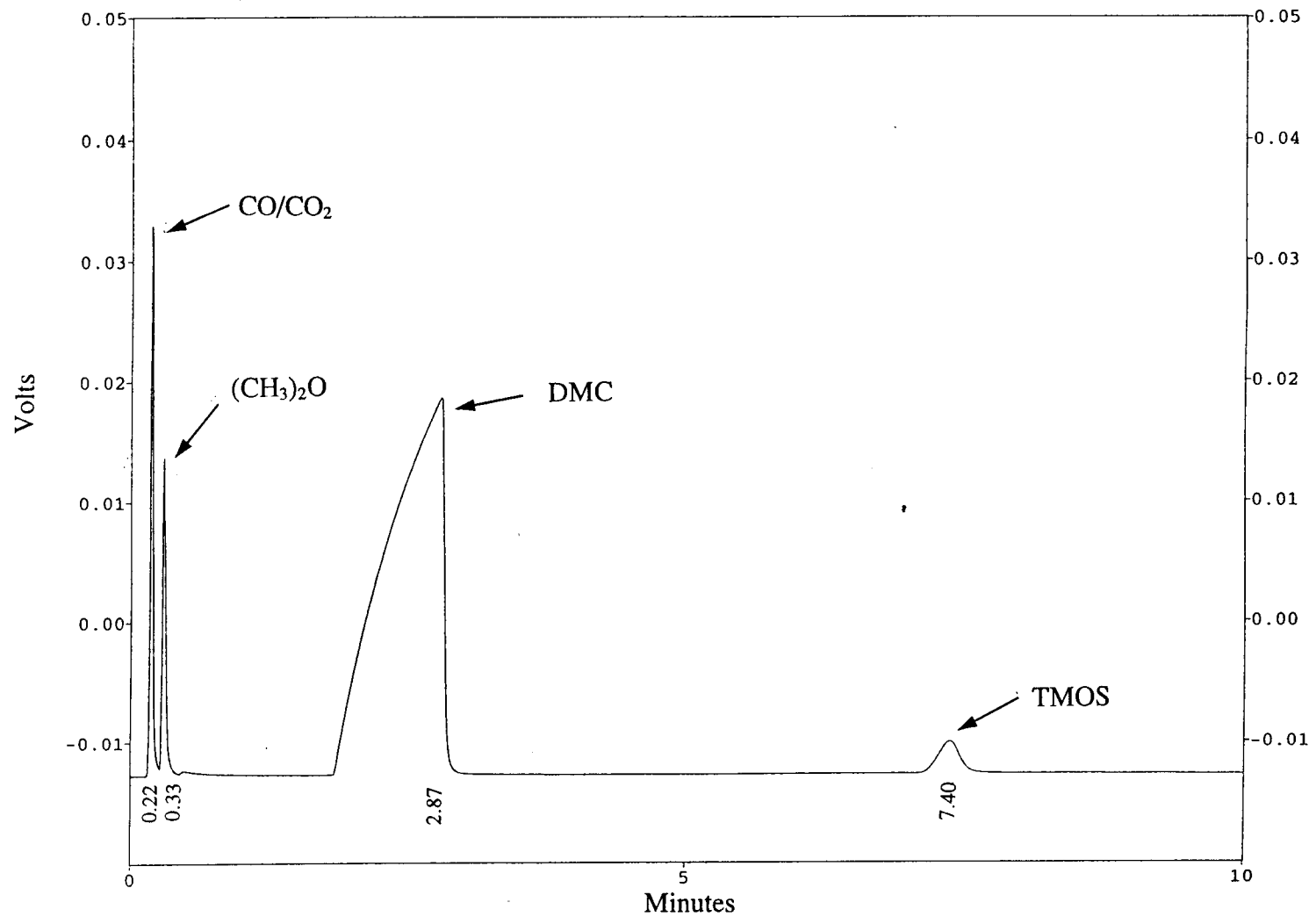
Figure 4.6 : The composition of reactor outlet gas in the BG-DMC reaction at 300 °C

Both Si and SiO_2 may have reacted with DMC. Hence, further investigation was conducted, which will be described later.

As shown in Table 4.2, the total masses of BG lost in both the DMC and CH_3OH reactions are almost identical, although the molar concentration of DMC is lower than that of CH_3OH, which is not sufficient, however, for choosing the effective reaction for BG based on the above results. Further study to identify which of DMC or CH_3OH reactions is suitable for converting BG will be provided in the next section.

Table 4.2 : Operating conditions for and results from the reaction of BG with DMC and CH_3OH

Conditions	DMC reaction	CH_3OH reaction
Palletization	0.3 g / 9,000 lb$_f$	0.3 g / 15,000 lb$_f$
Pretreatment temperature for 3 hr.	400 °C	500 °C
Gas for pretreatment	N_2	$N_2 + H_2$ (5 mol%)
Initial mass of sample	3 g	3 g
Operating pressure	101.3 KPa	144.7 KPa
Reaction temperature	300 °C	300 °C
Operating time	5 hr	5 hr
*Average concentration of reactant	2.9×10^{-2} mol/L	3.8×10^{-2} mol/L
Total mass of sample lost	0.21 g	0.20 g

* Calculated based on the total condensate collected in the ice trap during the 5-hr run.

4.4 TMOS formation from pure silicon powder

The major component of BG is Si (about 52 wt%). It is important to know which reaction can convert more Si to TMOS. Pure silicon powder (Shin-Etsu Chemical Company Ltd.) was used as a starting material for both the DMC and CH_3OH reactions. The sample preparation and operating conditions employed were identical so that the only difference was the reactant, i.e. Si powder instead of BG, for both the either CH_3OH or DMC reaction.

4.4.1 DMC reaction

The reactor outlet gas in the DMC reaction was analyzed by gas chromatography, which showed the same composition figures as in Figure 4.6. Analyzing the condensate collected in the ice trap identified TMOS as the only one product. This indicates that Si can react with DMC with KOH as a catalyst. The total mass of pure Si powder lost in the 5-hr reaction was 0.16 g, corresponding to 5.3 % of silicon. The total amount of TMOS produced is 4.0×10^{-3} mole, based on TMOS in the condensate, which is 70% of the amount of TMOS production estimated based on the Si consumption. The results are summarized in Table 4.3.

4.4.2 CH_3OH reaction

It was found that the mass of pure Si powder reduced by 0.06 g due to the reaction with CH_3OH. Based on the initial mass of pure Si powder, the conversion of Si

is about 2 %. Furthermore, the total amount of TMOS in the condensate collected in the ice trap is 1.4×10^{-3} mole, corresponding to 65% of the TMOS production based on the Si consumption. One of GC charts of outlet gas analysis is shown in Figure 4.7. There are five peaks corresponding to H_2, CH_3OH, TMS, TMOS, and one unknown. The additional pieces of information about this reaction are presented in Table 4.3.

Analyzing the condensate collected in the ice trap revealed that TMS was no longer produced after forty minutes from the beginning of the reaction. Because TMS is an intermediate product in the Si-CH_3OH reaction, it seems that TMS was converted to TMOS during the course of reaction[Suzuki et. al., 1991]. The rates of TMOS formation from both the DMC and CH_3OH reactions are calculated based on the condensate analysis, as shown in Figure 4.8. Obviously, the rate of TMOS formation from the DMC reaction is higher than that from the CH_3OH reaction. Table 4.3 shows that the total mass of Si conversion in the DMC reaction is also greater than that in the CH_3OH reaction, even though the average concentration of CH_3OH is slightly higher than that of DMC.

From the composition of outlet gas shown in Figures 4.5 and 4.7, the unknown peaks, observed in the CH_3OH reaction with BG and pure Si powder, are believed to be chlorine-containing compounds. Chlorine-containing compounds are also found in the products as impurities when using Cu(I)Cl or Cu(II)Cl_2 as a catalyst [Ono et. al., 1995]. Because TMS was produced in the CH_3OH reaction with either pure Si powder or BG during the first forty minutes, it will be necessary to separate TMS from TMOS in an actual process. When the CH_3OH reaction is employed, it leads to an increase in the cost of recovery .
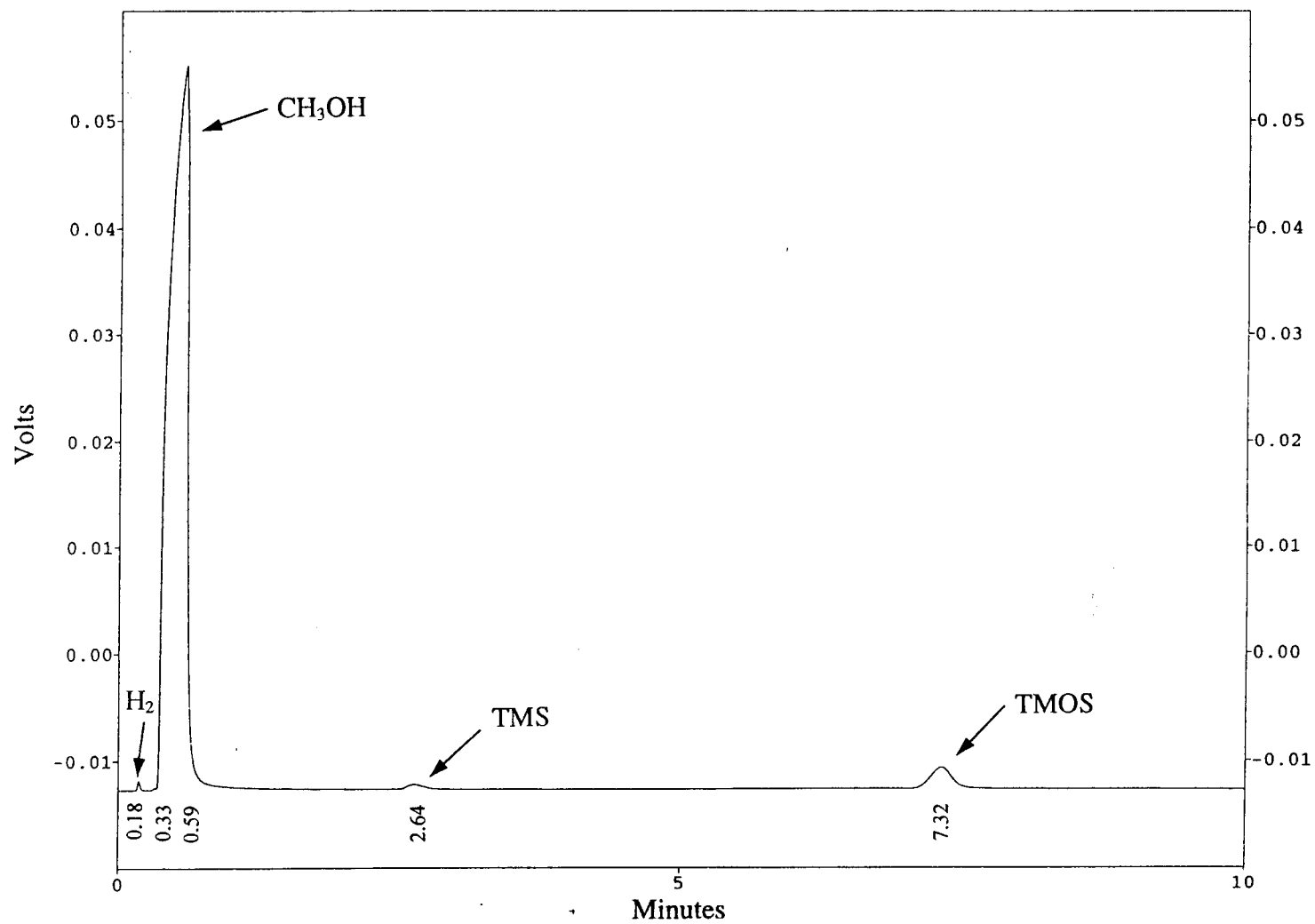
Figure 4.7 : The composition of reactor outlet gas when Si powder reacted with CH_3OH at 300 °C
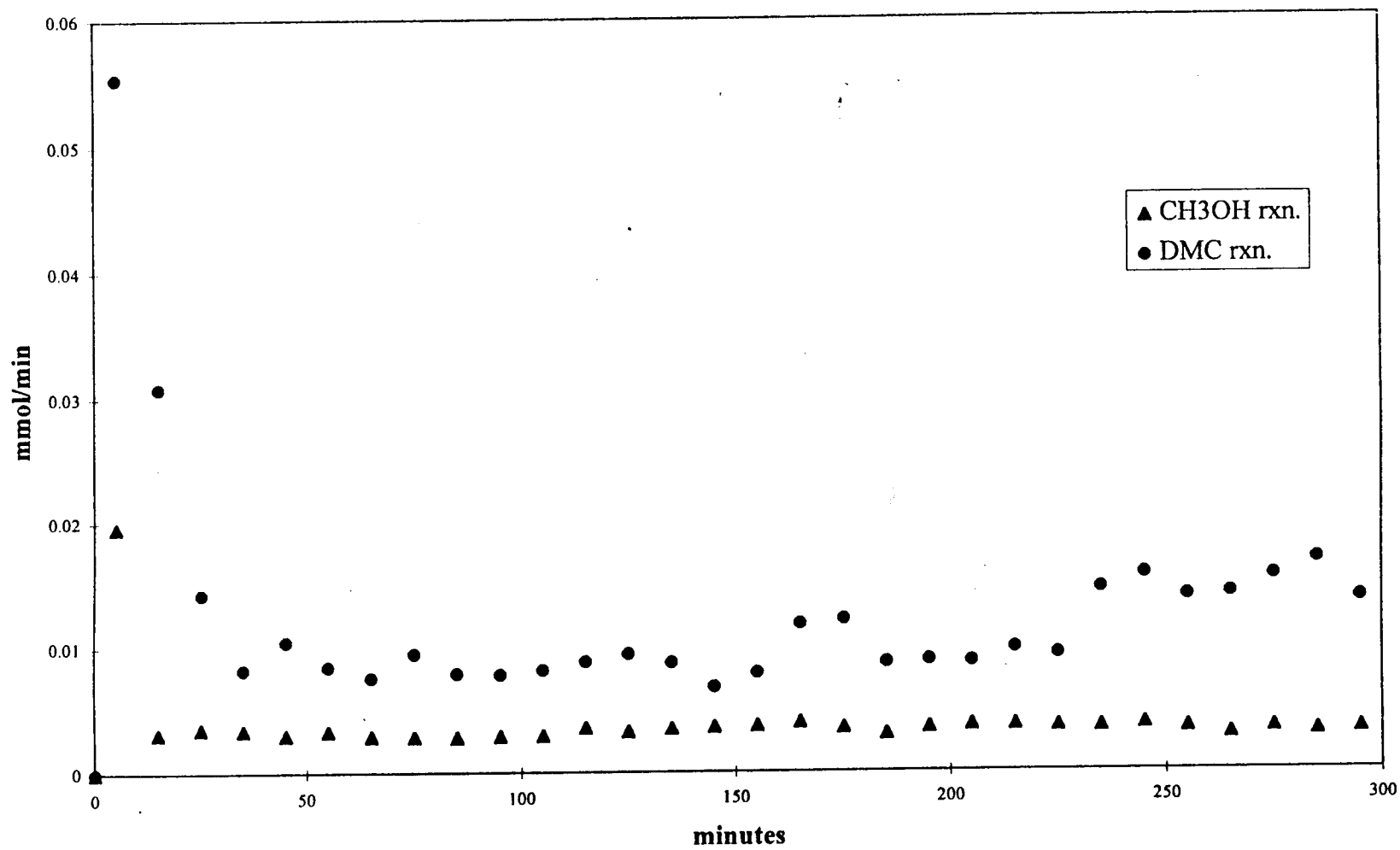
Figure 4.8 : The rates of TMOS formation from pure Si powder reacting with CH_3OH and DMC at 300 ^{o}C

Based on the results described above, it is implied that the DMC reaction is preferable when converting Si to TMOS is concerned. The DMC reaction can not only highly consume Si, a major component of BG, but also produce TMOS selectively. In addition, there are two more advantages of using the DMC reaction for BG over using the CH_3OH reaction. First, chlorine-containing compounds from $Cu(II)Cl_2$ used as a catalyst in the CH_3OH reaction can cause corrosion, as previously mentioned. Using KOH as a catalyst in the DMC reaction may be less costly in terms of materials in the process. Secondly, in addition to Si-DMC reaction, DMC can react with SiO_2 to produce TMOS. Hence, both Si and SiO_2 in BG can be converted to TMOS effectively.

Table 4.3 : Operating conditions and results from the reaction of pure Si powder with DMC and CH_3OH

Conditions	DMC reaction	CH_3OH reaction
Palletization	0.3 g / 3,000 lb$_f$	0.3 g / 3,000 lb$_f$
Pretreatment temperature	400 °C	500 °C
Gas for pretreatment	N_2	N_2
Initial mass of sample	3 g	3 g
Reaction temperature	300 °C	300 °C
Operating pressure	101.3 KPa	144.7 KPa
*Average concentration of reactant	2.8×10^{-2} mol/L	3.5×10^{-2} mol/L
*Average molar flow rate of reactant	322.8 mmol/hr	511.6 mmol/hr
Total mass of sample lost	0.16 g	0.06 g
Sample mass conversion	5.3 %	2 %
Total TMOS collected from ice trap	4.0×10^{-3} mole	1.4×10^{-3} mole

* Calculated based on the total condensate collected in the ice trap in the 5-hr run.

4.5 Synthesis of TMOS from BG via DMC reaction

4.5.1 Effect of temperature

Now that the DMC reaction was found to be more suitable for converting BG

silicon fines, effects of operating conditions on the reaction kinetics were studied. Thus

the reaction of BG with DMC was carried out at different temperatures for 5 hr. In order

to avoid the DMC decomposition during the reaction, the highest temperature applied was

325 °C. Figure 4.9 compares the rates of TMOS formation at four different operating

temperatures. It is indicated that there are two stages in the reaction: the initial and steady

stages. No induction period appeared in the reaction catalyzed by KOH, as evidenced in

Figure 4.9.

In the initial stage, the rate of TMOS formation drastically increased and attained

to a maximum value in a short time. Then, it decreased and reached a relatively constant

value in the steady stage. As shown in Figure 4.9, the maximum rate of TMOS formation

increased with the operating temperature. Also, the TMOS formation in the steady stage

was promoted by an increase in temperature. Therefore, an increase in the operating

temperature significantly enhances the TMOS formation process. Table 4.4 summarizes

the operating conditions and results at four different reaction temperatures.

During the reaction at operating temperatures ranging from 250 °C to 300 °C, the

effluent gas from the reactor was analyzed by gas chromatography every 15 minutes. As

shown in Figure 4.6, there were four peaks corresponding to CO/CO_2, dimethyl ether,
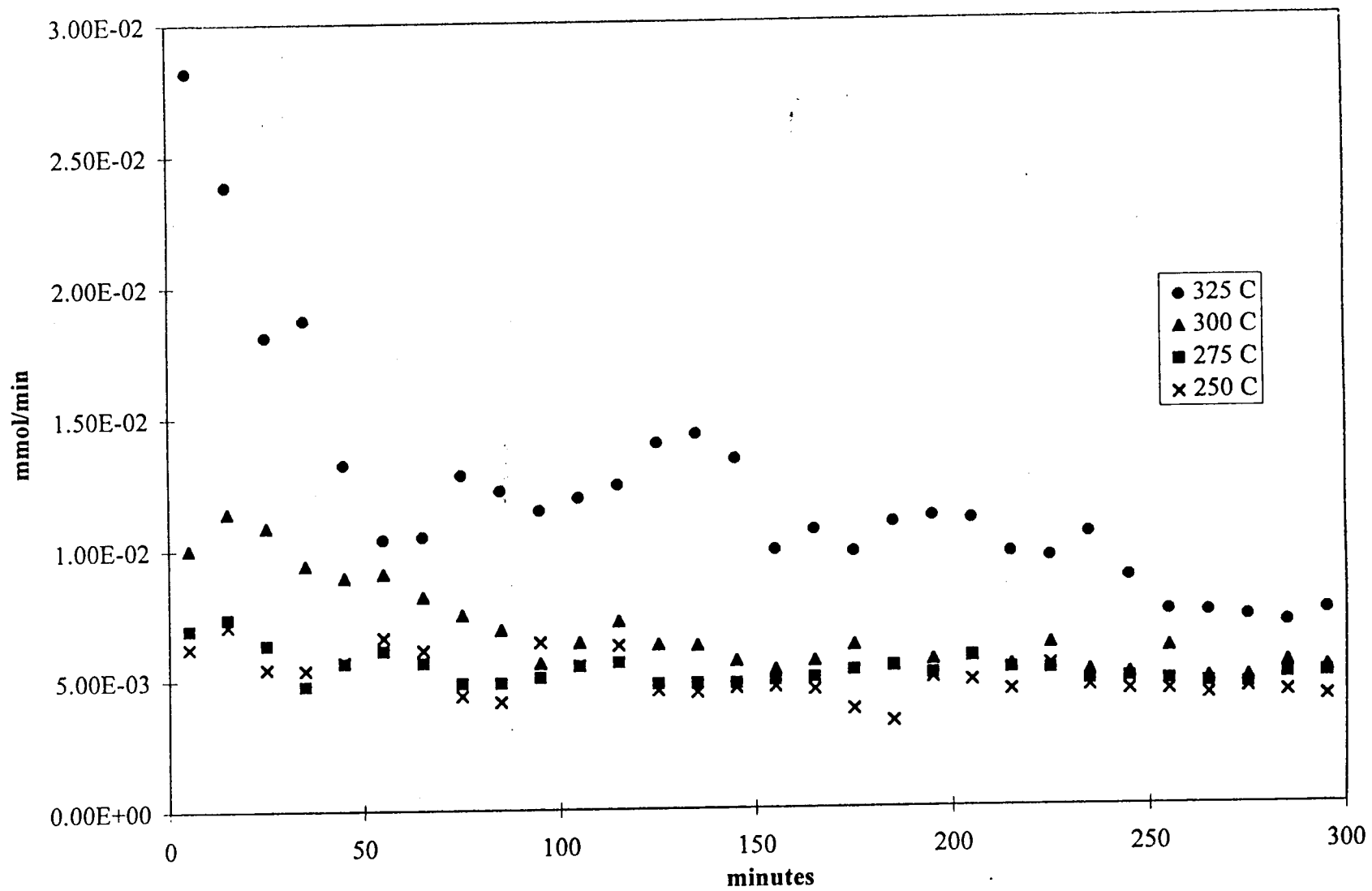
Figure 4.9 : The rate of TMOS formation from BG-DMC reaction at different temperatures

Table 4.4 : The operating conditions and results obtained from BG-DMC reaction at four different reaction temperatures

Conditions	250 °C	275 °C	300 °C	325 °C
1) * The concentration of DMC flow	2.71×10^{-2} mol/l	2.62×10^{-2} mol/l	2.74×10^{-2} mol/l	2.62×10^{-2} mol/l
2) * Molar flow rate of DMC	284.9 mmol/hr	271.2 mmol/hr	297.5 mmol/hr	253.7 mmol/hr
3) Mass of sample consumption	0.09 g	0.12 g	0.18 g	#N/A
4) Total of TMOS produced	1.7×10^{-3} mole	2.0×10^{-3} mole	2.3×10^{-3} mole	3.8×10^{-3} mole
5) TMOS yield	2.7 %	3.3 %	3.6 %	6.1 %

* Referred to room temperature

* Average values over the 5-hr operation

Due to the formation of carbonaceous materials

DMC, and TMOS. Hence, it is implied that possible reactions at these temperatures are: the reactions of DMC with Si and SiO_2 and the DMC decomposition.

At 325 °C, the GC analysis of gas collected in the gas sampling loop indicated two unknown peaks, appearing at 0.4 and 5.6 minute, as shown in Figure 4.10. The color of BG turned to dark-black after 5-hr. Also, there was no change in the mass of BG between before and after the reaction. It is suspected that some side reactions took place at 325 °C, leading to the formation of carbonaceous materials.

Since CO/CO_2 peaks in the gas chromatography analysis could not be separated, it is not possible to determine each extent of conversion of Si and SiO_2. The TMOS yield was hence calculated based on the initial total amount of Si and SiO_2 in the sample of BG, as (See Appendix 3).

$$\text{TMOS yield} = \frac{\text{Total moles of TMOS produced}}{\text{Total initial moles of Si and } SiO_2}$$

Even though a higher temperature promotes the reaction, leading to a higher conversion of solids and TMOS yield, the operating temperature at 300 °C should be selected as the most effective temperature for the DMC reaction. A lower selectivity of TMOS and more impurities result from 325 °C, which will increase the cost of separation and process treatment.

At the same concentration but at different temperatures, the temperature dependency of the reaction rate is often well fitted by the Arrhenius law.

$$\ln (r_1/r_2) = (-E_a/R) \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (4.5.1.1)$$
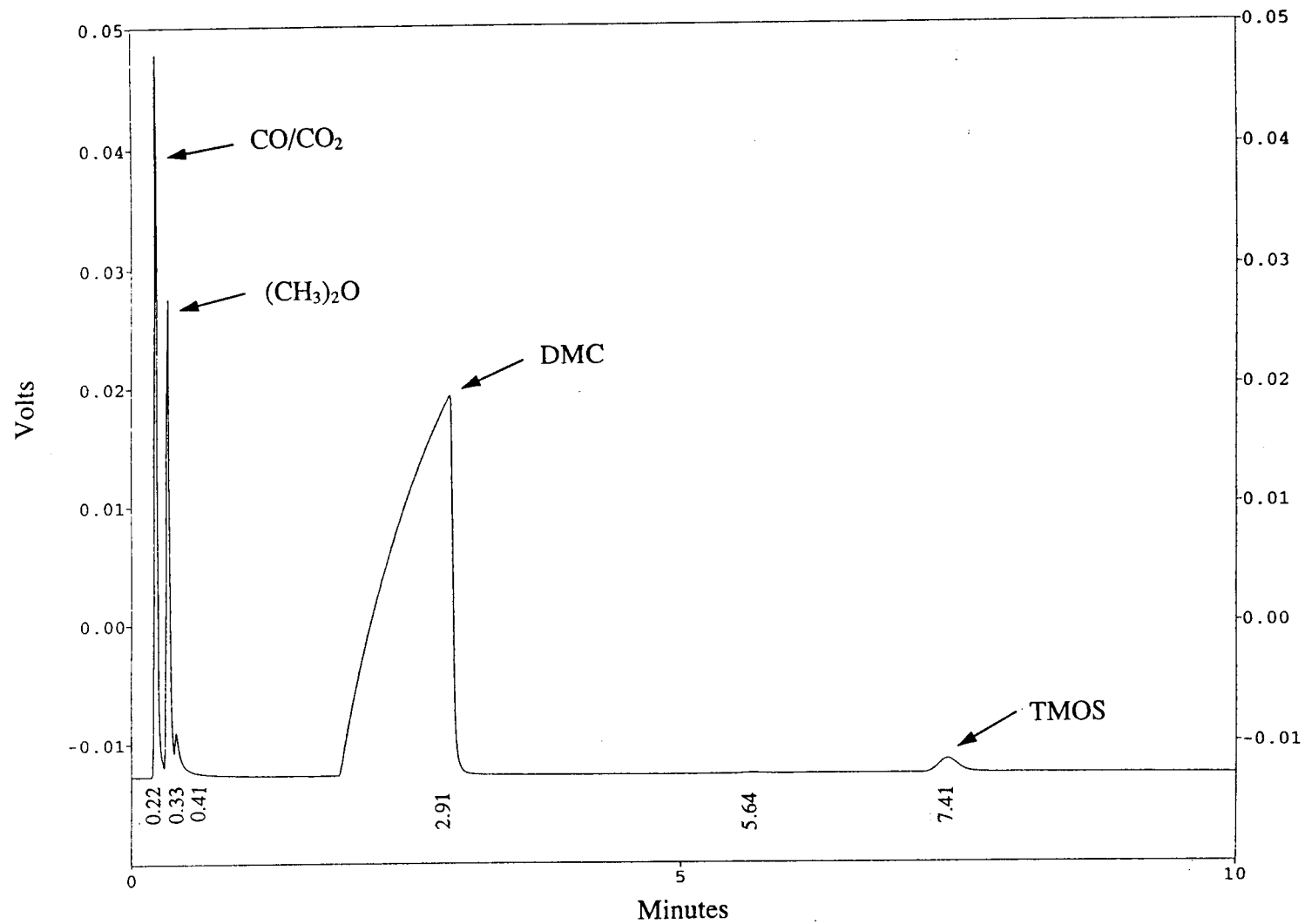
Figure 4.10 : The composition of reactor outlet gas in the BG-DMC reaction at 325 °C

where E_a is the apparent activation energy (J/mol), R is the gas constant (8.314 J/mol °K), and r_i is the observed rate of TMOS formation at a reaction temperature.

A plot of ln(r) vs 1/T will give $-E_a/R$ as the slope. Using the data given in Table 4.4, Figure 4.11 shows the Arrhenius relationship between the rate of TMOS formation and temperature in the range from 250 °C to 300 °C. Some side reactions taking place at 325 °C may have affected the data at that temperature. An apparent activation energy, E_a, evaluated for the temperature range of 250 °C to 300 °C is 15.07 KJ/mol. Compared to the activation energy of 89 KJ/mol for the SiO_2-DMC reaction reported by Ono [1993], the current result is lower probably because the solids used in this study contains both Si and SiO_2. However, the detail is not clear yet.

4.5.2 Effect of sample amount

The effect of the amount of sample solids on the DMC reaction with BG was tested at 300 °C. All the operating conditions were kept unchanged, except the initial mass of BG.

At 300 °C, the two possible main reactions are:

$$2\ (\ CH_3O\ )_2CO_{(g)}\ +\ Si_{(s)}\ \xrightarrow{\ KOH\ }\ (\ CH_3O\ )_4Si_{(g)}\ +\ CO_{(g)} \qquad (4.5.2.1)$$

$$2\ (\ CH_3O\ )_2CO_{(g)}\ +\ SiO_{2\ (s)}\ \xrightarrow{\ KOH\ }\ (\ CH_3O\ )_4Si_{(g)}\ +\ CO_{2\ (g)} \qquad (4.5.2.2)$$
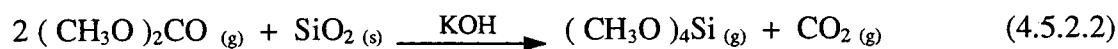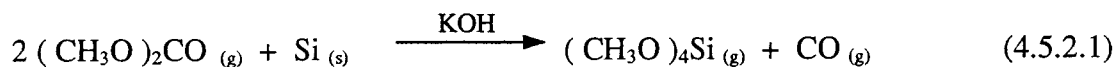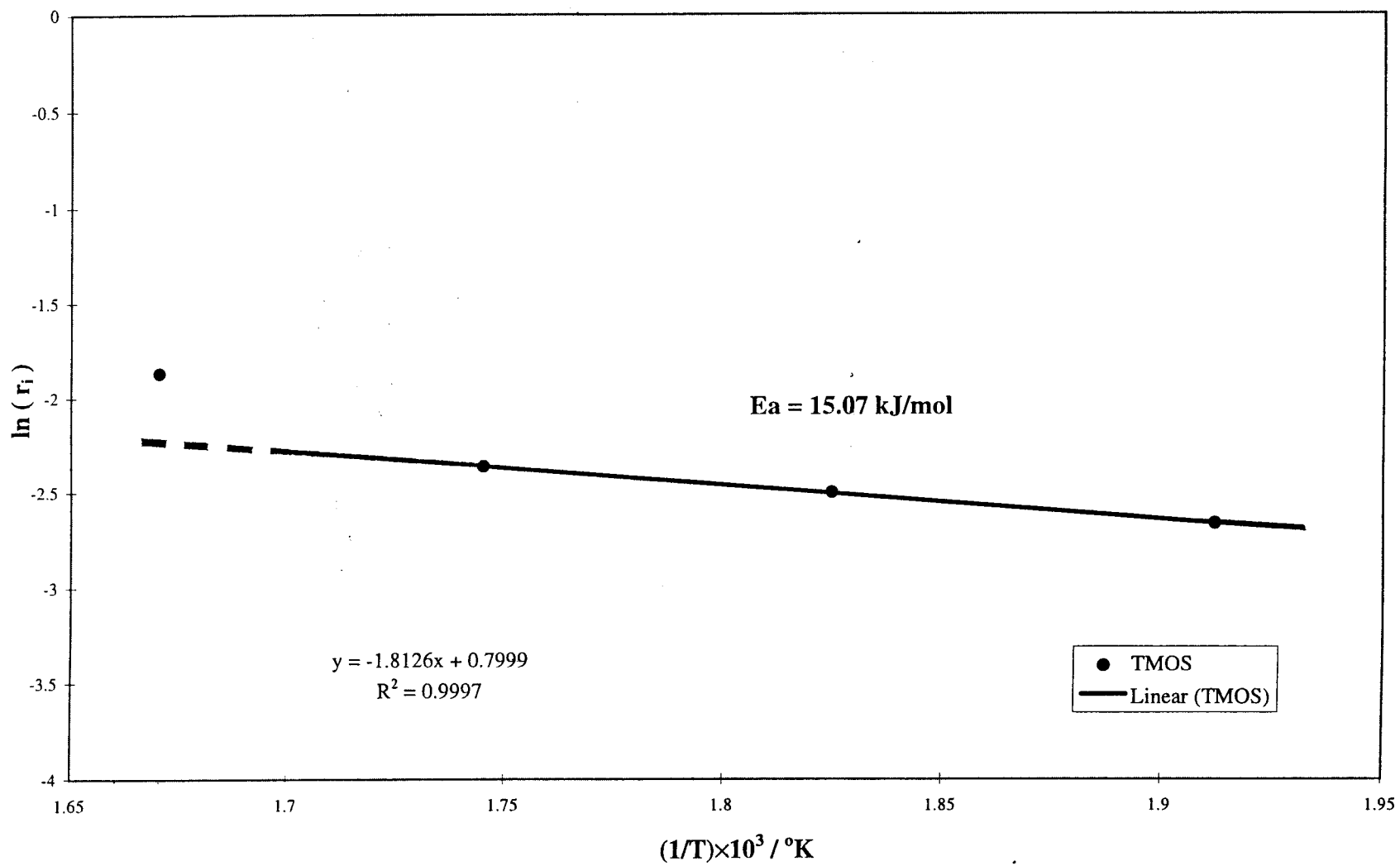
Figure 4.11 : Arrhenius relationship between the rate of TMOS formation and temperature

For plug flow reactors at steady state, the differential equation of the material balance based on solid mass is given as

$$F_{AO} \, dX_A = r'_A \, dW \qquad (4.5.2.3)$$

where F_{AO} is the molar feed rate of reactant A, X_A is the conversion of A, and W is the mass of solid.

Integrating equation 4.5.2.3 with an assumption that r'_A is constant, one obtains

$$\frac{W}{F_{AO}} = \frac{X_A}{-r'_{A,ave}} \qquad (4.5.2.4)$$

Using $F_{AO} = C_{AO} \, v_o$ rewrites equation 4.5.2.4 as

$$(\tau') = \frac{W}{v_o} = \frac{C_{AO} \, X_A}{-r'_{A,ave}} \qquad (4.5.2.5)$$

where τ' is the weight time, based on the weight of solid;

C_{AO} is the inlet concentration of A

v_o is the volumetric flow rate of the feed

A set of experimental data shown in Table 4.5 was applied to test the relationship, equation 4.5.2.5, between the initial mass of BG and the molar conversion of DMC, that is based on the constant rate assumption. Figure 4.12 presents the plot of the initial BG mass versus the overall molar conversion of DMC.

Table 4.5 : The overall molar conversion of DMC at 300 °C for 5 hour operation with the different initial mass of BG.

Initial BG mass (g)	DMC conversion (X_A)
3	3.45×10^{-3}
6	5.60×10^{-3}
10	0.01

It is implied that the overall molar conversion of DMC is proportional to the initial mass of BG. Since the conversion of Si and SiO_2 in BG is so small, the system can be considered as a differential flow reactor in the range investigated. However, the rate of TMOS formation varies with time as well as with the mass of BG, as shown in Figure 4.13. It is needed to investigate the time variation of TMOS formation, i.e., the conversion of solids, until all the solid is depleted by the reaction, though it is not included in this study.

4.6 Synthesis of TMOS from TS or SR via DMC reaction

As previously mentioned in chapter 3, TS contains SiO_2 at the highest fraction among the four types and in SR SiO_2 is the major component. Since the use of CH_3OH is not a favorable way to convert SiO_2 to TMOS, as described in section 2.3 and 4.3.1, the DMC reaction with these two was also studied. Using 3 g of TS or SR, the reaction with DMC was carried out at 300 °C. The operating conditions for both the DMC reactions with TS and SR are shown in Table 4.6. One of GC charts of outlet gas analysis, obtained

$$y = 0.001x$$
$$R^2 = 0.9838$$
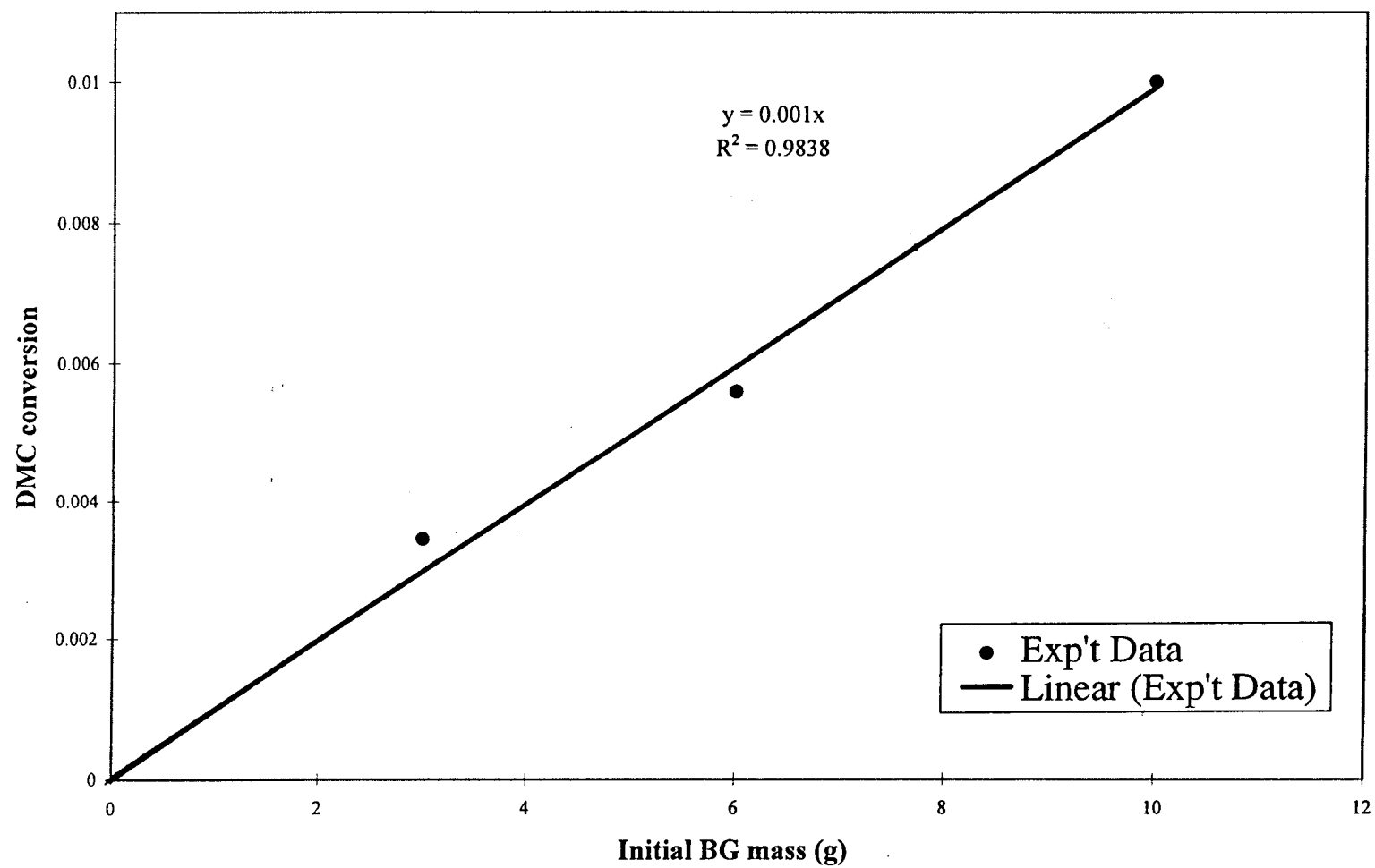
Figure 4:12 : Molar conversion of DMC changing with the initial mass of BG
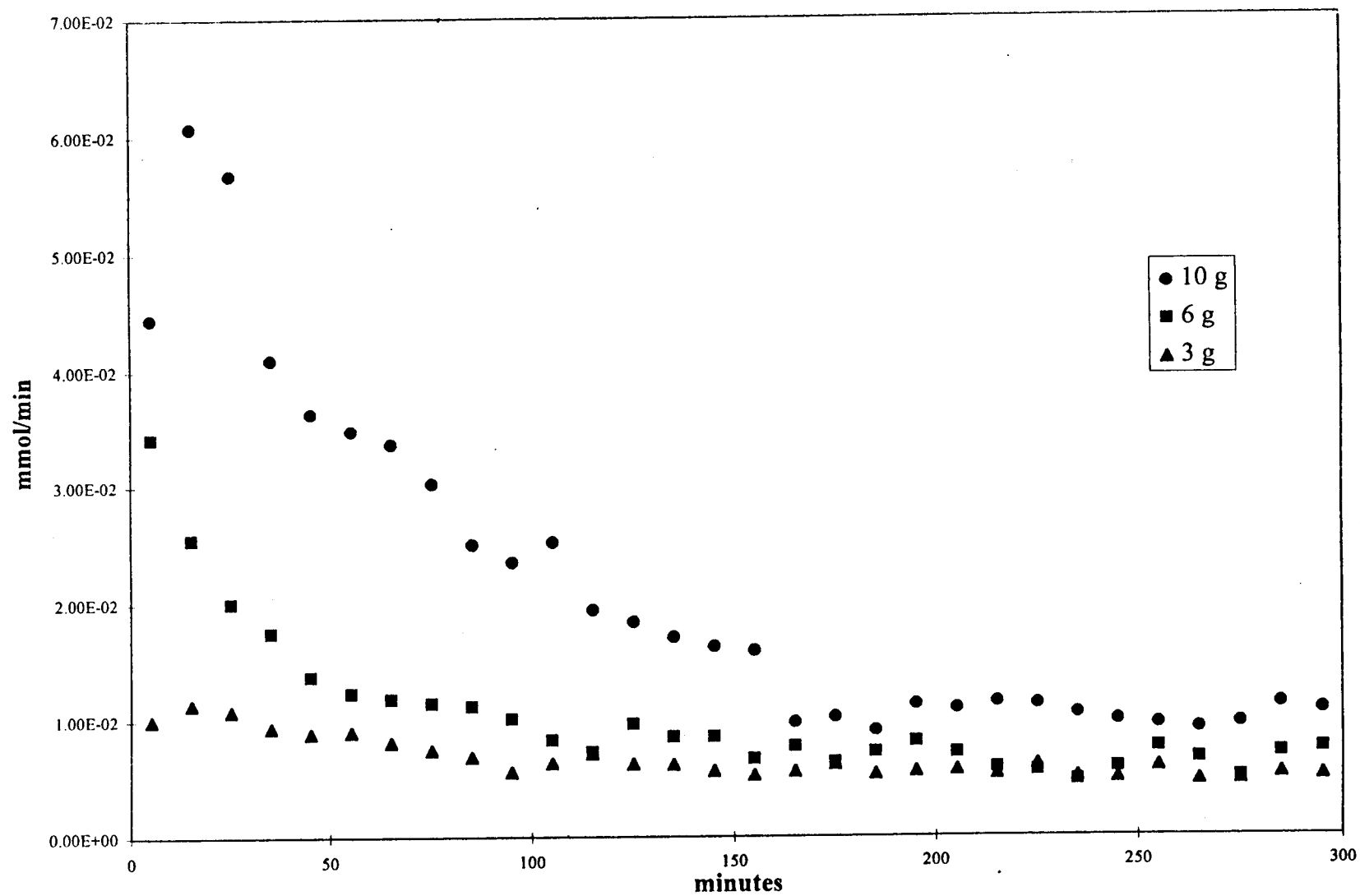
Figure 4.13 : TMOS formation from the BG-DMC reaction at 300 ^{o}C with different initial mass of samples

in the TS-DMC reaction is shown in Figure 4.14. There are four peaks corresponding to CO/CO_2, $(CH_3)_2O$, DMC, and TMOS.

There was no obvious TMOS peak observed in the GC chart of outlet gas analysis in the SR-DMC reaction. On the other hand, the analysis of condensate collected in the ice trap showed the TMOS peak at 7.54 minute, as shown in Figure 4.15. The reason for this is not clear.

Table 4.6 : Operating conditions for TS-DMC and SR-DMC reactions

Specifications	TS-DMC reaction	SR-DMC reaction
Catalyst	KOH (5 wt%)	KOH (5 wt%)
Palletization	0.4 g/12,000 lb$_f$	0.5 g/7,500 lb$_f$
Solvent for contact mass	CH_3OH	CH_3OH
Sieve opening	1.168 mm	1.168 mm
Pretreatment temperature	400 °C for 3 hr	400 °C for 3 hr
Gas for pretreatment	N_2	N_2
Reaction temperature	300 °C	300 °C
Operating pressure	101.3 KPa	101.3 KPa
Operating time	4 hr	2 hr
Carrier gas	Helium	Helium

Based on these results, it is implied that TMOS can also be produced from TS and SR via the reaction with DMC. It is appropriate to conclude that silicon fines can be converted into TMOS when DMC is used as a coreactant and KOH as a catalyst.
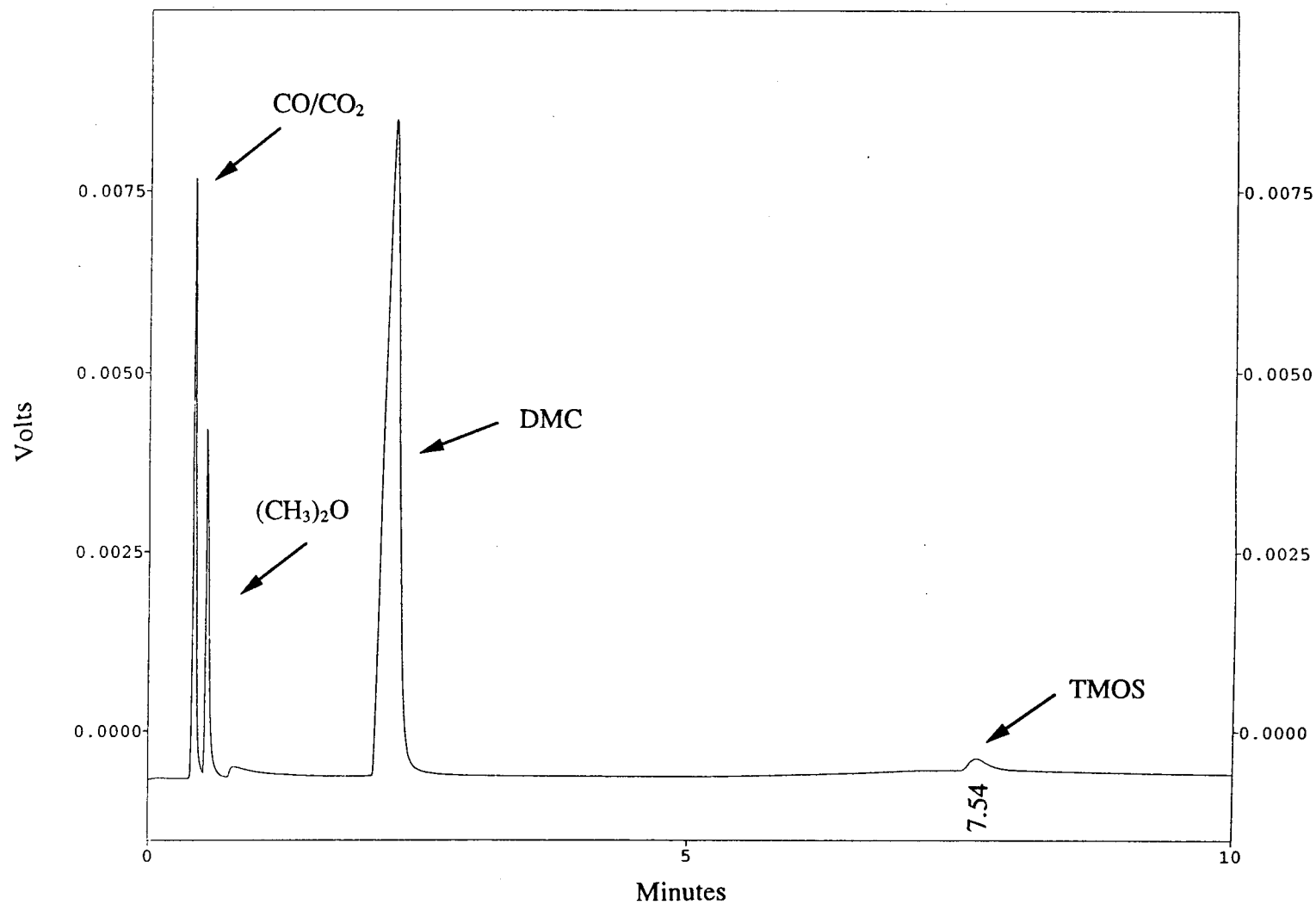
Figure 4.14 : The composition of reactor outlet gas in the TS-DMC reaction at 300 °C
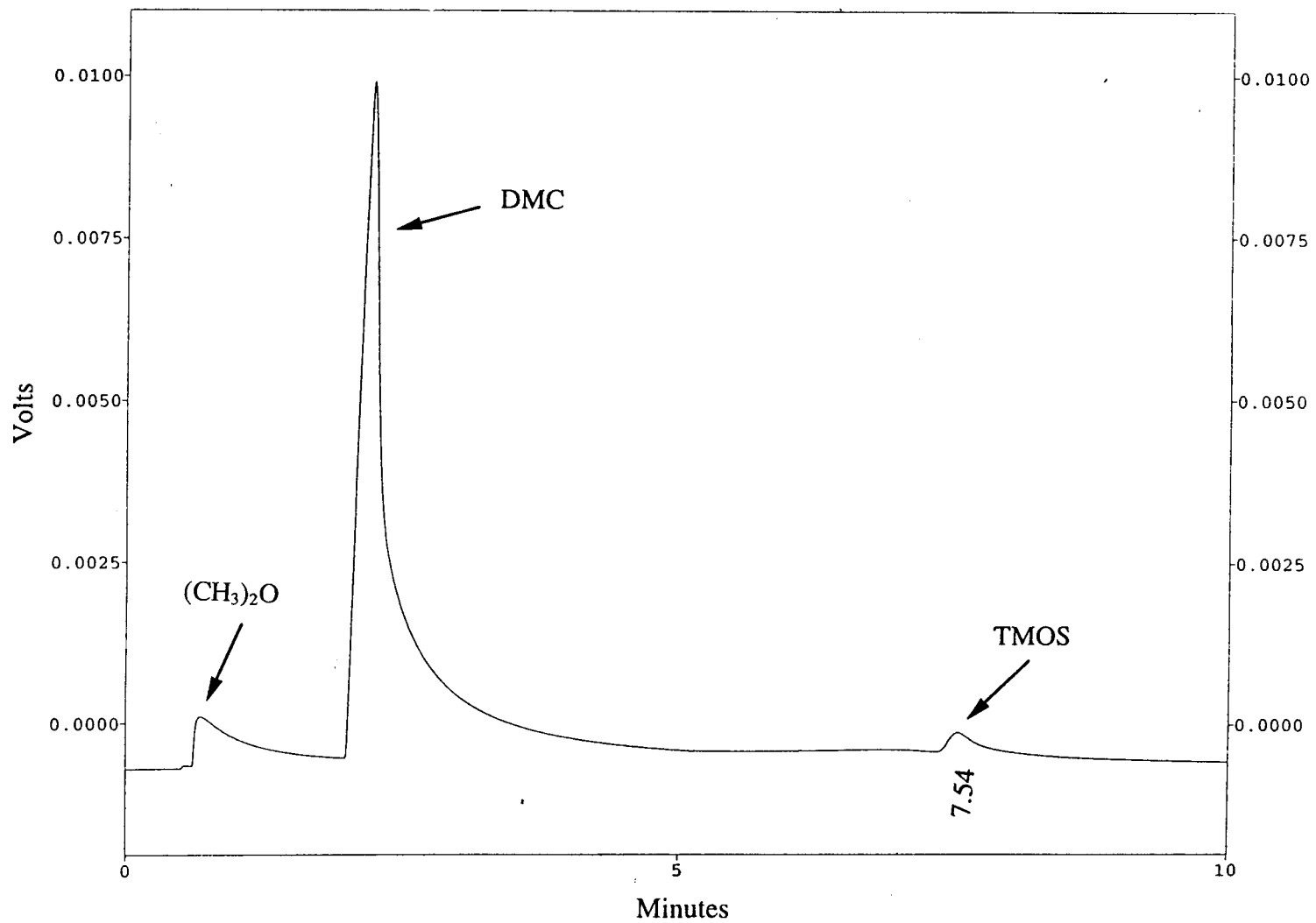
Figure 4.15 :   The composition of the condensate in the ice trap from the SR-DMC reaction at 300 °C

Chapter 5

Mass Transfer Limitation Analysis

In the synthesis of TMOS, the mass transfer limitation, one of the most important factors, may affect on the rate of reaction. Thus, it is necessary to determine which of mass transfer or chemical kinetics controls BG-DMC reaction. To do this, several assumptions were made for the following overall reaction.

$$4(CH_3O)_2CO_{(g)} + Si_{(s)} + SiO_{2 (s)} \xrightarrow{\text{KOH}} 2(CH_3O)_4Si_{(g)} + 2CO_{2 (g)} + 2CO_{(g)} \quad (5.1)$$
$$\text{(DMC)} \qquad\qquad\qquad\qquad \text{(TMOS)}$$
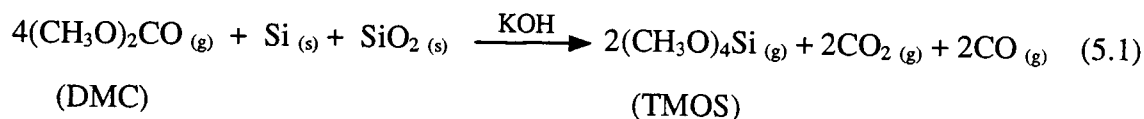
At steady state, for forced convection around a solid sphere, k_g (the mass transfer coefficient) may be predicted by [T.H. Chilton and A.P.Colborn, 1934].

$$\frac{k_g\, d}{D_{DMC\text{-}He}} = 2.0 + 0.6Re^{1/2}Sc^{1/3} \qquad (5.2)^{(35)}$$

where Re = Reynold number $= du\rho/\mu$ (5.2.1)

Sc = Schmidt number $= \mu/(\rho D_{DMC\text{-}He})$ (5.2.2)

d = diameter of particle (m)

$D_{DMC\text{-}He}$ = diffusivity of DMC gas in helium (m^2/s)

k_g = mass transfer coefficient (m/s)

u = average interstitial velocity of DMC/He gas

in the packed bed (m/s)

ρ = density of particle (kg/m^3)

μ = viscosity of DMC/He gas (μP)

Generally, the viscosity of pure gas at low pressure is best estimated by the corresponding-states method [Thodos et. al., 1961]. The viscosity of DMC-He at the current conditions is given as

$$\mu = 1.1\times10^{-5} \ N.s/m^2$$

(See Appendix 3 for details)

Furthermore, the diffusion coefficient for a binary mixture of gases DMC and He may be estimated from the Fuller, Schettler, and Giddings relation [1966]. (See Appendix 3) Thus,

$$D_{DMC\text{-}He} = 1.48\times10^{-4} \ m^2/s$$

The superficial gas velocity, u_∞, the volumetric flow rate of gases divided by the cross-sectional area of empty reactor tube, at 300 °C is 3.6×10^{-2} m/s. The average interstitial gas velocity, u, in the packed bed is then 0.12 m/s, where a bed void fraction of 0.3 has been assumed.

Based on the ideal gas approximation, the gas density (DMC) at 300 °C and 101.3 Kpa is

$$\rho = 3 \ kg/m^3$$

Inserting the values of d, u, ρ, μ, and $D_{DMC\text{-}He}$ into equation 5.2.1 and 5.2.2, Re and Sc can be calculated as:

$$Re = \frac{(1.168\times10^{-3} \text{ m})\times(0.12 \text{ m/s})\times(3 \text{ kg/m}^3)}{(1.1\times10^{-5} \text{ N.s/m}^2)}$$

$$= 38.23$$

$$Sc = \frac{(1.1\times10^{-5} \text{ N.s/m}^2)}{(3 \text{ kg/m}^3)\times(1.48\times10^{-4} \text{ m}^2\text{/s})}$$

$$= 0.025$$

Therefore, mass transfer coefficient (k_g) can be obtained by inserting the values for Re and Sc into equation 5.2 as:

$$\frac{k_g\times(1.168\times10^{-3} \text{ m})}{1.48\times10^{-4} \text{ m}^2\text{/s}} = 2 + 0.6\times(38.23)^{1/2}\times(0.025)^{1/3}$$

$$k_g = 0.39 \quad \text{m}^3\text{gas/m particle.s}$$

The ratio α of reaction resistance to mass transfer resistance is then

$$\alpha = \frac{(-r_{obs}''')_{avg}\times L}{k_g\times C_{ag,avg}} \qquad (5.3)^{(34)}$$

where $-r_{obs,avg}'''$ = the average observed reaction rate

$(\text{mol/m}^3 \text{ particle.s})$

C_{ag} = the average molar concentration of DMC

$(\text{mol/m}^3\text{gas})$

L = characteristic length for the spherical solid (m)

$= R / 3 \qquad (5.4)^{(34)}$

R = radius of particles (m)

Knowing that R = $(1.168 \times 10^{-3})/2$ m.,

$$L = (1.168 \times 10^{-3} \text{ m})/6$$

$$= 1.95 \times 10^{-4} \text{ m}$$

The average molar concentration of DMC ($C_{Ag,avg}$) at 300 °C is

$$C_{ag,Avg} = 27.4 \text{ mol/m}^3$$

The observed rate based on unit particle volume is given by

$$-r_{obs,Avg}''' = \frac{(\text{ TMOS formation rate })}{(M/\rho)}$$

where M is the mass of sample particles and ρ is the particle apparent density, 2.21×10^3 kg/m^3, based on a particle volume fraction of 0.85 assumed.

$$= \frac{(6.732 \times 10^{-6} \text{ mol/min})}{(1.36 \times 10^{-6} \text{ m}^3 \text{ particle})}$$

$$= 8.25 \times 10^{-2} \text{ mol/m}^3 \text{particle.s}$$

From equation 5.3,

$$\text{Fraction of resistance } (\alpha) = \frac{(8.25 \times 10^{-2} \text{ mol/m}^3 \text{ particle.s}) \times (1.95 \times 10^{-4} \text{ m})}{(0.39 \text{ m}^2\text{gas/m particle.s}) \times (27.4 \text{ mol/m}^3)}$$

$$= 1.51 \times 10^{-6}$$

Since the ratio of the two resistance is very small, the film mass transfer limitation is negligibly small and only chemical kinetics limitation controls this process.

Chapter 6

TMOS Process

Based on the findings in this study that TMOS can be produced from silicon fines using the reaction with DMC, this chapter proposes an idea for the process to produce TMOS from silicon fines, a waste material, as shown in Figure 6.1.

First, silicon fines obtained from the landfill are mixed with a KOH/CH_3OH solution in a stirred tank. The mixture is sent to an extruder which palletizes the mixture. Next, the pallets are dried in a dryer where a heated-air stream is supplied to evaporate CH_3OH. Then, dried pallets of silicon fines impregnated with KOH are sent to a moving bed reactor.

DMC vapor, evaporated in a boiler heated with steam, is supplied to the reactor to react with silicon fines. The pallets of silicon fines are loaded to the top of the reactor, and move downward as the reaction takes place. Any inerts in silicon fines are discharged from the reactor with catalyst KOH.

The gas product from the top of the reactor is condensed in a separator where unreacted DMC and product TMOS are condensed into liquid. The vapor phase containing small amounts of uncondensed DMC, TMOS, CO, CO_2, and ether, produced as a byproduct, is sent to an incinerator, because it is not economical to recover them. The unreacted DMC and product TMOS are separated in a distillation column, from which unreacted DMC vapor is recycled back to the reactor. The CH_3OH vapor from the

dryer, mixed with a heated-air stream, is condensed in a cooling system, and the liquid CH_3OH is sent back to be uses as a solvent for the catalyst impregnation.

Because DMC, TMOS and CH_3OH are all toxic chemicals, the air stream from the dryer needs to be treated even after CH_3OH removed. One way is to combine the stream with the outlet from the separator to be sent to the incineration process. The mixture of catalyst KOH and inerts needs to be treated to recover KOH.

Even though the purchasing cost of DMC is on the order of $1.00/kg. and that of TMOS is in the range from $6.00/kg to $20.00/kg, more experimental data and calculations, ie., the major cost of equipment or manufacturing cost estimation, need to be investigated further in order to know the possibility of commercializing profitable TMOS process, which is not included in this study.
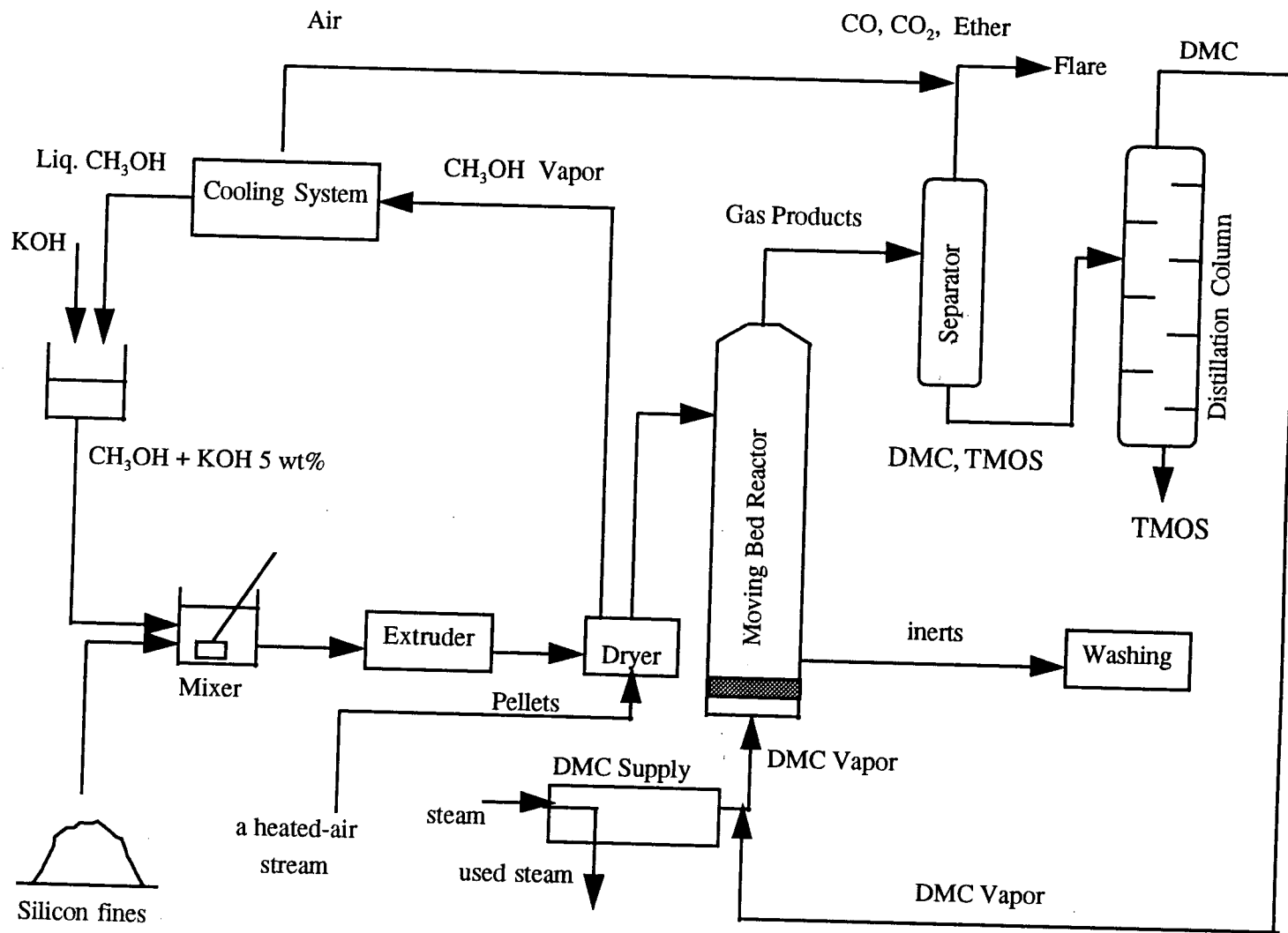
Figure 6.1 : The schematic of TMOS process

Chapter 7

Conclusions and Recommendations for Future Study

7.1 Conclusions

- KOH is useful for catalytically converting both Si and SiO_2 with DMC into TMOS while $Cu(II)Cl_2$ is useful for converting only Si with CH_3OH.

- The thermal decomposition of CH_3OH at any temperatures below 300 °C and that of DMC at any temperatures below 325 °C, used in this study, can be neglected.

- CH_3OH can convert Si, a component of silicon fines, to TMOS as a major product. TMS is also produced as a minor product only during the beginning stage of reaction. However, CH_3OH can not react with SiO_2, another major component. On the other hand, DMC can convert both Si and SiO_2 into TMOS without any major byproducts at temperature below 300 °C.

- DMC is more appropriate reactant to utilize silicon fines impregnated with KOH as a catalyst.

- No induction period was observed in the DMC-silicon fines reaction catalyzed by KOH.

- The TMOS formation in the DMC-silicon fines reaction can be divided into two stages: the initial and steady stages. Side reactions took place at 325 °C, leading to the formation of undesired by-products. The operating temperature for the DMC reaction should be lower than 300 °C.

- The overall molar conversion of DMC is proportional to the initial mass of silicon fines in the range investigated.

- The film mass transfer limitation can be neglected in the operating conditions investigated.

- An increase in the operating temperature, in the range from 250 °C to 300 °C, significantly enhances the TMOS formation process.

7.2 Recommendations for Future Study

The synthesis of TMOS from silicon fines via the reaction with DMC is dependent on the reaction temperature and sample preparations. Thus, further study is needed in several areas before this process is considered for its commercialization. Some suggestions are listed below.

- Since the DMC decomposition increases with an increase in the operating temperature, the kinetic study of DMC decomposition should be done.

- The time variation of TMOS formation, ie., the conversion of solids, until all the solid is depleted by the reaction, needs to be investigated.

- To find a simple kinetics expression for this reaction, the experiment with varying reactant concentration should be performed.

- Further study to find a method to determine the extent of conversion of each Si and SiO_2 in the DMC reaction is needed.

Bibliography

(1) Rochow, E. G., "The Direct Synthesis of Organosilicon Compounds", Journal of American Chemical Society, Vol.67, p.963, 1945.

(2) Hurd, D. T., and Rochow, E. G., "On the Mechanism of the Reaction between Methyl Chloride and Silicon-Copper", Journal of American Chemical Society, Vol.67, p.1057, 1945.

(3) Newton, W. E., and Rochow, E. G., "The Direct Synthesis of Organic Derivatives of Silicon Using Nonhalogenated Organic Compounds", Inorganic Chemistry, Vol.9, No.5, p.1071, 1970.

(4) Klebansky, W. E., and Fikhtengotts, V. S., "The Mechanism of the Reaction between Methyl Chloride and Silicon in presence of Copper", Journal of General Chemistry of the USSR (English Translation)", Vol.26, p.2795, 1956.

(5) Voorhoeve, R. J. H., and Vlugter, J. C., "The Catalytically Active Form of the Copper Catalyst". Journal of Catalysis, Vol.4, p.123, 1965.

(6) Voorhoeve, R. J. H., Geertsema, B. J. H., and Vlugter, J. C., "The Kinetics of the Copper-Catalyzed Reaction of Methyl Chloride and Silicon", Journal of Catalysis, Vol.4, p.43, 1965.

(7) Weber, G., Gillot, B., and Barret, P., "Interfaces Structure in Relation with the Mechanisms in the Reaction Copper-Silicon", Physica Status Solidi, Vol.75, p.567, 1983.

(8) Viale, D., Weber, G., and Gillot, B., "Effect of Silicon-Cleaning Procedures on the Growth of Cu_3Si on Si(100)-Oriented Wafers", Oxidation of Metals, Vol.35, No.5/6, 1991.

(9) Weber, G., Gourgouillo, N., Gillot, B., and Barret, P., "Study of the Reactivity of A Single Crystal of Silicon with Molten Copper(I)Chloride", Reactivity of Solids, Vol.3, p.127, 1987.

(10) Souha, H., Viale, D., Weber, G., amd Gillot, B., "Effects of a Silicon Oxide layer on Reactivity of Silicon with Copper(I)Chloride", Journal of Materials Science, Vol.24, p.1767, 1989.

(11) Banholzer, W. F., and Burrell, m. C., "Characterization of Reactive Areas in the Direct Process for the Production of Methyl Chlorosilane", Journal of Catalysis, Vol.114, p.259, 1988.

(12) Banholzer, W. F., Lewis, N., and Ward, W., "Active Site Formation in the Direct Process for Methylchlorosilanes", Journal of Catalysis, Vol.101, p.405, 1986.

(13) Okamoto, M., Watanabe, N., Suzuki, E., and Ono, Y., "Direct Synthesis of ethylmethoxysilanes by the liquid-phase reaction of silicon, methanol, and ethylene", Journal of Organometallic Chemistry, Vol.489, 1995.

(14) Suzuki, E., Kamata, T., and Ono, Y., "Direct Synthesis of Trimethoxysilane from Methanol and Hydrogen-Treated Silicon using Copper(II)Chloride as a Catalyst", Bulletin. Chemical Society of Japan, Vol.64, p.3445, 1991.

(15) Suzuki, E., Okamoto, M., and Ono, Y., "A Kinetics Study on the Copper-Catalyzed Reaction of Silicon with Methanol into Trimethoxysilane", Chemistry Letters, Iss 2, p.199-202, 1991.

(16) Suzuki, E., and Ono, Y., "Mechanism of Active-Site Formation in Copper-Catalyzed Synthesis of Trimethoxysilane by the Reaction of Silicon with Methanol", Journal of Catalysis, Vol.125, p.390, 1990.

(17) Okamoto, M., Suzuki, E., amd Ono, Y., "Reaction Pathway of Formation of Methoxysilanes in the Reaction of Silicon with Methanol Catalyzed by Copper(I)Chloride", Journal of Catalysis, Vol.145, p.537, 1994.

(18) Okamoto, M., Osaka, M., Yamamoto, K., Suzuki, E., and Ono, Y., "Effect of Pretreatment Conditions of Si-CuCl Mixtures on the Rate and Selectivity in the Reaction of Silicon with Methanol Using Copper(I)Chloride Catalyst", Journal of Catalysis, Vol.143, p.64, 1993.

(19) Okamoto, M., Yamamoto, K., Suzuki, E., and Ono, Y., "Selective Synthesis of Trialkoxysilanes by the Reaction of Metallic Silicon with Alcohols Using Copper(I)Chloride as the Catalyst", Journal of Catalysis, Vol.147, p.15, 1994.

(20) Suzuki, E., and Ono, Y., "Reaction of Methanol Vapor with Silicon into Trimethoxysilane with High Selectivity", Chemistry Letters, Iss 1, p.47, 1990.

(21) Rochow, E. G., "Methyl Silicate from Silicon and Methanol", Journal of American Society, Vol.70, p.2170, 1948.

(22) Okamoto, M., Suzuki, E., and Ono, Y., "Direct Formation of Organosilicon Compounds from Silicon, Methanol, and Alkenes", Journal of the Chemical Society-Chemical Communications, Iss 4, p. 507-508 1994.

(23) Suzuki, E., Okamoto, M., and Ono, Y. "Effect of oxide layers on the reaction of silicon with methanol into trimethoxysilane using copper(I)chloride catalyst", Solid State Ionics", Vol.47, p.97-104, 1991.

(24) Frank, D. M., "Process for producing trialkoxysilanes from the reaction of silicon methanol and alcohol", United State Patent 4,727,173 (Feb. 23, 1988).

(25) Okamoto, M., Mimura, N., Suzuki, E., and Ono, Y., "Synthesis of methoxysilanes by the reaction of metallic silicon with methanol using copper(II)acetate as the catalyst", Catalysis Letters, Vol.33, p.421-427, 1995.

(26) Boudin, A., Cerveau, G., Chuit, C., Corriu, R. J. P., and Reye, C., "Reactivity of hypervalent silicon derivatives (One step synthesis of mono- and di-hydrogenosilanes)", Journal of Oganometallic Chemistry, Vol.362, p.265, 1989.

(27) Boudin, A., Cerveau, G., Chuit, C., Corriu, R. J. P., and Reye, C., "Reactivity of Dianionic Hexacoordinated Silicon Complexes toward Nucleophiles: A New Route to Organosilanes from Silica", Organometallics, Vol.7, p.1165, 1988.

(28) Ono, Y., Akiyama, M., and Suzuki, E., "Direct Synthesis of Tetramethoxysilanes from Silica by Reaction with Dialkyl Carbonates", Chemistry of Materials, Vol.5, p.442, 1993.

(29) Suzuki, E., Akiyama, M., and Ono, Y., "Direct Transformation of Silica into Alkoxysilanes by Gas-Solid Reactions", Journal of American Chemical Society, Iss 2, p.136-137, 1992.

(30) Richard, M. L., Kay, Y. B., and et. al., "Synthesis of pentacoordinate silicon complexes from SiO_2", Letters of Nature, Vol.353, p.642-644, 1991.

(31) Goodwin, G. B., and Kenney, M. E., "A New Route to Alkoxysilanes and Alkoxysiloxanes of Use for the Preparation of Ceramics by the Sol-Gel Techniques", Inorganic Chemistry, Vol.29, p.1216-1220, 1990.

(32) Akiyama, M., Suzuki, E., and Ono, Y., "Direct Synthesis of Tetramethoxysilane from rice hull ash by reaction with dimethyl carbonate", Inorganica Chemica Acta, Vol.207, p.259-261, 1993.

(33) Thynne, J. C. J., and Peter, G., "The Methyl-Radical-Sensitized Decomposition of Gaseous Dimethyl Carbonates", Journal Chemical Society Faraday Transactions, Vol.58, p.2403-2409, 1962.

(34) Levenspiel, O., "The Chemical Reactor Omnibook", OSU Book Stores Inc., Oregon, 1993.

(35) Cussler, E. L., "Diffusion Mass Transfer in Fluid Systems", Cambridge University Press, 1984.

(36) Robert H. P., Don G., "Perry's Chemical Engineer's Handbook", McGraw-Hill Int. Editions (Sixth Edition), 1984.

(37) Krevelen, D. W. V., and Chermin, H. A., "Estimation of the free enthalpy(Gibbs free energy) of formation of organic compounds from group contributions", Chemical Engineering Science, Vol.1, p.66-80, 1951.

(38) Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena", Wiley International Edition, Jon Wiley&Sons, Inc., 1960.

APPENDICES

Appendix 1

Experimental Data and Results of DMC and CH$_3$OH Decomposition

A.1.1 : The study of Methanol Decomposition at 300 'C

Table A.1.1 : Operating Conditions

Helium flow rate	10 ml/min
He side stream flow	36.5 ml/min
Bath temperature	76 'C
Initial DMC inside bubbler	90 ml
Final DMC inside bubbler	31 ml

Table A.1.1 : Experimental data (Continue)

Tube No.	Time	Cond. Liq	Liq. mass	Gas film flow	MeOH flow	MeOH flow	MeOH gas	MeOH + He
	(min.)	(ml)	(g)	(ml/min)	(mol/10 min)	(mmol/min)	(ml/min)	(ml/min)
Waiting	30	9.7	7.28	-	-	-	-	-
1	5	3.4	2.53	52.6	2.81E-02	2.81	68.63	115.13
2	15	2.5	1.82	50	2.02E-02	2.02	49.37	95.87
3	25	2.45	1.78	50.2	1.98E-02	1.98	48.29	94.79
4	35	3	2.27	51.1	2.52E-02	2.52	61.58	108.08
5	45	2.45	1.81	49.8	2.01E-02	2.01	49.10	95.60
6	55	2.5	1.83	51.1	2.03E-02	2.03	49.64	·96.14
7	65	2.4	1.73	50.4	1.92E-02	1.92	46.93	93.43
8	75	2.6	1.89	51.3	2.10E-02	2.10	51.27	97.77
9	85	2.45	1.8	51.7	2.00E-02	2.00	48.83	95.33
10	95	2.7	1.98	50.6	2.20E-02	2.20	53.71	100.21
11	105	2.4	1.74	48	1.93E-02	1.93	47.20	93.70
12	115	2.2	1.58	49	1.75E-02	1.75	42.86	89.36
Purge & EV-91		14.45	-					
		55.2						

Table A.1.1 : Calculation (Continue)

Time	H2 area	H2	H2	Total H2	MeOH area	MeOH	MeOH	Total MeOH
(min)	per 1 cc	mol/cc	mol/min	by graph	per 1 cc	mol/cc	mol/min	by graph
2	1676	1.58E-06	1.81E-04	9.07E-04	355779	8.11E-05	9.33E-03	0.047
8	1593	1.50E-06	1.72E-04	8.62E-04	355827	8.11E-05	9.34E-03	0.047
13	1908	1.79E-06	1.72E-04	8.60E-04	355859	8.11E-05	7.77E-03	0.039
18	2062	1.94E-06	1.86E-04	9.29E-04	355772	8.11E-05	7.77E-03	0.039
23	1887	1.77E-06	1.68E-04	8.41E-04	355696	8.11E-05	7.68E-03	0.038
28	1818	1.71E-06	1.62E-04	8.10E-04	355690	8.11E-05	7.68E-03	0.038
33	1511	1.42E-06	1.53E-04	7.67E-04	355552	8.10E-05	8.76E-03	0.044
38	1312	1.23E-06	1.33E-04	6.66E-04	355568	8.10E-05	8.76E-03	0.044
43	1682	1.58E-06	1.51E-04	7.56E-04	355621	8.10E-05	7.75E-03	0.039
48	1710	1.61E-06	1.54E-04	7.68E-04	355524	8.10E-05	7.75E-03	0.039
53	1580	1.48E-06	1.43E-04	7.14E-04	355651	8.10E-05	7.79E-03	0.039
58	1563	1.47E-06	1.41E-04	7.06E-04	355650	8.10E-05	7.79E-03	0.039
63	1611	1.51E-06	1.41E-04	7.07E-04	355641	8.10E-05	7.57E-03	0.038
68	1557	1.46E-06	1.37E-04	6.84E-04	355610	8.10E-05	7.57E-03	0.038
73	1438	1.35E-06	1.32E-04	6.61E-04	355722	8.11E-05	7.93E-03	0.040
78	1437	1.35E-06	1.32E-04	6.60E-04	355611	8.10E-05	7.92E-03	0.040
83	1449	1.36E-06	1.30E-04	6.49E-04	355652	8.10E-05	7.73E-03	0.039
88	1442	1.36E-06	1.29E-04	6.46E-04	355552	8.10E-05	7.72E-03	0.039
93	1285	1.21E-06	1.21E-04	6.05E-04	355681	8.11E-05	8.12E-03	0.041
98	1320	1.24E-06	1.24E-04	6.22E-04	355649	8.10E-05	8.12E-03	0.041
103	1417	1.33E-06	1.25E-04	6.24E-04	355624	8.10E-05	7.59E-03	0.038
108	1390	1.31E-06	1.22E-04	6.12E-04	355694	8.11E-05	7.59E-03	0.038
113	1354	1.27E-06	1.14E-04	5.69E-04	355652	8.10E-05	7.24E-03	0.036
118	1354	1.27E-06	1.14E-04	5.69E-04	355734	8.11E-05	7.24E-03	0.036
				1.72E-02				0.953

A.1.2 : The study of Dimethyl Carbonate Decomposition at 300 'C

Table A.1.2 : Operating Conditions

Helium flow rate	25 ml/min
Bath temperature	93 'C
Initial DMC inside bubbler	100 ml
Final DMC inside bubbler	42 ml

Table A.1.2 : Experimantal data (Continue)

Tube No.	Time	Cond. Liq	Liq. mass	Gas film flow	DMC flow	DMC flow	*DMC gas	DMC + He
	(min.)	(ml)	(g)	(ml/min)	(mol/10 min)	(mmol/min)	(ml/min)	(ml/min)
Waiting	80	8.8	9.21	-	-	-	-	-
1	5	4	4.03	25.4	4.47E-02	4.47	109.3	134.3
2	15	3.95	4.01	24.1	4.45E-02	4.45	108.8	133.8
3	25	3.5	3.57	24.4	3.96E-02	3.96	96.8	121.8
4	35	3.2	3.2	25.1	3.55E-02	3.55	86.8	111.8
5	45	3.2	3.22	24.6	3.57E-02	3.57	87.3	112.3
6	55	3.15	3.16	24.6	3.51E-02	3.51	85.7	110.7
7	65	3.4	3.41	25.6	3.79E-02	3.79	92.5	117.5
8	75	3.4	3.4	24.2	3.77E-02	3.77	92.2	117.2
9	85	3.1	3.1	25.1	3.44E-02	3.44	84.1	109.1
10	95	3.1	3.09	24.7	3.43E-02	3.43	83.8	108.8
11	105	3.1	3.13	24.4	3.47E-02	3.47	84.9	109.9
12	115	3.45	3.5	27.1	3.89E-02	3.89	94.9	119.9
Purge & EV-91		7.3	-					
		56.65						

Table A.1.2 : Calculation (Continue)

Time	CO2 area	CO2	CO2	Total CO2	DMC area	DMC	DMC	Total DMC
(min)	per 1 cc	mol/cc	mol/min	by graph	per 1 cc	mol/cc	mol/min	by graph
5	20292	5.26E-07	7.05E-05	5.29E-04	1487111	1.54E-04	2.07E-02	0.155
12	16948	4.39E-07	5.84E-05	4.38E-04	1574641	1.63E-04	2.17E-02	0.163
18	19777	5.13E-07	6.87E-05	5.15E-04	1477580	1.53E-04	2.06E-02	0.154
25	20253	5.25E-07	6.35E-05	4.77E-04	1467786	1.52E-04	1.84E-02	0.138
32	21561	5.59E-07	6.26E-05	3.13E-04	1446392	1.50E-04	1.68E-02	0.084
39	21896	5.68E-07	6.36E-05	4.77E-04	1420605	1.47E-04	1.65E-02	0.124
45	20255	5.25E-07	5.88E-05	2.94E-04	1458110	1.51E-04	1.70E-02	0.085
53	21332	5.53E-07	6.14E-05	6.14E-04	1434703	1.49E-04	1.65E-02	0.165
61	19861	5.15E-07	6.05E-05	4.54E-04	1443961	1.50E-04	1.76E-02	0.132
67	19082	4.95E-07	5.81E-05	2.91E-04	1458639	1.51E-04	1.78E-02	0.089
74	17889	4.64E-07	5.43E-05	4.07E-04	1480507	1.54E-04	1.80E-02	0.135
81	20049	5.20E-07	5.67E-05	4.25E-04	1439496	1.49E-04	1.63E-02	0.122
87	21261	5.51E-07	6.01E-05	4.51E-04	1415274	1.47E-04	1.60E-02	0.120
96	20566	5.33E-07	5.81E-05	4.36E-04	1427816	1.48E-04	1.62E-02	0.121
103	19703	5.11E-07	5.62E-05	4.21E-04	1432411	1.49E-04	1.64E-02	0.123
112	21025	5.45E-07	6.54E-05	8.18E-04	1413552	1.47E-04	1.76E-02	0.220
				7.36E-03				**2.131**

A.1.3 : The study of Dimethyl Carbonate Decomposition at 325 C

Table A.1.3 : Operating Conditions

Helium flow rate	25 ml/min
Bath temperature	93 'C
Initial DMC inside bubbler	110 ml
Final DMC inside bubbler	54 ml

Table A.1.3 : Experimantal data (Continue)

Tube No.	Time	Cond. Liq	Liq. mass	Gas film flow	DMC flow	DMC flow	*DMC gas	DMC + He
	(min.)	(ml)	(g)	(ml/min)	(mol/10 min)	(mmol/min)	(ml/min)	(ml/min)
Waiting	80	12.45	13	-	-	-	-	-
1	5	3.3	3.28	25.8	3.64E-02	3.64	88.98	114.98
2	15	3.2	3.17	25.5	3.52E-02	3.52	85.99	111.99
3	25	2.45	2.41	27.4	2.68E-02	2.68	65.38	91.38
4	35	2.5	2.45	24.4	2.72E-02	2.72	66.46	92.46
5	45	3.5	3.52	26.3	3.91E-02	3.91	95.49	121.49
6	55	3.2	3.18	25	3.53E-02	3.53	86.26	112.26
7	65	2.9	2.89	26.2	3.21E-02	3.21	78.40	104.40
8	75	2.7	2.65	24	2.94E-02	2.94	71.89	97.89
9	85	2.7	2.71	26.9	3.01E-02	3.01	73.51	99.51
10	95	2.4	2.32	26.2	2.58E-02	2.58	62.93	88.93
11	105	2.55	2.53	28.2	2.81E-02	2.81	68.63	94.63
12	115	3.3	3.3	27.3	3.66E-02	3.66	89.52	115.52
Purge & EV-91		7.8	-					
		54.95						

Table A.1.3 : Calculation (Continue)

Time	CO2 area	CO2	CO2	Total CO2	DMC area	DMC	DMC	Total DMC
(min)	per 1 cc	mol/cc	mol/min	by graph	per 1 cc	mol/cc	mol/min	by graph
2	32029	8.30E-07	9.55E-05	4.78E-04	1406091	1.46E-04	1.68E-02	0.084
8	26431	6.85E-07	7.88E-05	5.91E-04	1466826	1.52E-04	1.75E-02	0.131
15	25328	6.57E-07	7.36E-05	5.52E-04	1469579	1.53E-04	1.71E-02	0.128
23	32967	8.55E-07	7.81E-05	3.91E-04	1312191	1.36E-04	1.25E-02	0.062
30	33904	8.79E-07	8.13E-05	8.13E-04	1301447	1.35E-04	1.25E-02	0.125
37	25666	6.66E-07	6.16E-05	3.08E-04	1342863	1.39E-04	1.29E-02	0.064
44	18656	4.84E-07	5.88E-05	4.41E-04	1480570	1.54E-04	1.87E-02	0.140
52	22976	5.96E-07	6.67E-05	5.00E-04	1475399	1.53E-04	1.72E-02	0.129
59	29012	7.52E-07	8.43E-05	6.32E-04	1358716	1.41E-04	1.58E-02	0.118
66	29118	7.55E-07	7.85E-05	5.89E-04	1366045	1.42E-04	1.47E-02	0.111
73	25091	6.51E-07	6.38E-05	4.78E-04	1419193	1.47E-04	1.44E-02	0.108
80	26440	6.86E-07	6.82E-05	3.41E-04	1441268	1.50E-04	1.49E-02	0.074
87	28253	7.33E-07	7.29E-05	5.47E-04	1339318	1.39E-04	1.38E-02	0.104
94	32478	8.42E-07	7.49E-05	5.65E-04	1267641	1.32E-04	1.17E-02	0.088
102	29887	7.75E-07	7.33E-05	7.33E-04	1324952	1.38E-04	1.30E-02	0.130
111	22678	5.88E-07	6.79E-05	8.49E-04	1436292	1.49E-04	1.72E-02	0.215
				8.81E-03				1.813

Appendix 2

Experimental Data and Results of TMOS Process

Table A.2.1: Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Cond. Liq. Vol. (ml)	Gas flow (ml/min)	TMOS (mole/10 min)	Avg. Rate of TMOS formation (mole/min)	Rate (mmol/min)
1	5	1.8	2.4	60.9	2.2E-05	2.2E-06	2.2E-03
2	15	1.97	2.6	60.3	2.6E-05	2.6E-06	2.6E-03
3	25	1.99	2.7	57.1	1.6E-05	1.6E-06	1.6E-03
4	35	1.63	2.3	56.6	1.5E-05	1.5E-06	1.5E-03
5	45	1.92	2.6	59.4	1.5E-05	1.5E-06	1.5E-03
6	55	1.99	2.7	59.4	2.0E-05	2.0E-06	2.0E-03
7	65	1.98	2.7	58.8	1.7E-05	1.7E-06	1.7E-03
8	75	1.94	2.6	56.9	1.5E-05	1.5E-06	1.5E-03
9	85	1.91	2.6	58.3	1.5E-05	1.5E-06	1.5E-03
10	95	1.93	2.6	57.4	1.4E-05	1.4E-06	1.4E-03
11	105	1.88	2.5	57.1	1.3E-05	1.3E-06	1.3E-03
12	115	1.91	2.6	58.0	1.3E-05	1.3E-06	1.3E-03
13	125	1.82	2.5	58.0	1.5E-05	1.5E-06	1.5E-03
14	135	1.85	2.5	58.0	1.4E-05	1.4E-06	1.4E-03
15	145	1.79	2.4	57.4	1.3E-05	1.3E-06	1.3E-03
16	155	1.91	2.6	57.4	1.2E-05	1.2E-06	1.2E-03
17	165	1.88	2.5	57.7	1.2E-05	1.2E-06	1.2E-03
18	175	1.87	2.5	58.3	1.2E-05	1.2E-06	1.2E-03
19	185	1.87	2.5	57.70	1.2E-05	1.2E-06	1.2E-03
20	195	1.84	2.5	57.7	1.2E-05	1.2E-06	1.2E-03
21	205	1.6	2.2	56.1	1.1E-05	1.1E-06	1.1E-03
22	215	1.81	2.4	64.5	1.1E-05	1.1E-06	1.1E-03
23	225	1.82	2.5	64.5	1.2E-05	1.2E-06	1.2E-03
24	235	1.86	2.5	65.6	1.2E-05	1.2E-06	1.2E-03
25	245	1.88	2.5	64.5	1.2E-05	1.2E-06	1.2E-03
26	255	1.83	2.5	64.9	1.2E-05	1.2E-06	1.2E-03
27	265	1.79	2.4	64.2	1.1E-05	1.1E-06	1.1E-03
28	275	1.83	2.5	65.2	1.2E-05	1.2E-06	1.2E-03
29	285	1.83	2.5	64.5	1.2E-05	1.2E-06	1.2E-03
30	295	1.66	2.3	63.8	1.1E-05	1.1E-06	1.1E-03
				Total	4.21E-04		

Table A.2.1 : Experimental results (Continue)

Tube	Mole of TMOS (mol in10 min)	Unreacted MeOH (mol in 10 min)	Mole MeOH reacted (mol in 10 min.)	Total MeOH flow (mol in 10 min)	Total MeOH flow (mmol/min)
1	2.16E-05	5.61E-02	8.66E-05	5.62E-02	5.62
2	2.60E-05	6.14E-02	1.04E-04	6.15E-02	6.15
3	1.63E-05	6.21E-02	6.51E-05	6.22E-02	6.22
4	1.51E-05	5.09E-02	6.03E-05	5.09E-02	5.09
5	1.50E-05	5.99E-02	6.01E-05	6.00E-02	6.00
6	2.01E-05	6.21E-02	8.03E-05	6.22E-02	6.22
7	1.67E-05	6.18E-02	6.68E-05	6.19E-02	6.19
8	1.53E-05	6.06E-02	6.11E-05	6.06E-02	6.06
9	1.53E-05	5.96E-02	6.10E-05	5.97E-02	5.97
10	1.41E-05	6.02E-02	5.65E-05	6.03E-02	6.03
11	1.31E-05	5.87E-02	5.25E-05	5.87E-02	5.87
12	1.32E-05	5.96E-02	5.26E-05	5.97E-02	5.97
13	1.54E-05	5.68E-02	6.17E-05	5.69E-02	5.69
14	1.36E-05	5.77E-02	5.43E-05	5.78E-02	5.78
15	1.31E-05	5.59E-02	5.22E-05	5.59E-02	5.59
16	1.25E-05	5.96E-02	5.00E-05	5.97E-02	5.97
17	1.21E-05	5.87E-02	4.83E-05	5.87E-02	5.87
18	1.20E-05	5.84E-02	4.78E-05	5.84E-02	5.84
19	1.20E-05	5.84E-02	4.80E-05	5.84E-02	5.84
20	1.20E-05	5.74E-02	4.79E-05	5.75E-02	5.75
21	1.06E-05	4.99E-02	4.22E-05	5.00E-02	5.00
22	1.14E-05	5.65E-02	4.56E-05	5.66E-02	5.66
23	1.21E-05	5.68E-02	4.83E-05	5.69E-02	5.69
24	1.21E-05	5.81E-02	4.86E-05	5.81E-02	5.81
25	1.19E-05	5.87E-02	4.75E-05	5.87E-02	5.87
26	1.21E-05	5.71E-02	4.82E-05	5.72E-02	5.72
27	1.14E-05	5.59E-02	4.58E-05	5.59E-02	5.59
28	1.21E-05	5.71E-02	4.85E-05	5.72E-02	5.72
29	1.20E-05	5.71E-02	4.81E-05	5.72E-02	5.72
30	1.11E-05	5.18E-02	4.44E-05	5.19E-02	5.19
					173.69
				Average MeOH flow	5.79

Table A.2.1 : Experimental results (Continue)

Tube	Mole of TMOS (mol in10 min)	Unreacted MeOH (mol in 10 min)	Mole MeOH reacted (mol in 10 min.)	Total MeOH flow (mol in 10 min)	Total MeOH flow (mmol/min)
1	2.16E-05	5.61E-02	8.66E-05	5.62E-02	5.62
2	2.60E-05	6.14E-02	1.04E-04	6.15E-02	6.15
3	1.63E-05	6.21E-02	6.51E-05	6.22E-02	6.22
4	1.51E-05	5.09E-02	6.03E-05	5.09E-02	5.09
5	1.50E-05	5.99E-02	6.01E-05	6.00E-02	6.00
6	2.01E-05	6.21E-02	8.03E-05	6.22E-02	6.22
7	1.67E-05	6.18E-02	6.68E-05	6.19E-02	6.19
8	1.53E-05	6.06E-02	6.11E-05	6.06E-02	6.06
9	1.53E-05	5.96E-02	6.10E-05	5.97E-02	5.97
10	1.41E-05	6.02E-02	5.65E-05	6.03E-02	6.03
11	1.31E-05	5.87E-02	5.25E-05	5.87E-02	5.87
12	1.32E-05	5.96E-02	5.26E-05	5.97E-02	5.97
13	1.54E-05	5.68E-02	6.17E-05	5.69E-02	5.69
14	1.36E-05	5.77E-02	5.43E-05	5.78E-02	5.78
15	1.31E-05	5.59E-02	5.22E-05	5.59E-02	5.59
16	1.25E-05	5.96E-02	5.00E-05	5.97E-02	5.97
17	1.21E-05	5.87E-02	4.83E-05	5.87E-02	5.87
18	1.20E-05	5.84E-02	4.78E-05	5.84E-02	5.84
19	1.20E-05	5.84E-02	4.80E-05	5.84E-02	5.84
20	1.20E-05	5.74E-02	4.79E-05	5.75E-02	5.75
21	1.06E-05	4.99E-02	4.22E-05	5.00E-02	5.00
22	1.14E-05	5.65E-02	4.56E-05	5.66E-02	5.66
23	1.21E-05	5.68E-02	4.83E-05	5.69E-02	5.69
24	1.21E-05	5.81E-02	4.86E-05	5.81E-02	5.81
25	1.19E-05	5.87E-02	4.75E-05	5.87E-02	5.87
26	1.21E-05	5.71E-02	4.82E-05	5.72E-02	5.72
27	1.14E-05	5.59E-02	4.58E-05	5.59E-02	5.59
28	1.21E-05	5.71E-02	4.85E-05	5.72E-02	5.72
29	1.20E-05	5.71E-02	4.81E-05	5.72E-02	5.72
30	1.11E-05	5.18E-02	4.44E-05	5.19E-02	5.19
					173.69
				Average MeOH flow	5.79

A.2.2 : BG-DMC reaction in presence of KOH (5 wt%) as a catalyst at 300 'C

Table A.2.2 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 3 g.	1.6	0.3	1.1

Table A.2.2 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	3 g.
Final BG mass	2.82 g.

Table A.2.2 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles $*10^{-7}$	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mol)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	2.48	5	1865.20	2.01	2.50	1.00E-04	1.53E-02	2.46	2.74E-02
2	3.94	5	1089.60	1.46	3.90	1.14E-04	1.74E-02	3.92	4.35E-02
3	4.01	5	988.30	1.39	3.90	1.09E-04	1.65E-02	3.99	4.43E-02
4	3.61	5	864.30	1.31	3.60	9.41E-05	1.43E-02	3.60	3.99E-02
5	3.89	5	634.30	1.15	3.90	8.94E-05	1.36E-02	3.88	4.30E-02
6	4.11	5	617.40	1.13	4.00	9.07E-05	1.38E-02	4.10	4.55E-02
7	3.53	5	670.00	1.17	3.50	8.20E-05	1.25E-02	3.52	3.90E-02
8	3.15	5	722.20	1.21	3.10	7.49E-05	1.14E-02	3.14	3.48E-02
9	3.13	5	589.68	1.11	3.10	6.91E-05	1.05E-02	3.12	3.46E-02
10	3.06	5	334.40	0.94	3.00	5.62E-05	8.55E-03	3.05	3.39E-02
11	3.65	5	268.80	0.89	3.60	6.41E-05	9.75E-03	3.64	4.04E-02
12	4.28	5	223.50	0.86	4.20	7.21E-05	1.10E-02	4.27	4.74E-02
13	3.75	5	212.80	0.85	3.70	6.30E-05	9.58E-03	3.74	4.15E-02
14	3.66	5	240.80	0.87	3.60	6.27E-05	9.54E-03	3.65	4.05E-02
15	3.59	5	151.40	0.81	3.50	5.65E-05	8.61E-03	3.58	3.98E-02
16	3.59	5	79.50	0.76	3.50	5.30E-05	8.07E-03	3.58	3.98E-02
17	3.62	5	132.80	0.79	3.55	5.64E-05	8.59E-03	3.61	4.01E-02
18	3.84	5	169.00	0.82	3.80	6.23E-05	9.49E-03	3.83	4.25E-02
19	3.39	5	169.00	0.82	3.30	5.41E-05	8.24E-03	3.38	3.75E-02
20	3.62	5	129.50	0.79	3.55	5.63E-05	8.56E-03	3.61	4.01E-02
21	3.23	5	281.90	0.90	3.20	5.75E-05	8.76E-03	3.22	3.58E-02
22	3.33	5	166.50	0.82	3.30	5.40E-05	8.22E-03	3.32	3.69E-02
23	3.99	5	136.50	0.80	3.90	6.22E-05	9.47E-03	3.98	4.42E-02
24	3.14	5	186.00	0.83	3.10	5.16E-05	7.85E-03	3.13	3.48E-02
25	3.11	5	160.00	0.81	3.10	5.05E-05	7.68E-03	3.10	3.44E-02
26	3.89	5	134.10	0.80	3.80	6.05E-05	9.20E-03	3.88	4.31E-02
27	3.12	5	112.10	0.78	3.10	4.84E-05	7.36E-03	3.11	3.46E-02
28	2.88	5	197.00	0.84	2.90	4.87E-05	7.41E-03	2.87	3.19E-02
29	3.41	5	135.20	0.80	3.40	5.42E-05	8.24E-03	3.40	3.78E-02
30	3.19	5	161.00	0.81	3.20	5.21E-05	7.93E-03	3.18	3.53E-02
EV-91	13.98	5	159.50	0.81	14.50	2.36E-04	-	-	-

2.26E-03

Table A.2.2 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	2.48	2.50	31.8	1.00E-04	1.00E-05	1.00E-02
2	15	3.94	3.90	33.4	1.14E-04	1.14E-05	1.14E-02
3	25	4.01	3.90	30.2	1.09E-04	1.09E-05	1.09E-02
4	35	3.61	3.60	29.6	9.41E-05	9.41E-06	9.41E-03
5	45	3.89	3.90	31.0	8.94E-05	8.94E-06	8.94E-03
6	55	4.11	4.00	29.6	9.07E-05	9.07E-06	9.07E-03
7	65	3.53	3.50	26.8	8.20E-05	8.20E-06	8.20E-03
8	75	3.15	3.10	30.3	7.49E-05	7.49E-06	7.49E-03
9	85	3.13	3.10	32.0	6.91E-05	6.91E-06	6.91E-03
10	95	3.06	3.00	30.8	5.62E-05	5.62E-06	5.62E-03
11	105	3.65	3.60	30.0	6.41E-05	6.41E-06	6.41E-03
12	115	4.28	4.20	29.9	7.21E-05	7.21E-06	7.21E-03
13	125	3.75	3.70	28.5	6.30E-05	6.30E-06	6.30E-03
14	135	3.66	3.60	30.2	6.27E-05	6.27E-06	6.27E-03
15	145	3.59	3.50	29.7	5.65E-05	5.65E-06	5.65E-03
16	155	3.59	3.50	30.5	5.30E-05	5.30E-06	5.30E-03
17	165	3.62	3.55	29.9	5.64E-05	5.64E-06	5.64E-03
18	175	3.84	3.80	30.9	6.23E-05	6.23E-06	6.23E-03
19	185	3.39	3.30	28.8	5.41E-05	5.41E-06	5.41E-03
20	195	3.62	3.55	32.6	5.63E-05	5.63E-06	5.63E-03
21	205	3.23	3.20	32.0	5.75E-05	5.75E-06	5.75E-03
22	215	3.33	3.30	32.4	5.40E-05	5.40E-06	5.40E-03
23	225	3.99	3.90	31.0	6.22E-05	6.22E-06	6.22E-03
24	235	3.14	3.10	29.6	5.16E-05	5.16E-06	5.16E-03
25	245	3.11	3.10	33.0	5.05E-05	5.05E-06	5.05E-03
26	255	3.89	3.80	32.3	6.05E-05	6.05E-06	6.05E-03
27	265	3.12	3.10	30.2	4.84E-05	4.84E-06	4.84E-03
28	275	2.88	2.90	33.6	4.87E-05	4.87E-06	4.87E-03
29	285	3.41	3.40	34.9	5.42E-05	5.42E-06	5.42E-03
30	295	3.19	3.20	31.0	5.21E-05	5.21E-06	5.21E-03
Waiting	-	-	17.10	-	-		
			120.90		2.02E-03		

Table A.2.2 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	1.00E-04	2.74E-02	2.01E-04	2.76E-02	2.76
2	1.14E-04	4.35E-02	2.28E-04	4.38E-02	4.38
3	1.09E-04	4.43E-02	2.17E-04	4.45E-02	4.45
4	9.41E-05	3.99E-02	1.88E-04	4.01E-02	4.01
5	8.94E-05	4.30E-02	1.79E-04	4.32E-02	4.32
6	9.07E-05	4.55E-02	1.81E-04	4.57E-02	4.57
7	8.20E-05	3.90E-02	1.64E-04	3.92E-02	3.92
8	7.49E-05	3.48E-02	1.50E-04	3.50E-02	3.50
9	6.91E-05	3.46E-02	1.38E-04	3.48E-02	3.48
10	5.62E-05	3.39E-02	1.12E-04	3.40E-02	3.40
11	6.41E-05	4.04E-02	1.28E-04	4.05E-02	4.05
12	7.21E-05	4.74E-02	1.44E-04	4.75E-02	4.75
13	6.30E-05	4.15E-02	1.26E-04	4.16E-02	4.16
14	6.27E-05	4.05E-02	1.25E-04	4.06E-02	4.06
15	5.65E-05	3.98E-02	1.13E-04	3.99E-02	3.99
16	5.30E-05	3.98E-02	1.06E-04	3.99E-02	3.99
17	5.64E-05	4.01E-02	1.13E-04	4.02E-02	4.02
18	6.23E-05	4.25E-02	1.25E-04	4.26E-02	4.26
19	5.41E-05	3.75E-02	1.08E-04	3.77E-02	3.77
20	5.63E-05	4.01E-02	1.13E-04	4.02E-02	4.02
21	5.75E-05	3.58E-02	1.15E-04	3.59E-02	3.59
22	5.40E-05	3.69E-02	1.08E-04	3.70E-02	3.70
23	6.22E-05	4.42E-02	1.24E-04	4.43E-02	4.43
24	5.16E-05	3.48E-02	1.03E-04	3.49E-02	3.49
25	5.05E-05	3.44E-02	1.01E-04	3.45E-02	3.45
26	6.05E-05	4.31E-02	1.21E-04	4.32E-02	4.32
27	4.84E-05	3.46E-02	9.68E-05	3.47E-02	3.47
28	4.87E-05	3.19E-02	9.74E-05	3.20E-02	3.20
29	5.42E-05	3.78E-02	1.08E-04	3.79E-02	3.79
30	5.21E-05	3.53E-02	1.04E-04	3.54E-02	3.54
					116.84
				Average DMC flow	3.89

A.2.3 : Pure Si powder-CH3OH reaction in a presence of CuCl2 (5 wt%) as a catalyst at 300 'C

Table A.2.3 : BG Composition

	Si	SIO2	SiC
Composition (wt%)	100	0	0
Component of BG 3 g.	3.0	0.0	0.0

Table A.2.3 : Operating Conditions (Continue)

Pretreatment	500 'C for 3 hr. in N2+H2
Bath temperature	76 'C
He flow rate	10 ml/min
He side stream	38 ml/min
Initial BG mass	3 g.
Final BG mass	2.94 g.

Table A.2.3 : Experimental results (Continue)

Cond. Liq. Tube No.	Vol of Inj. (uL)	Mass (g)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 mins (mole)	Mass TMOS in 10 min. (g)	Mass MeOH unreacted (g)	Mole MeOH unreacted
1	2	1.76	4164.00	1.6331	2.40	1.96E-04	2.98E-02	1.73	5.41E-02
2	4	2.03	674.25	0.4622	2.70	3.12E-05	4.75E-03	2.03	6.33E-02
3	4	1.85	969.00	0.5611	2.50	3.51E-05	5.34E-03	1.84	5.76E-02
4	4	1.8	913.00	0.5423	2.50	3.39E-05	5.16E-03	1.79	5.61E-02
5	4	1.88	729.75	0.4808	2.50	3.01E-05	4.57E-03	1.88	5.86E-02
6	4	1.96	804.00	0.5057	2.60	3.29E-05	5.00E-03	1.95	6.11E-02
7	4	1.81	685.75	0.4661	2.50	2.91E-05	4.43E-03	1.81	5.64E-02
8	4	1.77	711.00	0.4745	2.40	2.85E-05	4.33E-03	1.77	5.52E-02
9	4	1.76	686.75	0.4664	2.40	2.80E-05	4.26E-03	1.76	5.49E-02
10	4	1.82	676.25	0.4629	2.50	2.89E-05	4.40E-03	1.82	5.67E-02
11	4	1.84	706.75	0.4731	2.50	2.96E-05	4.50E-03	1.84	5.74E-02
12	4	1.84	996.00	0.5702	2.50	3.56E-05	5.42E-03	1.83	5.73E-02
13	4	1.86	852.00	0.5219	2.50	3.26E-05	4.96E-03	1.86	5.80E-02
14	4	1.86	948.25	0.5541	2.50	3.46E-05	5.27E-03	1.85	5.80E-02
15	4	1.86	1012.50	0.5757	2.50	3.60E-05	5.48E-03	1.85	5.80E-02
16	4	1.85	1055.50	0.5901	2.50	3.69E-05	5.61E-03	1.84	5.76E-02
17	4	1.9	1112.25	0.6092	2.60	3.96E-05	6.03E-03	1.89	5.92E-02
18	4	1.77	1052.50	0.5891	2.40	3.53E-05	5.38E-03	1.76	5.51E-02
19	4	1.63	1072.50	0.5958	2.00	2.98E-05	4.53E-03	1.63	5.08E-02
20	4	1.82	965.75	0.5600	2.50	3.50E-05	5.33E-03	1.81	5.67E-02
21	4	1.83	1060.25	0.5917	2.50	3.70E-05	5.63E-03	1.82	5.70E-02
22	4	1.85	1050.25	0.5884	2.50	3.68E-05	5.60E-03	1.84	5.76E-02
23	4	1.83	989.25	0.5679	2.50	3.55E-05	5.40E-03	1.82	5.70E-02
24	4	1.82	965.50	0.5599	2.50	3.50E-05	5.33E-03	1.81	5.67E-02
25	4	1.78	1116.50	0.6106	2.45	3.74E-05	5.69E-03	1.77	5.54E-02
26	4	1.76	993.00	0.5692	2.40	3.41E-05	5.20E-03	1.75	5.48E-02
27	4	1.71	805.00	0.5061	2.30	2.91E-05	4.43E-03	1.71	5.33E-02
28	4	1.78	970.25	0.5615	2.40	3.37E-05	5.13E-03	1.77	5.55E-02
29	4	1.8	818.25	0.5105	2.45	3.13E-05	4.76E-03	1.80	5.61E-02
30	4	1.75	924.75	0.5463	2.40	3.28E-05	4.99E-03	1.75	5.45E-02
PURGE	4	3.04	937.00	0.5504	4.00	5.50E-05			
EV-91	4	11.45	417.50	0.3761	15.50	1.46E-04			
						Total	1.36E-03		

Table A.2.3 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas flow (ml/min)	TMOS (mole/10 min)	Avg. Rate of TMOS formation (mole/min)	Rate (mmol/min)
1	5	1.76	2.4	58.5	1.96E-04	2.0E-05	1.96E-02
2	15	2.03	2.70	56.0	3.12E-05	3.1E-06	3.12E-03
3	25	1.85	2.50	54.5	3.51E-05	3.5E-06	3.51E-03
4	35	1.8	2.50	55.6	3.39E-05	3.4E-06	3.39E-03
5	45	1.88	2.50	56.1	3.01E-05	3.0E-06	3.01E-03
6	55	1.96	2.60	58.0	3.29E-05	3.3E-06	3.29E-03
7	65	1.81	2.50	59.4	2.91E-05	2.9E-06	2.91E-03
8	75	1.77	2.40	60.0	2.85E-05	2.8E-06	2.85E-03
9	85	1.76	2.40	53.4	2.80E-05	2.8E-06	2.80E-03
10	95	1.82	2.50	59.7	2.89E-05	2.9E-06	2.89E-03
11	105	1.84	2.50	60.0	2.96E-05	3.0E-06	2.96E-03
12	115	1.84	2.50	59.7	3.56E-05	3.6E-06	3.56E-03
13	125	1.86	2.50	60.0	3.26E-05	3.3E-06	3.26E-03
14	135	1.86	2.50	60.3	3.46E-05	3.5E-06	3.46E-03
15	145	1.86	2.50	57.1	3.60E-05	3.6E-06	3.60E-03
16	155	1.85	2.50	60.6	3.69E-05	3.7E-06	3.69E-03
17	165	1.9	2.6	60.3	3.96E-05	4.0E-06	3.96E-03
18	175	1.77	2.4	62.8	3.53E-05	3.5E-06	3.53E-03
19	185	1.63	2	62.20	2.98E-05	3.0E-06	2.98E-03
20	195	1.82	2.5	63.2	3.50E-05	3.5E-06	3.50E-03
21	205	1.83	2.5	62.2	3.70E-05	3.7E-06	3.70E-03
22	215	1.85	2.5	61.9	3.68E-05	3.7E-06	3.68E-03
23	225	1.83	2.5	61.5	3.55E-05	3.5E-06	3.55E-03
24	235	1.82	2.5	61.2	3.50E-05	3.5E-06	3.50E-03
25	245	1.78	2.45	61.5	3.74E-05	3.7E-06	3.74E-03
26	255	1.76	2.4	61.2	3.41E-05	3.4E-06	3.41E-03
27	265	1.71	2.3	60.3	2.91E-05	2.9E-06	2.91E-03
28	275	1.78	2.4	60.3	3.37E-05	3.4E-06	3.37E-03
29	285	1.8	2.45	60	3.13E-05	3.1E-06	3.13E-03
30	295	1.75	2.4	61.9	3.28E-05	3.3E-06	3.28E-03
PURGE	-	3.04	4.0	-	5.50E-05		
EV-91	-	11.45	15.5	-	1.46E-04		
					1.36E-03		

Table A.2.3 : Experimental results (Continue)

Tube	Mole of TMOS (mol in10 min)	Unreacted MeOH (mol in 10 min)	Mole MeOH reacted (mol in 10 min.)	Total MeOH flow (mol in 10 min)	Total MeOH flow (mmol/min)
1	1.96E-04	5.41E-02	7.84E-04	5.49E-02	5.49
2	3.12E-05	6.33E-02	1.25E-04	6.34E-02	6.34
3	3.51E-05	5.76E-02	1.40E-04	5.78E-02	5.78
4	3.39E-05	5.61E-02	1.36E-04	5.62E-02	5.62
5	3.01E-05	5.86E-02	1.20E-04	5.87E-02	5.87
6	3.29E-05	6.11E-02	1.31E-04	6.12E-02	6.12
7	2.91E-05	5.64E-02	1.17E-04	5.65E-02	5.65
8	2.85E-05	5.52E-02	1.14E-04	5.53E-02	5.53
9	2.80E-05	5.49E-02	1.12E-04	5.50E-02	5.50
10	2.89E-05	5.67E-02	1.16E-04	5.69E-02	5.69
11	2.96E-05	5.74E-02	1.18E-04	5.75E-02	5.75
12	3.56E-05	5.73E-02	1.43E-04	5.75E-02	5.75
13	3.26E-05	5.80E-02	1.30E-04	5.81E-02	5.81
14	3.46E-05	5.80E-02	1.39E-04	5.81E-02	5.81
15	3.60E-05	5.80E-02	1.44E-04	5.81E-02	5.81
16	3.69E-05	5.76E-02	1.48E-04	5.78E-02	5.78
17	3.96E-05	5.92E-02	1.58E-04	5.93E-02	5.93
18	3.53E-05	5.51E-02	1.41E-04	5.53E-02	5.53
19	2.98E-05	5.08E-02	1.19E-04	5.09E-02	5.09
20	3.50E-05	5.67E-02	1.40E-04	5.68E-02	5.68
21	3.70E-05	5.70E-02	1.48E-04	5.72E-02	5.72
22	3.68E-05	5.76E-02	1.47E-04	5.78E-02	5.78
23	3.55E-05	5.70E-02	1.42E-04	5.72E-02	5.72
24	3.50E-05	5.67E-02	1.40E-04	5.68E-02	5.68
25	3.74E-05	5.54E-02	1.50E-04	5.56E-02	5.56
26	3.41E-05	5.48E-02	1.37E-04	5.50E-02	5.50
27	2.91E-05	5.33E-02	1.16E-04	5.34E-02	5.34
28	3.37E-05	5.55E-02	1.35E-04	5.56E-02	5.56
29	3.13E-05	5.61E-02	1.25E-04	5.62E-02	5.62
30	3.28E-05	5.45E-02	1.31E-04	5.47E-02	5.47
					170.47
				Average MeOH flow	5.68

A.2.4 : Pure Si powder-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 300 'C

Table A.2.4 : BG Composition

	Si	SiO2	SiC
Composition (5 wt%)	100	0	0
Component of BG 3 g.	3.0	0.0	0.0

Table A.2.4 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	3 g.
Final BG mass	2.84 g.

Table A.2.4 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Mole *10^-7	Cond. Liq. vol. (ml)	Total TMOS in periods (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	5.4	4	5083	4.260	5.2	5.54E-04	8.43E-02	5.32	5.90E-02
2	6.46	4	1837	1.988	6.2	3.08E-04	4.69E-02	6.41	7.12E-02
3	4.22	4	981.5	1.389	4.1	1.42E-04	2.17E-02	4.20	4.66E-02
4	3.02	4	564	1.097	3.00	8.22E-05	1.25E-02	3.01	3.34E-02
5	3.76	4	613.4	1.131	3.70	1.05E-04	1.59E-02	3.74	4.16E-02
6	3.87	4	269.3	0.890	3.80	8.46E-05	1.29E-02	3.86	4.28E-02
7	3.57	4	236.9	0.868	3.50	7.59E-05	1.16E-02	3.56	3.95E-02
8	4.88	4	130.86	0.793	4.80	9.52E-05	1.45E-02	4.87	5.40E-02
9	4.68	5	259.1	0.883	4.50	7.95E-05	1.21E-02	4.67	5.18E-02
10	3.99	5	432.8	1.005	3.90	7.84E-05	1.19E-02	3.98	4.42E-02
11	3.54	5	666.7	1.168	3.50	8.18E-05	1.25E-02	3.53	3.92E-02
12	4.19	5	539.7	1.080	4.10	8.85E-05	1.35E-02	4.18	4.64E-02
13	4.9	5	408	0.987	4.80	9.48E-05	1.44E-02	4.89	5.42E-02
14	4.53	5	417.4	0.994	4.40	8.75E-05	1.33E-02	4.52	5.01E-02
15	2.16	5	1202	1.543	2.20	6.79E-05	1.03E-02	2.15	2.39E-02
16	2.29	5	1456.8	1.722	2.30	7.92E-05	1.21E-02	2.28	2.53E-02
17	4.05	5	1106	1.476	4.00	1.18E-04	1.80E-02	4.03	4.48E-02
18	4.89	5	805.7	1.266	4.80	1.22E-04	1.85E-02	4.87	5.41E-02
19	3.16	5	941.3	1.361	3.20	8.71E-05	1.33E-02	3.15	3.49E-02
20	2.81	5	1270	1.591	2.80	8.91E-05	1.36E-02	2.80	3.10E-02
21	2.96	5	1080	1.458	3.00	8.75E-05	1.33E-02	2.95	3.27E-02
22	2.58	5	1596	1.819	2.70	9.82E-05	1.50E-02	2.57	2.85E-02
23	2.2	5	2027	2.121	2.20	9.33E-05	1.42E-02	2.19	2.43E-02
24	4.4	5	1356.1	1.651	4.40	1.45E-04	2.21E-02	4.38	4.86E-02
25	4.69	5	1431	1.704	4.60	1.57E-04	2.39E-02	4.67	5.18E-02
26	4.2	5	1355.6	1.651	4.20	1.39E-04	2.11E-02	4.18	4.64E-02
27	3.73	5	1716.6	1.903	3.70	1.41E-04	2.14E-02	3.71	4.12E-02
28	4.11	5	1763.7	1.936	4.00	1.55E-04	2.36E-02	4.09	4.54E-02
29	3.68	5	2235	2.266	3.70	1.68E-04	2.55E-02	3.65	4.06E-02
30	3.39	5	1868.6	2.010	3.40	1.37E-04	2.08E-02	3.37	3.74E-02
Purge	-	5	247.9	0.875	10.40	1.82E-04	-	-	-
						4.02E-03			

Table A.2.4 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS (mol/10 min)	Avg. Rate of TMOS formation (mole/min)	Rate (mmol/min)
1	5	5.4	5.2	38.3	5.54E-04	5.54E-05	5.54E-02
2	15	6.46	6.2	31.0	3.08E-04	3.08E-05	3.08E-02
3	25	4.22	4.1	24.4	1.42E-04	1.42E-05	1.42E-02
4	35	3.02	3.00	28.6	8.22E-05	8.22E-06	8.22E-03
5	45	3.76	3.70	29.3	1.05E-04	1.05E-05	1.05E-02
6	55	3.87	3.80	27.2	8.46E-05	8.46E-06	8.46E-03
7	65	3.57	3.50	29.1	7.59E-05	7.59E-06	7.59E-03
8	75	4.88	4.80	27.3	9.52E-05	9.52E-06	9.52E-03
9	85	4.68	4.50	24.3	7.95E-05	7.95E-06	7.95E-03
10	95	3.99	3.90	25.5	7.84E-05	7.84E-06	7.84E-03
11	105	3.54	3.50	24.3	8.18E-05	8.18E-06	8.18E-03
12	115	4.19	4.10	28.8	8.85E-05	8.85E-06	8.85E-03
13	125	4.9	4.80	29.8	9.48E-05	9.48E-06	9.48E-03
14	135	4.53	4.40	26.1	8.75E-05	8.75E-06	8.75E-03
15	145	2.16	2.20	27.1	6.79E-05	6.79E-06	6.79E-03
16	155	2.29	2.30	32.8	7.92E-05	7.92E-06	7.92E-03
17	165	4.05	4.00	32.3	1.18E-04	1.18E-05	1.18E-02
18	175	4.89	4.80	29.1	1.22E-04	1.22E-05	1.22E-02
19	185	3.16	3.20	30.9	8.71E-05	8.71E-06	8.71E-03
20	195	2.81	2.80	32.3	8.91E-05	8.91E-06	8.91E-03
21	205	2.96	3.00	33.3	8.75E-05	8.75E-06	8.75E-03
22	215	2.58	2.70	33.0	9.82E-05	9.82E-06	9.82E-03
23	225	2.2	2.20	35.1	9.33E-05	9.33E-06	9.33E-03
24	235	4.4	4.40	40.1	1.45E-04	1.45E-05	1.45E-02
25	245	4.69	4.60	36.1	1.57E-04	1.57E-05	1.57E-02
26	255	4.2	4.20	36.3	1.39E-04	1.39E-05	1.39E-02
27	265	3.73	3.70	36.3	1.41E-04	1.41E-05	1.41E-02
28	275	4.11	4.00	41.4	1.55E-04	1.55E-05	1.55E-02
29	285	3.68	3.70	40.8	1.68E-04	1.68E-05	1.68E-02
30	295	3.39	3.40	44.8	1.37E-04	1.37E-05	1.37E-02
Purge	-	-	10.40	-	1.82E-04	-	-
			125.1		3.84E-03		

Table A.2.4 : Experimental results (Continue)

Time (min)	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	5.54E-04	5.90E-02	1.11E-03	6.01E-02	6.01
2	3.08E-04	7.12E-02	6.16E-04	7.18E-02	7.18
3	1.42E-04	4.66E-02	2.85E-04	4.69E-02	4.69
4	8.22E-05	3.34E-02	1.64E-04	3.36E-02	3.36
5	1.05E-04	4.16E-02	2.09E-04	4.18E-02	4.18
6	8.46E-05	4.28E-02	1.69E-04	4.30E-02	4.30
7	7.59E-05	3.95E-02	1.52E-04	3.97E-02	3.97
8	9.52E-05	5.40E-02	1.90E-04	5.42E-02	5.42
9	7.95E-05	5.18E-02	1.59E-04	5.20E-02	5.20
10	7.84E-05	4.42E-02	1.57E-04	4.43E-02	4.43
11	8.18E-05	3.92E-02	1.64E-04	3.93E-02	3.93
12	8.85E-05	4.64E-02	1.77E-04	4.65E-02	4.65
13	9.48E-05	5.42E-02	1.90E-04	5.44E-02	5.44
14	8.75E-05	5.01E-02	1.75E-04	5.03E-02	5.03
15	6.79E-05	2.39E-02	1.36E-04	2.40E-02	2.40
16	7.92E-05	2.53E-02	1.58E-04	2.54E-02	2.54
17	1.18E-04	4.48E-02	2.36E-04	4.50E-02	4.50
18	1.22E-04	5.41E-02	2.43E-04	5.43E-02	5.43
19	8.71E-05	3.49E-02	1.74E-04	3.51E-02	3.51
20	8.91E-05	3.10E-02	1.78E-04	3.12E-02	3.12
21	8.75E-05	3.27E-02	1.75E-04	3.29E-02	3.29
22	9.82E-05	2.85E-02	1.96E-04	2.87E-02	2.87
23	9.33E-05	2.43E-02	1.87E-04	2.45E-02	2.45
24	1.45E-04	4.86E-02	2.91E-04	4.89E-02	4.89
25	1.57E-04	5.18E-02	3.13E-04	5.21E-02	5.21
26	1.39E-04	4.64E-02	2.77E-04	4.67E-02	4.67
27	1.41E-04	4.12E-02	2.82E-04	4.15E-02	4.15
28	1.55E-04	4.54E-02	3.10E-04	4.57E-02	4.57
29	1.68E-04	4.06E-02	3.35E-04	4.09E-02	4.09
30	1.37E-04	3.74E-02	2.73E-04	3.77E-02	3.77
					129.24
				Average DMC flow	**4.31**

A.2.5 : BG-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 250 'C

Table A.2.5 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 3 g.	1.6	0.3	1.1

Table A.2.5 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	3 g.
Final BG mass	2.91 g.

Table A.2.5 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	3.29	5	352.44	0.95	3.30	6.26E-05	9.53E-03	3.28	3.64E-02
2	4.58	5	125.60	0.79	4.50	7.11E-05	1.08E-02	4.57	5.07E-02
3	3.42	5	145.60	0.80	3.40	5.47E-05	8.32E-03	3.41	3.79E-02
4	3.32	5	166.10	0.82	3.30	5.40E-05	8.22E-03	3.31	3.68E-02
5	3.83	5	72.00	0.75	3.80	5.72E-05	8.70E-03	3.82	4.24E-02
6	4.05	5	181.50	0.83	4.00	6.63E-05	1.01E-02	4.04	4.48E-02
7	3.91	5	139.20	0.80	3.85	6.15E-05	9.37E-03	3.90	4.33E-02
8	2.73	5	151.96	0.81	2.70	4.36E-05	6.64E-03	2.72	3.02E-02
9	2.90	5	17.40	0.71	2.90	4.14E-05	6.30E-03	2.89	3.21E-02
10	4.55	5	15.70	0.71	4.50	6.42E-05	9.77E-03	4.54	5.04E-02
11	3.80	5	34.25	0.73	3.80	5.52E-05	8.40E-03	3.79	4.21E-02
12	4.10	5	90.80	0.77	4.10	6.28E-05	9.55E-03	4.09	4.54E-02
13	3.15	5	23.10	0.72	3.15	4.52E-05	6.89E-03	3.14	3.49E-02
14	2.95	5	59.30	0.74	3.00	4.46E-05	6.79E-03	2.94	3.27E-02
15	2.98	5	94.50	0.77	3.00	4.61E-05	7.01E-03	2.97	3.30E-02
16	3.19	5	32.95	0.72	3.20	4.64E-05	7.06E-03	3.18	3.53E-02
17	3.16	5	23.70	0.72	3.15	4.53E-05	6.89E-03	3.15	3.50E-02
18	2.57	5	32.65	0.72	2.60	3.77E-05	5.74E-03	2.56	2.85E-02
19	2.29	5	20.90	0.72	2.30	3.30E-05	5.02E-03	2.28	2.54E-02
20	3.47	5	22.50	0.72	3.45	4.95E-05	7.54E-03	3.46	3.84E-02
21	3.47	5	11.84	0.71	3.40	4.83E-05	7.35E-03	3.46	3.84E-02
22	3.13	5	24.84	0.72	3.10	4.46E-05	6.79E-03	3.12	3.47E-02
23	3.71	5	43.75	0.73	3.70	5.42E-05	8.25E-03	3.70	4.11E-02
24	3.26	5	17.00	0.71	3.20	4.57E-05	6.95E-03	3.25	3.61E-02
25	3.17	5	15.00	0.71	3.10	4.42E-05	6.72E-03	3.16	3.51E-02
26	2.97	5	42.60	0.73	3.00	4.39E-05	6.68E-03	2.96	3.29E-02
27	2.85	5	34.60	0.73	2.90	4.21E-05	6.41E-03	2.84	3.16E-02
28	3.06	5	57.42	0.74	3.00	4.45E-05	6.78E-03	3.05	3.39E-02
29	2.93	5	56.20	0.74	2.90	4.30E-05	6.54E-03	2.92	3.25E-02
30	2.67	5	86.40	0.76	2.70	4.12E-05	6.27E-03	2.66	2.96E-02
EV-91	11.83	5	104.60	0.78	13.00	2.02E-04	-	-	-

1.70E-03

Table A.2.5: Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	3.29	3.30	25.9	6.26E-05	6.26E-06	6.26E-03
2	15	4.58	4.50	24.0	7.11E-05	7.11E-06	7.11E-03
3	25	3.42	3.40	23.9	5.47E-05	5.47E-06	5.47E-03
4	35	3.32	3.30	26.0	5.40E-05	5.40E-06	5.40E-03
5	45	3.83	3.80	25.8	5.72E-05	5.72E-06	5.72E-03
6	55	4.05	4.00	24.5	6.63E-05	6.63E-06	6.63E-03
7	65	3.91	3.85	23.1	6.15E-05	6.15E-06	6.15E-03
8	75	2.73	2.70	24.1	4.36E-05	4.36E-06	4.36E-03
9	85	2.90	2.90	27.3	4.14E-05	4.14E-06	4.14E-03
10	95	4.55	4.50	25.3	6.42E-05	6.42E-06	6.42E-03
11	105	3.80	3.80	24.5	5.52E-05	5.52E-06	5.52E-03
12	115	4.10	4.10	24.5	6.28E-05	6.28E-06	6.28E-03
13	125	3.15	3.15	24.0	4.52E-05	4.52E-06	4.52E-03
14	135	2.95	3.00	25.6	4.46E-05	4.46E-06	4.46E-03
15	145	2.98	3.00	25.7	4.61E-05	4.61E-06	4.61E-03
16	155	3.19	3.20	24.9	4.64E-05	4.64E-06	4.64E-03
17	165	3.16	3.15	24.7	4.53E-05	4.53E-06	4.53E-03
18	175	2.57	2.60	24.8	3.77E-05	3.77E-06	3.77E-03
19	185	2.29	2.30	26.9	3.30E-05	3.30E-06	3.30E-03
20	195	3.47	3.45	26.8	4.95E-05	4.95E-06	4.95E-03
21	205	3.47	3.40	25.1	4.83E-05	4.83E-06	4.83E-03
22	215	3.13	3.10	24.9	4.46E-05	4.46E-06	4.46E-03
23	225	3.71	3.70	26.5	5.42E-05	5.42E-06	5.42E-03
24	235	3.26	3.20	26.6	4.57E-05	4.57E-06	4.57E-03
25	245	3.17	3.10	26.3	4.42E-05	4.42E-06	4.42E-03
26	255	2.97	3.00	26.4	4.39E-05	4.39E-06	4.39E-03
27	265	2.85	2.90	27.2	4.21E-05	4.21E-06	4.21E-03
28	275	3.06	3.00	26.8	4.45E-05	4.45E-06	4.45E-03
29	285	2.93	2.90	26.5	4.30E-05	4.30E-06	4.30E-03
30	295	2.67	2.70	26.9	4.12E-05	4.12E-06	4.12E-03
Wait&EV-91	-	-	20.45	-	-		
			119.45		1.49E-03		

Table A.2.5 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	6.26E-05	3.64E-02	1.25E-04	3.65E-02	3.65
2	7.11E-05	5.07E-02	1.42E-04	5.09E-02	5.09
3	5.47E-05	3.79E-02	1.09E-04	3.80E-02	3.80
4	5.40E-05	3.68E-02	1.08E-04	3.69E-02	3.69
5	5.72E-05	4.24E-02	1.14E-04	4.25E-02	4.25
6	6.63E-05	4.48E-02	1.33E-04	4.50E-02	4.50
7	6.15E-05	4.33E-02	1.23E-04	4.34E-02	4.34
8	4.36E-05	3.02E-02	8.73E-05	3.03E-02	3.03
9	4.14E-05	3.21E-02	8.28E-05	3.22E-02	3.22
10	6.42E-05	5.04E-02	1.28E-04	5.05E-02	5.05
11	5.52E-05	4.21E-02	1.10E-04	4.22E-02	4.22
12	6.28E-05	4.54E-02	1.26E-04	4.55E-02	4.55
13	4.52E-05	3.49E-02	9.05E-05	3.50E-02	3.50
14	4.46E-05	3.27E-02	8.92E-05	3.28E-02	3.28
15	4.61E-05	3.30E-02	9.22E-05	3.31E-02	3.31
16	4.64E-05	3.53E-02	9.28E-05	3.54E-02	3.54
17	4.53E-05	3.50E-02	9.05E-05	3.51E-02	3.51
18	3.77E-05	2.85E-02	7.54E-05	2.85E-02	2.85
19	3.30E-05	2.54E-02	6.59E-05	2.54E-02	2.54
20	4.95E-05	3.84E-02	9.90E-05	3.85E-02	3.85
21	4.83E-05	3.84E-02	9.66E-05	3.85E-02	3.85
22	4.46E-05	3.47E-02	8.92E-05	3.48E-02	3.48
23	5.42E-05	4.11E-02	1.08E-04	4.12E-02	4.12
24	4.57E-05	3.61E-02	9.14E-05	3.62E-02	3.62
25	4.42E-05	3.51E-02	8.83E-05	3.52E-02	3.52
26	4.39E-05	3.29E-02	8.78E-05	3.30E-02	3.30
27	4.21E-05	3.16E-02	8.42E-05	3.17E-02	3.17
28	4.45E-05	3.39E-02	8.90E-05	3.40E-02	3.40
29	4.30E-05	3.25E-02	8.60E-05	3.25E-02	3.25
30	4.12E-05	2.96E-02	8.23E-05	2.97E-02	2.97
				1.105	110.46
			Average DMC flow		3.68

A.2.6 : BG-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 275 'C

Table A.2.6 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 3 g.	1.6	0.3	1.1

Table A.2.6 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	3 g.
Final BG mass	2.88 g.

Table A.2.6 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	3.46	5	460.20	1.02	3.40	6.96E-05	1.06E-02	3.45	3.83E-02
2	3.96	5	345.50	0.94	3.90	7.36E-05	1.12E-02	3.95	4.38E-02
3	3.71	5	242.00	0.87	3.65	6.36E-05	9.68E-03	3.70	4.11E-02
4	2.86	5	172.00	0.82	2.90	4.77E-05	7.26E-03	2.85	3.17E-02
5	3.46	5	163.90	0.82	3.45	5.63E-05	8.58E-03	3.45	3.83E-02
6	3.76	5	175.00	0.82	3.70	6.10E-05	9.29E-03	3.75	4.16E-02
7	3.41	5	180.10	0.83	3.40	5.63E-05	8.57E-03	3.40	3.78E-02
8	2.89	5	188.70	0.83	2.90	4.84E-05	7.36E-03	2.88	3.20E-02
9	2.94	5	193.30	0.84	2.90	4.86E-05	7.39E-03	2.93	3.26E-02
10	3.07	5	178.70	0.83	3.05	5.04E-05	7.68E-03	3.06	3.40E-02
11	3.60	5	98.80	0.77	3.55	5.47E-05	8.33E-03	3.59	3.99E-02
12	3.62	5	126.30	0.79	3.55	5.61E-05	8.54E-03	3.61	4.01E-02
13	3.15	5	97.30	0.77	3.10	4.77E-05	7.27E-03	3.14	3.49E-02
14	2.74	5	240.00	0.87	2.75	4.78E-05	7.28E-03	2.73	3.03E-02
15	2.79	5	213.80	0.85	2.80	4.77E-05	7.26E-03	2.78	3.09E-02
16	2.75	5	243.60	0.87	2.80	4.88E-05	7.44E-03	2.74	3.04E-02
17	2.85	5	224.90	0.86	2.90	4.98E-05	7.59E-03	2.84	3.16E-02
18	3.21	5	167.80	0.82	3.20	5.24E-05	7.98E-03	3.20	3.55E-02
19	3.20	5	202.40	0.84	3.20	5.40E-05	8.22E-03	3.19	3.54E-02
20	3.06	5	168.70	0.82	3.10	5.08E-05	7.74E-03	3.05	3.39E-02
21	3.30	5	242.40	0.87	3.30	5.75E-05	8.76E-03	3.29	3.65E-02
22	3.07	5	231.40	0.86	3.05	5.27E-05	8.02E-03	3.06	3.40E-02
23	3.02	5	241.20	0.87	3.00	5.22E-05	7.95E-03	3.01	3.34E-02
24	2.66	5	265.70	0.89	2.70	4.79E-05	7.30E-03	2.65	2.94E-02
25	2.74	5	238.90	0.87	2.80	4.87E-05	7.41E-03	2.73	3.03E-02
26	2.70	5	252.40	0.88	2.70	4.74E-05	7.22E-03	2.69	2.99E-02
27	2.74	5	180.10	0.83	2.80	4.64E-05	7.06E-03	2.73	3.03E-02
28	2.53	5	259.30	0.88	2.60	4.59E-05	6.99E-03	2.52	2.80E-02
29	2.88	5	215.90	0.85	2.90	4.95E-05	7.53E-03	2.87	3.19E-02
30	2.94	5	205.90	0.85	2.95	4.99E-05	7.60E-03	2.93	3.26E-02
EV-91	28.53	5	149.00	0.81	28.00	4.51E-04	-	-	-
						2.04E-03			

Table A.2.6 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	3.46	3.40	23.0	6.96E-05	6.96E-06	6.96E-03
2	15	3.96	3.90	24.2	7.36E-05	7.36E-06	7.36E-03
3	25	3.71	3.65	20.6	6.36E-05	6.36E-06	6.36E-03
4	35	2.86	2.90	21.9	4.77E-05	4.77E-06	4.77E-03
5	45	3.46	3.45	22.3	5.63E-05	5.63E-06	5.63E-03
6	55	3.76	3.70	22.9	6.10E-05	6.10E-06	6.10E-03
7	65	3.41	3.40	22.0	5.63E-05	5.63E-06	5.63E-03
8	75	2.89	2.90	23.1	4.84E-05	4.84E-06	4.84E-03
9	85	2.94	2.90	20.5	4.86E-05	4.86E-06	4.86E-03
10	95	3.07	3.05	23.1	5.04E-05	5.04E-06	5.04E-03
11	105	3.60	3.55	21.9	5.47E-05	5.47E-06	5.47E-03
12	115	3.62	3.55	20.8	5.61E-05	5.61E-06	5.61E-03
13	125	3.15	3.10	22.2	4.77E-05	4.77E-06	4.77E-03
14	135	2.74	2.75	23.3	4.78E-05	4.78E-06	4.78E-03
15	145	2.79	2.80	23.3	4.77E-05	4.77E-06	4.77E-03
16	155	2.75	2.80	24.0	4.88E-05	4.88E-06	4.88E-03
17	165	2.85	2.90	22.4	4.98E-05	4.98E-06	4.98E-03
18	175	3.21	3.20	22.9	5.24E-05	5.24E-06	5.24E-03
19	185	3.20	3.20	24.4	5.40E-05	5.40E-06	5.40E-03
20	195	3.06	3.10	23.9	5.08E-05	5.08E-06	5.08E-03
21	205	3.30	3.30	23.9	5.75E-05	5.75E-06	5.75E-03
22	215	3.07	3.05	25.1	5.27E-05	5.27E-06	5.27E-03
23	225	3.02	3.00	24.3	5.22E-05	5.22E-06	5.22E-03
24	235	2.66	2.70	26.2	4.79E-05	4.79E-06	4.79E-03
25	245	2.74	2.80	26.3	4.87E-05	4.87E-06	4.87E-03
26	255	2.70	2.70	25.5	4.74E-05	4.74E-06	4.74E-03
27	265	2.74	2.80	25.8	4.64E-05	4.64E-06	4.64E-03
28	275	2.53	2.60	26.8	4.59E-05	4.59E-06	4.59E-03
29	285	2.88	2.90	29.7	4.95E-05	4.95E-06	4.95E-03
30	295	2.94	2.95	30.3	4.99E-05	4.99E-06	4.99E-03
Wait&EV-91	-	-	28.0	-	-		
			121.00		1.58E-03		

Table A.2.6 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	6.96E-05	3.83E-02	1.39E-04	3.84E-02	3.84
2	7.36E-05	4.38E-02	1.47E-04	4.40E-02	4.40
3	6.36E-05	4.11E-02	1.27E-04	4.12E-02	4.12
4	4.77E-05	3.17E-02	9.54E-05	3.18E-02	3.18
5	5.63E-05	3.83E-02	1.13E-04	3.84E-02	3.84
6	6.10E-05	4.16E-02	1.22E-04	4.18E-02	4.18
7	5.63E-05	3.78E-02	1.13E-04	3.79E-02	3.79
8	4.84E-05	3.20E-02	9.67E-05	3.21E-02	3.21
9	4.86E-05	3.26E-02	9.71E-05	3.27E-02	3.27
10	5.04E-05	3.40E-02	1.01E-04	3.41E-02	3.41
11	5.47E-05	3.99E-02	1.09E-04	4.00E-02	4.00
12	5.61E-05	4.01E-02	1.12E-04	4.02E-02	4.02
13	4.77E-05	3.49E-02	9.55E-05	3.50E-02	3.50
14	4.78E-05	3.03E-02	9.57E-05	3.04E-02	3.04
15	4.77E-05	3.09E-02	9.54E-05	3.10E-02	3.10
16	4.88E-05	3.04E-02	9.77E-05	3.05E-02	3.05
17	4.98E-05	3.16E-02	9.97E-05	3.17E-02	3.17
18	5.24E-05	3.55E-02	1.05E-04	3.57E-02	3.57
19	5.40E-05	3.54E-02	1.08E-04	3.55E-02	3.55
20	5.08E-05	3.39E-02	1.02E-04	3.40E-02	3.40
21	5.75E-05	3.65E-02	1.15E-04	3.67E-02	3.67
22	5.27E-05	3.40E-02	1.05E-04	3.41E-02	3.41
23	5.22E-05	3.34E-02	1.04E-04	3.35E-02	3.35
24	4.79E-05	2.94E-02	9.59E-05	2.95E-02	2.95
25	4.87E-05	3.03E-02	9.73E-05	3.04E-02	3.04
26	4.74E-05	2.99E-02	9.49E-05	3.00E-02	3.00
27	4.64E-05	3.03E-02	9.27E-05	3.04E-02	3.04
28	4.59E-05	2.80E-02	9.19E-05	2.81E-02	2.81
29	4.95E-05	3.19E-02	9.89E-05	3.20E-02	3.20
30	4.99E-05	3.26E-02	9.98E-05	3.27E-02	3.27
					103.37
				Average DMC flow	3.45

A.2.7 : BG-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 325 'C

Table A.2.7 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 3 g.	1.6	0.3	1.1

Table A.2.7 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	3 g.
Final BG mass	N/A

Table A.2.7 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	2.86	5	5946.3	4.86	2.90	2.82E-04	4.29E-02	2.82	3.13E-02
2	3.44	5	4010.2	3.51	3.40	2.39E-04	3.63E-02	3.40	3.78E-02
3	3.29	5	2914.5	2.74	3.30	1.81E-04	2.75E-02	3.26	3.62E-02
4	3.36	5	2931.8	2.75	3.40	1.87E-04	2.85E-02	3.33	3.70E-02
5	3.03	5	2142.3	2.20	3.00	1.32E-04	2.01E-02	3.01	3.34E-02
6	2.81	5	1597.7	1.82	2.85	1.04E-04	1.58E-02	2.79	3.10E-02
7	3.01	5	1490.3	1.75	3.00	1.05E-04	1.59E-02	2.99	3.32E-02
8	4.39	5	1075.9	1.45	4.40	1.28E-04	1.95E-02	4.37	4.85E-02
9	3.55	5	1449.2	1.72	3.55	1.22E-04	1.85E-02	3.53	3.92E-02
10	3.31	5	1473.1	1.73	3.30	1.14E-04	1.74E-02	3.29	3.66E-02
11	2.50	5	2273.8	2.29	2.60	1.19E-04	1.82E-02	2.48	2.76E-02
12	2.62	5	2274.5	2.29	2.70	1.24E-04	1.89E-02	2.60	2.89E-02
13	3.13	5	2116.0	2.18	3.20	1.40E-04	2.13E-02	3.11	3.45E-02
14	3.01	5	2294.7	2.31	3.10	1.43E-04	2.18E-02	2.99	3.32E-02
15	2.65	5	2527.0	2.47	2.70	1.33E-04	2.03E-02	2.63	2.92E-02
16	2.95	5	1350.2	1.65	3.00	9.88E-05	1.50E-02	2.93	3.26E-02
17	2.62	5	1810.4	1.97	2.70	1.06E-04	1.62E-02	2.60	2.89E-02
18	2.39	5	1794.3	1.96	2.50	9.79E-05	1.49E-02	2.38	2.64E-02
19	2.75	5	1729.9	1.91	2.85	1.09E-04	1.66E-02	2.73	3.03E-02
20	3.15	5	1477.7	1.74	3.20	1.11E-04	1.69E-02	3.13	3.48E-02
21	2.64	5	1798.9	1.96	2.80	1.10E-04	1.67E-02	2.62	2.91E-02
22	2.31	5	1887.5	2.02	2.40	9.71E-05	1.48E-02	2.30	2.55E-02
23	2.81	5	1344.0	1.64	2.90	9.53E-05	1.45E-02	2.80	3.10E-02
24	3.22	5	1254.2	1.58	3.30	1.04E-04	1.59E-02	3.20	3.56E-02
25	2.80	5	1152.4	1.51	2.90	8.75E-05	1.33E-02	2.79	3.09E-02
26	2.26	5	1206.5	1.55	2.40	7.42E-05	1.13E-02	2.25	2.50E-02
27	2.00	5	1500.0	1.75	2.10	7.36E-05	1.12E-02	1.99	2.21E-02
28	2.04	5	1331.6	1.63	2.20	7.19E-05	1.09E-02	2.03	2.25E-02
29	2.16	5	1155.7	1.51	2.30	6.95E-05	1.06E-02	2.15	2.39E-02
30	2.32	5	1201.9	1.54	2.40	7.41E-05	1.13E-02	2.31	2.56E-02
EV-91	12.74	5	104.6	0.78	13.00	2.02E-04	-	-	-
						3.84E-03			

Table A.2.7 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	2.86	2.90	40.7	2.82E-04	2.82E-05	2.82E-02
2	15	3.44	3.40	39.5	2.39E-04	2.39E-05	2.39E-02
3	25	3.29	3.30	38.3	1.81E-04	1.81E-05	1.81E-02
4	35	3.36	3.40	38.6	1.87E-04	1.87E-05	1.87E-02
5	45	3.03	3.00	37.7	1.32E-04	1.32E-05	1.32E-02
6	55	2.81	2.85	40.0	1.04E-04	1.04E-05	1.04E-02
7	65	3.01	3.00	41.2	1.05E-04	1.05E-05	1.05E-02
8	75	4.39	4.40	45.3	1.28E-04	1.28E-05	1.28E-02
9	85	3.55	3.55	46.7	1.22E-04	1.22E-05	1.22E-02
10	95	3.31	3.30	46.7	1.14E-04	1.14E-05	1.14E-02
11	105	2.50	2.60	49.6	1.19E-04	1.19E-05	1.19E-02
12	115	2.62	2.70	51.5	1.24E-04	1.24E-05	1.24E-02
13	125	3.13	3.20	57.1	1.40E-04	1.40E-05	1.40E-02
14	135	3.01	3.10	58.3	1.43E-04	1.43E-05	1.43E-02
15	145	2.65	2.70	58.8	1.33E-04	1.33E-05	1.33E-02
16	155	2.95	3.00	59.7	9.88E-05	9.88E-06	9.88E-03
17	165	2.62	2.70	62.2	1.06E-04	1.06E-05	1.06E-02
18	175	2.39	2.50	60.9	9.79E-05	9.79E-06	9.79E-03
19	185	2.75	2.85	62.5	1.09E-04	1.09E-05	1.09E-02
20	195	3.15	3.20	63.5	1.11E-04	1.11E-05	1.11E-02
21	205	2.64	2.80	64.5	1.10E-04	1.10E-05	1.10E-02
22	215	2.31	2.40	62.8	9.71E-05	9.71E-06	9.71E-03
23	225	2.81	2.90	66.7	9.53E-05	9.53E-06	9.53E-03
24	235	3.22	3.30	67.0	1.04E-04	1.04E-05	1.04E-02
25	245	2.80	2.90	64.9	8.75E-05	8.75E-06	8.75E-03
26	255	2.26	2.40	63.2	7.42E-05	7.42E-06	7.42E-03
27	265	2.00	2.10	63.2	7.36E-05	7.36E-06	7.36E-03
28	275	2.04	2.20	63.5	7.19E-05	7.19E-06	7.19E-03
29	285	2.16	2.30	61.9	6.95E-05	6.95E-06	6.95E-03
30	295	2.32	2.40	69.8	7.41E-05	7.41E-06	7.41E-03
EV-91	-	-	20.45	-	-		
			107.80		3.63E-03		

Table A.2.7 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	2.82E-04	3.13E-02	5.64E-04	3.18E-02	3.18
2	2.39E-04	3.78E-02	4.77E-04	3.83E-02	3.83
3	1.81E-04	3.62E-02	3.62E-04	3.66E-02	3.66
4	1.87E-04	3.70E-02	3.75E-04	3.74E-02	3.74
5	1.32E-04	3.34E-02	2.64E-04	3.37E-02	3.37
6	1.04E-04	3.10E-02	2.08E-04	3.12E-02	3.12
7	1.05E-04	3.32E-02	2.09E-04	3.34E-02	3.34
8	1.28E-04	4.85E-02	2.56E-04	4.88E-02	4.88
9	1.22E-04	3.92E-02	2.44E-04	3.94E-02	3.94
10	1.14E-04	3.66E-02	2.29E-04	3.68E-02	3.68
11	1.19E-04	2.76E-02	2.39E-04	2.78E-02	2.78
12	1.24E-04	2.89E-02	2.48E-04	2.91E-02	2.91
13	1.40E-04	3.45E-02	2.79E-04	3.48E-02	3.48
14	1.43E-04	3.32E-02	2.86E-04	3.35E-02	3.35
15	1.33E-04	2.92E-02	2.67E-04	2.95E-02	2.95
16	9.88E-05	3.26E-02	1.98E-04	3.28E-02	3.28
17	1.06E-04	2.89E-02	2.13E-04	2.91E-02	2.91
18	9.79E-05	2.64E-02	1.96E-04	2.66E-02	2.66
19	1.09E-04	3.03E-02	2.18E-04	3.06E-02	3.06
20	1.11E-04	3.48E-02	2.22E-04	3.50E-02	3.50
21	1.10E-04	2.91E-02	2.20E-04	2.93E-02	2.93
22	9.71E-05	2.55E-02	1.94E-04	2.57E-02	2.57
23	9.53E-05	3.10E-02	1.91E-04	3.12E-02	3.12
24	1.04E-04	3.56E-02	2.09E-04	3.58E-02	3.58
25	8.75E-05	3.09E-02	1.75E-04	3.11E-02	3.11
26	7.42E-05	2.50E-02	1.48E-04	2.51E-02	2.51
27	7.36E-05	2.21E-02	1.47E-04	2.22E-02	2.22
28	7.19E-05	2.25E-02	1.44E-04	2.27E-02	2.27
29	6.95E-05	2.39E-02	1.39E-04	2.40E-02	2.40
30	7.41E-05	2.56E-02	1.48E-04	2.58E-02	2.58
					94.90
				Average DMC flow	3.16

A.2.8 : BG-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 300 'C

Table A.2.8 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 10 g.	5.3	1.1	3.7

Table A.2.8 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	10 g.
Final BG mass	9.11 g.

Table A.2.8 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	2.87	5	9940	7.66	2.90	4.44E-04	6.76E-02	2.80	3.11E-02
2	4.80	5	8232	6.46	4.70	6.08E-04	9.25E-02	4.71	5.23E-02
3	5.60	5	6501	5.25	5.40	5.67E-04	8.64E-02	5.51	6.12E-02
4	4.75	5	5224	4.36	4.70	4.10E-04	6.24E-02	4.69	5.20E-02
5	4.20	5	5250	4.38	4.15	3.63E-04	5.53E-02	4.14	4.60E-02
6	3.96	5	5370	4.46	3.90	3.48E-04	5.30E-02	3.91	4.34E-02
7	4.03	5	5012	4.21	4.00	3.37E-04	5.13E-02	3.98	4.42E-02
8	4.14	5	4277	3.70	4.10	3.03E-04	4.61E-02	4.09	4.54E-02
9	4.34	5	3214	2.95	4.25	2.51E-04	3.82E-02	4.30	4.78E-02
10	4.22	5	3008	2.81	4.20	2.36E-04	3.59E-02	4.18	4.64E-02
11	4.20	5	3348	3.05	4.15	2.53E-04	3.85E-02	4.16	4.62E-02
12	3.63	5	2869	2.71	3.60	1.95E-04	2.97E-02	3.60	4.00E-02
13	3.38	5	2881	2.72	3.40	1.85E-04	2.81E-02	3.35	3.72E-02
14	3.58	5	2408	2.39	3.60	1.72E-04	2.62E-02	3.55	3.95E-02
15	3.62	5	2253	2.28	3.60	1.64E-04	2.50E-02	3.60	3.99E-02
16	3.64	5	2182	2.23	3.60	1.61E-04	2.44E-02	3.62	4.01E-02
17	4.03	5	758	1.23	4.00	9.86E-05	1.50E-02	4.01	4.46E-02
18	3.60	5	1049	1.44	3.60	1.03E-04	1.57E-02	3.58	3.98E-02
19	3.16	5	1044	1.43	3.20	9.17E-05	1.40E-02	3.15	3.49E-02
20	3.16	5	1542	1.78	3.20	1.14E-04	1.74E-02	3.14	3.49E-02
21	3.91	5	1015	1.41	3.90	1.10E-04	1.68E-02	3.89	4.32E-02
22	3.66	5	1292	1.61	3.60	1.16E-04	1.76E-02	3.64	4.04E-02
23	3.40	5	1386	1.67	3.40	1.14E-04	1.73E-02	3.38	3.76E-02
24	3.39	5	1222	1.56	3.40	1.06E-04	1.61E-02	3.37	3.75E-02
25	3.15	5	1268	1.59	3.15	1.00E-04	1.52E-02	3.13	3.48E-02
26	2.81	5	1426	1.70	2.85	9.69E-05	1.47E-02	2.80	3.10E-02
27	2.72	5	1373	1.66	2.80	9.31E-05	1.42E-02	2.71	3.00E-02
28	2.76	5	1480	1.74	2.80	9.73E-05	1.48E-02	2.75	3.05E-02
29	3.31	5	1462	1.72	3.30	1.14E-04	1.73E-02	3.29	3.66E-02
30	3.54	5	1212	1.55	3.50	1.09E-04	1.65E-02	3.52	3.91E-02

6.459E-03

Table A.2.8 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	2.87	2.90	43.3	4.44E-04	4.44E-05	4.44E-02
2	15	4.80	4.70	44.0	6.08E-04	6.08E-05	6.08E-02
3	25	5.60	5.40	43.5	5.67E-04	5.67E-05	5.67E-02
4	35	4.75	4.70	39.6	4.10E-04	4.10E-05	4.10E-02
5	45	4.20	4.15	38.8	3.63E-04	3.63E-05	3.63E-02
6	55	3.96	3.90	38.2	3.48E-04	3.48E-05	3.48E-02
7	65	4.03	4.00	37.9	3.37E-04	3.37E-05	3.37E-02
8	75	4.14	4.10	37.5	3.03E-04	3.03E-05	3.03E-02
9	85	4.34	4.25	37.6	2.51E-04	2.51E-05	2.51E-02
10	95	4.22	4.20	37.3	2.36E-04	2.36E-05	2.36E-02
11	105	4.20	4.15	37.6	2.53E-04	2.53E-05	2.53E-02
12	115	3.63	3.60	36.1	1.95E-04	1.95E-05	1.95E-02
13	125	3.38	3.40	37.5	1.85E-04	1.85E-05	1.85E-02
14	135	3.58	3.60	37.3	1.72E-04	1.72E-05	1.72E-02
15	145	3.62	3.60	36.9	1.64E-04	1.64E-05	1.64E-02
16	155	3.64	3.60	38.1	1.61E-04	1.61E-05	1.61E-02
17	165	4.03	4.00	38.6	9.86E-05	9.86E-06	9.86E-03
18	175	3.60	3.60	37.7	1.03E-04	1.03E-05	1.03E-02
19	185	3.16	3.20	38.0	9.17E-05	9.17E-06	9.17E-03
20	195	3.16	3.20	38.8	1.14E-04	1.14E-05	1.14E-02
21	205	3.91	3.90	39.0	1.10E-04	1.10E-05	1.10E-02
22	215	3.66	3.60	37.2	1.16E-04	1.16E-05	1.16E-02
23	225	3.40	3.40	38.5	1.14E-04	1.14E-05	1.14E-02
24	235	3.39	3.40	40.1	1.06E-04	1.06E-05	1.06E-02
25	245	3.15	3.15	39.9	1.00E-04	1.00E-05	1.00E-02
26	255	2.81	2.85	41.1	9.69E-05	9.69E-06	9.69E-03
27	265	2.72	2.80	41.1	9.31E-05	9.31E-06	9.31E-03
28	275	2.76	2.80	42.6	9.73E-05	9.73E-06	9.73E-03
29	285	3.31	3.30	43.3	1.14E-04	1.14E-05	1.14E-02
30	295	3.54	3.50	43.6	1.09E-04	1.09E-05	1.09E-02
Waiting	-	-	20.20	-	-		
			131.15		6.46E-03		

Table A.2.8 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	4.44E-04	3.11E-02	8.89E-04	3.20E-02	3.20
2	6.08E-04	5.23E-02	1.22E-03	5.35E-02	5.35
3	5.67E-04	6.12E-02	1.13E-03	6.23E-02	6.23
4	4.10E-04	5.20E-02	8.19E-04	5.29E-02	5.29
5	3.63E-04	4.60E-02	7.27E-04	4.67E-02	4.67
6	3.48E-04	4.34E-02	6.96E-04	4.41E-02	4.41
7	3.37E-04	4.42E-02	6.74E-04	4.48E-02	4.48
8	3.03E-04	4.54E-02	6.06E-04	4.61E-02	4.61
9	2.51E-04	4.78E-02	5.02E-04	4.83E-02	4.83
10	2.36E-04	4.64E-02	4.72E-04	4.69E-02	4.69
11	2.53E-04	4.62E-02	5.05E-04	4.67E-02	4.67
12	1.95E-04	4.00E-02	3.90E-04	4.04E-02	4.04
13	1.85E-04	3.72E-02	3.70E-04	3.76E-02	3.76
14	1.72E-04	3.95E-02	3.44E-04	3.98E-02	3.98
15	1.64E-04	3.99E-02	3.28E-04	4.02E-02	4.02
16	1.61E-04	4.01E-02	3.21E-04	4.05E-02	4.05
17	9.86E-05	4.46E-02	1.97E-04	4.48E-02	4.48
18	1.03E-04	3.98E-02	2.07E-04	4.00E-02	4.00
19	9.17E-05	3.49E-02	1.83E-04	3.51E-02	3.51
20	1.14E-04	3.49E-02	2.28E-04	3.51E-02	3.51
21	1.10E-04	4.32E-02	2.20E-04	4.34E-02	4.34
22	1.16E-04	4.04E-02	2.31E-04	4.07E-02	4.07
23	1.14E-04	3.76E-02	2.27E-04	3.78E-02	3.78
24	1.06E-04	3.75E-02	2.12E-04	3.77E-02	3.77
25	1.00E-04	3.48E-02	2.00E-04	3.50E-02	3.50
26	9.69E-05	3.10E-02	1.94E-04	3.12E-02	3.12
27	9.31E-05	3.00E-02	1.86E-04	3.02E-02	3.02
28	9.73E-05	3.05E-02	1.95E-04	3.07E-02	3.07
29	1.14E-04	3.66E-02	2.28E-04	3.68E-02	3.68
30	1.09E-04	3.91E-02	2.17E-04	3.93E-02	3.93
					124.05
				Average DMC flow	4.13

A.2.9 : BG-DMC reaction in a presence of KOH (5 wt%) as a catalyst at 300 'C

Table A.2.9 : BG Composition

	Si	SiO2	SiC
Composition (wt%)	52.52	10.91	36.56
Component of BG 6 g.	3.2	0.7	2.2

Table A.2.9 : Operating Conditions (Continue)

Pretreatment	400 'C for 3 hr. in N2
Bath temperature	93 'C
He flow rate	26 ml/min
Initial BG mass	6 g.
Final BG mass	5.65 g.

Table A.2.9 : Experimental results (Continue)

Cond. Liq. No.	Mass (g)	Vol of Inj. (uL)	GC Area	Moles *10^-7	Cond. Liq. vol. (ml)	Total TMOS per 10 min. (mole)	Mass TMOS per 10 min. (g)	Mass DMC unreacted (g)	Mole DMC unreacted (mole)
1	4.31	5	4803.00	4.06	4.20	3.41E-04	5.20E-02	4.26	4.73E-02
2	4.87	5	2794.43	2.66	4.80	2.55E-04	3.88E-02	4.83	5.36E-02
3	3.81	5	2815.10	2.67	3.75	2.00E-04	3.05E-02	3.78	4.20E-02
4	3.49	5	2580.40	2.51	3.50	1.76E-04	2.67E-02	3.46	3.84E-02
5	3.58	5	1818.40	1.97	3.50	1.38E-04	2.10E-02	3.56	3.95E-02
6	3.00	5	1939.50	2.06	3.00	1.24E-04	1.88E-02	2.98	3.31E-02
7	2.91	5	1921.64	2.05	2.90	1.19E-04	1.81E-02	2.89	3.21E-02
8	4.06	5	1051.76	1.44	4.00	1.15E-04	1.75E-02	4.04	4.49E-02
9	4.15	5	960.30	1.37	4.10	1.13E-04	1.72E-02	4.13	4.59E-02
10	3.79	5	964.60	1.38	3.70	1.02E-04	1.55E-02	3.77	4.19E-02
11	2.75	5	1130.90	1.49	2.80	8.36E-05	1.27E-02	2.74	3.04E-02
12	2.56	5	1013.45	1.41	2.60	7.34E-05	1.12E-02	2.55	2.83E-02
13	3.98	5	777.24	1.25	3.90	9.72E-05	1.48E-02	3.97	4.40E-02
14	3.72	5	664.50	1.17	3.70	8.64E-05	1.31E-02	3.71	4.12E-02
15	3.27	5	866.60	1.31	3.30	8.64E-05	1.31E-02	3.26	3.62E-02
16	3.20	5	497.50	1.05	3.20	6.72E-05	1.02E-02	3.19	3.54E-02
17	3.06	5	791.70	1.26	3.10	7.79E-05	1.19E-02	3.05	3.38E-02
18	2.94	5	514.80	1.06	3.00	6.37E-05	9.70E-03	2.93	3.25E-02
19	3.48	5	500.90	1.05	3.45	7.26E-05	1.11E-02	3.47	3.85E-02
20	3.80	5	537.30	1.08	3.80	8.19E-05	1.25E-02	3.79	4.20E-02
21	3.28	5	558.30	1.09	3.30	7.21E-05	1.10E-02	3.27	3.63E-02
22	2.74	5	498.22	1.05	2.80	5.88E-05	8.96E-03	2.73	3.03E-02
23	2.52	5	573.60	1.10	2.55	5.63E-05	8.57E-03	2.51	2.79E-02
24	2.36	5	417.68	0.99	2.40	4.77E-05	7.26E-03	2.35	2.61E-02
25	2.91	5	396.54	0.98	3.00	5.88E-05	8.94E-03	2.90	3.22E-02
26	4.05	5	363.70	0.96	4.00	7.65E-05	1.16E-02	4.04	4.48E-02
27	2.89	5	632.90	1.14	2.90	6.64E-05	1.01E-02	2.88	3.20E-02
28	2.11	5	636.93	1.15	2.20	5.05E-05	7.69E-03	2.10	2.33E-02
29	2.83	5	752.65	1.23	2.90	7.13E-05	1.08E-02	2.82	3.13E-02
30	3.56	5	532.70	1.07	3.50	7.52E-05	1.15E-02	3.55	3.94E-02
EV-91	10.85	5	233.70	0.87	11.00	1.90E-04	-	-	-

3.297E-03

Table A.2.9 : Experimental results (Continue)

Tube No.	Avg. time (min)	Mass (g)	Collecting Vol. (ml)	Gas film flow (ml/min)	Total TMOS in periods	Avg. Rate of TMOS formation (mole/ min)	Rate (mmol/min)
1	5	4.31	4.20	35.7	3.41E-04	3.41E-05	3.41E-02
2	15	4.87	4.80	33.8	2.55E-04	2.55E-05	2.55E-02
3	25	3.81	3.75	32.7	2.00E-04	2.00E-05	2.00E-02
4	35	3.49	3.50	33.8	1.76E-04	1.76E-05	1.76E-02
5	45	3.58	3.50	33.5	1.38E-04	1.38E-05	1.38E-02
6	55	3.00	3.00	32.3	1.24E-04	1.24E-05	1.24E-02
7	65	2.91	2.90	33.2	1.19E-04	1.19E-05	1.19E-02
8	75	4.06	4.00	32.6	1.15E-04	1.15E-05	1.15E-02
9	85	4.15	4.10	31.8	1.13E-04	1.13E-05	1.13E-02
10	95	3.79	3.70	32.4	1.02E-04	1.02E-05	1.02E-02
11	105	2.75	2.80	33.1	8.36E-05	8.36E-06	8.36E-03
12	115	2.56	2.60	34.9	7.34E-05	7.34E-06	7.34E-03
13	125	3.98	3.90	32.9	9.72E-05	9.72E-06	9.72E-03
14	135	3.72	3.70	31.6	8.64E-05	8.64E-06	8.64E-03
15	145	3.27	3.30	31.3	8.64E-05	8.64E-06	8.64E-03
16	155	3.20	3.20	34.1	6.72E-05	6.72E-06	6.72E-03
17	165	3.06	3.10	33.1	7.79E-05	7.79E-06	7.79E-03
18	175	2.94	3.00	33.5	6.37E-05	6.37E-06	6.37E-03
19	185	3.48	3.45	35.6	7.26E-05	7.26E-06	7.26E-03
20	195	3.80	3.80	32.8	8.19E-05	8.19E-06	8.19E-03
21	205	3.28	3.30	32.8	7.21E-05	7.21E-06	7.21E-03
22	215	2.74	2.80	33.5	5.88E-05	5.88E-06	5.88E-03
23	225	2.52	2.55	34.9	5.63E-05	5.63E-06	5.63E-03
24	235	2.36	2.40	32.7	4.77E-05	4.77E-06	4.77E-03
25	245	2.91	3.00	32.7	5.88E-05	5.88E-06	5.88E-03
26	255	4.05	4.00	36.9	7.65E-05	7.65E-06	7.65E-03
27	265	2.89	2.90	30.6	6.64E-05	6.64E-06	6.64E-03
28	275	2.11	2.20	29.8	5.05E-05	5.05E-06	5.05E-03
29	285	2.83	2.90	38.9	7.13E-05	7.13E-06	7.13E-03
30	295	3.56	3.50	32.9	7.52E-05	7.52E-06	7.52E-03
EV-91	-	-	27.45	31.0	-		
			127.30		3.11E-03		

Table A.2.9 : Experimental results (Continue)

Tube	Mole of TMOS (mol in 10 min)	Unreacted DMC (mol in 10 min)	Mole DMC reacted (mol in 10 min.)	Total DMC flow (mol in 10 min)	Total DMC flow (mmol/min)
1	3.41E-04	4.73E-02	6.83E-04	4.80E-02	4.80
2	2.55E-04	5.36E-02	5.10E-04	5.41E-02	5.41
3	2.00E-04	4.20E-02	4.01E-04	4.24E-02	4.24
4	1.76E-04	3.84E-02	3.51E-04	3.88E-02	3.88
5	1.38E-04	3.95E-02	2.76E-04	3.98E-02	3.98
6	1.24E-04	3.31E-02	2.47E-04	3.33E-02	3.33
7	1.19E-04	3.21E-02	2.37E-04	3.23E-02	3.23
8	1.15E-04	4.49E-02	2.30E-04	4.51E-02	4.51
9	1.13E-04	4.59E-02	2.25E-04	4.61E-02	4.61
10	1.02E-04	4.19E-02	2.04E-04	4.21E-02	4.21
11	8.36E-05	3.04E-02	1.67E-04	3.06E-02	3.06
12	7.34E-05	2.83E-02	1.47E-04	2.84E-02	2.84
13	9.72E-05	4.40E-02	1.94E-04	4.42E-02	4.42
14	8.64E-05	4.12E-02	1.73E-04	4.13E-02	4.13
15	8.64E-05	3.62E-02	1.73E-04	3.63E-02	3.63
16	6.72E-05	3.54E-02	1.34E-04	3.55E-02	3.55
17	7.79E-05	3.38E-02	1.56E-04	3.40E-02	3.40
18	6.37E-05	3.25E-02	1.27E-04	3.27E-02	3.27
19	7.26E-05	3.85E-02	1.45E-04	3.87E-02	3.87
20	8.19E-05	4.20E-02	1.64E-04	4.22E-02	4.22
21	7.21E-05	3.63E-02	1.44E-04	3.64E-02	3.64
22	5.88E-05	3.03E-02	1.18E-04	3.04E-02	3.04
23	5.63E-05	2.79E-02	1.13E-04	2.80E-02	2.80
24	4.77E-05	2.61E-02	9.54E-05	2.62E-02	2.62
25	5.88E-05	3.22E-02	1.18E-04	3.23E-02	3.23
26	7.65E-05	4.48E-02	1.53E-04	4.50E-02	4.50
27	6.64E-05	3.20E-02	1.33E-04	3.21E-02	3.21
28	5.05E-05	2.33E-02	1.01E-04	2.34E-02	2.34
29	7.13E-05	3.13E-02	1.43E-04	3.14E-02	3.14
30	7.52E-05	3.94E-02	1.50E-04	3.95E-02	3.95
					111.09
				Average DMC flow	3.70

Appendix 3

Data Analysis Procedures

The Calculations of the Mass Transfer Limitation

For DMC gas which is a polar gas and has the hydrogen-bonding, $T_r < 2.0$:

$$\mu\xi = (0.775T_r - 0.055)Z_c^{-5/4} \qquad (A.3.1)^{(36)}$$

where $\quad\xi\quad =\quad$ gas-viscosity parameter

$$= \quad T_c^{1/6}M^{-1/2}P_c^{-2/3} \qquad (A.3.2)^{(36)}$$

$M\quad =\quad$ molecular weight of DMC (g.mol)

$T_c\quad =\quad$ critical temperature (°K)

$P_c\quad =\quad$ critical pressure (atm)

$Z_c\quad =\quad$ critical compressibility factor

$T_r\quad =\quad$ reduced temperature

The critical compressibility factor Z_c is obtained from T_c, P_c, and V_c as follows:

$$Z_c = P_cV_c/RT_c \qquad (A.3.3)^{(36)}$$

where $\quad V_c\quad =\quad$ critical volume (cm³/mol)

$R\quad =\quad$ gas constant (cm³ atm/mol °K)

From equation A.3.3, the critical variables of organic compounds are best estimated from Lydersen's correlation by using Lydersen's group contributions of critical-property increments. Thus

$$Tc = \frac{T_b}{0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2} \qquad (A.3.4)^{(36)}$$

where $\quad\Delta_T\quad =\quad$ Lydersen's critical-temperature increment

$$T_b \quad = \quad \text{normal boiling point of DMC (°K)}$$

From Table 3-330[36], T_c can be calculated as

$$Tc \quad = \quad \frac{363}{0.567 + 0.101 - (0.101)^2} \qquad (A.3.5)^{(36)}$$

So $\qquad T_c \quad = \quad 551.84 \text{ °K}$

For the critical volume of DMC:

$$V_c \quad = \quad 33.04 + (\sum_i M_i \times \Delta V_i)^{1.029} \qquad (A.3.6)^{(36)}$$

where $\qquad \Delta Vi \quad = \quad$ volume contribution of group i

From Table 3-330[36], V_c can be calculated as

$$= \quad 33.04 + [(2 \times 15 \times 2.888) + (2 \times 16 \times 0.79) + (28 \times 1.5)]^{1.029}$$

So $\qquad V_c \quad = \quad 211.2 \text{ cm}^3/\text{mol}$

For the critical pressure of DMC:

$$P_c \quad = \quad \frac{M}{(0.34 + \Sigma \Delta_p)^2} \qquad (A.3.7)^{(36)}$$

where $\qquad \Delta_p \quad = \quad$ pressure contribution of group i

From Table 3-330[36], P_c can be calculated as

$$= \quad \frac{90}{[0.34 + (2 \times 0.227) + (2 \times 0.12) + 0.2]^2}$$

So $\qquad P_c \quad = \quad 59.1 \text{ atm}$

Therefore, the critical compressibility factor Z_c can be calculated by inserting the values of T_c, V_c, and P_c into equation A.3.3.

$$= \frac{(59.1 \text{ atm}) \times (211.2 \text{ cm}^3/\text{mol})}{(551.84 \text{ }^\circ\text{K}) \times (82.06 \text{ cm}^3 \text{ atm/mol } ^\circ\text{K})}$$

So Z_c = 0.276

From equation A.3.2, gas-viscosity parameter ξ can be calculated as follows:

$$= (551.84)^{1/6} \times (90)^{-1/2} \times (59.1)^{-2/3}$$

So ξ = 0.02

In addition, the reduced temperature T_r is given by

$$T_r = T / T_c \qquad (A.3.8)^{(36)}$$

$$= 363 / 551.84$$

So T_r = 0.66

In order to obtain gas viscosity μ, the values of ξ, T_r, and Z_c are inserted into equation A.3.1:

$$(0.02) \times \mu = [(0.755 \times 0.66) - 0.055] \times (0.276)^{-5/4}$$

$$= 110.8 \text{ } \mu\text{P}$$

Since 1 cP $= 10^{-3} \text{ N.s/m}^2$

Thus $\mu = 1.1 \times 10^{-5} \text{ N.s/m}^2 \text{ (Pa.s)}$

The diffusion coefficient for a binary mixture of gases DMC and He may be estimated from the Fuller, Schettler, and Giddings relation as:

$$D_{DMC-He} = \frac{10^{-3} T^{1.75} [(M_{DMC} + M_{He}) / M_{DMC} \times M_{He}]^{1/2}}{P \times [(\Sigma v)^{1/3}_{DMC} + (\Sigma v)^{1/3}_{He}]^2} \qquad (A.3.9)^{(36)}$$

where M_{DMC} = molecular weight of dimethyl carbonate

$$M_{He} \quad = \quad \text{molecular weight of helium}$$

$$v \quad = \quad \text{atomic diffusion volume}$$

$$P \quad = \quad \text{pressure (atm)}$$

At the reaction temperature and atmospheric pressure, D_{DMC-He} can be estimated as followed:

$$= \quad \frac{10^{-3} \times 573^{1.75} \times [(90+2)/(90 \times 2)]^{1/2}}{1 \times [\{(16.5 \times 3)+(5.48 \times 3)+(1.98 \times 6)\}^{1/3} + \{2.88\}^{1/3}]^2}$$

$$= \quad 1.48 \quad cm^2/s$$

In the packed bed reactor, the relationship between the superficial and the average gas velocity can be written as

$$u_\infty \quad = \quad u \times \varepsilon \qquad\qquad (A.3.10)^{(38)}$$

where

$$u_\infty \quad = \quad \text{superficial gas velocity (m/s)}$$

$$u \quad = \quad \text{average gas velocity (m/s)}$$

$$\varepsilon \quad = \quad \text{void fraction in the packed bed}$$

The superficial gas velocity, u_∞, the volumetric flow rate of gases divided by the cross-sectional area of empty reactor tube at 300 °C as

$$u_\infty \quad = \quad \frac{\text{total volumetric flow rate of gases (cm}^3/\text{s)}}{\text{cross-sectional area of empty reactor (cm}^2)}$$

Cross-sectional area of empty reactor tube is 1.27 cm^2

Based on the experimental results of 3-g BG-DMC reaction at 300 °C, the superficial gas velocity can be estimated as:

$$= \quad \frac{(273.4 \ cm^2/min)}{(1.27 \ cm^2)}$$

$$= \quad 3.6 \times 10^{-2} \, m/s$$

The gas density (DMC), ρ, can be calculated, based on the ideal gas assumption at 300 °C and 101.3 KP, as follows:

$$PV \quad = \quad RT \qquad\qquad (A.3.11)^{(36)}$$

where $\quad V \quad = \quad$ vapor density (m^3/mol)

Appling the molecular weight of DMC = 90.08 g/mol, the vapor density of DMC is obtained.

Also, The apparent particle density can be estimated by

$$\rho_P \quad = \quad \rho \times \varepsilon_v \qquad\qquad (A.3.12)^{(34)}$$

where $\quad \rho_P \quad = \quad$ apparent particle density (kg/m^3)

$\quad\rho \quad = \quad$ silicon-fine density (kg/m^3)

$\quad\varepsilon_v \quad = \quad$ volume fraction of particle

Analytical Composition of Silicon fines

Analytical composition of 3 g BG: 53 % wt Si, 11 % wt SiO_2

$$\text{Mass of Si} \quad = \quad \frac{53}{100} \times 3 \quad = \quad 1.59 \, g.$$

$$\text{Mole of Si} \quad = \quad \frac{\text{Mass of Si}}{\text{MW. Si}} \quad = \quad \frac{1.59}{28} \quad = \quad 5.7 \times 10^{-2}$$

$$\text{Mass of SiO}_2 \;=\; \frac{11}{100} \times 3 \;=\; 0.33 \text{ g.}$$

$$\text{Mole of SiO}_2 \;=\; \frac{\text{Mass of SiO}_2}{\text{MW. SiO}_2} \;=\; \frac{0.33}{60} \;=\; 5.5 \times 10^{-3}$$

$$\text{Total mole of Si and SiO}_2 \;=\; 5.7 \times 10^{-2} + 5.5 \times 10^{-3}$$

$$= 6.25 \times 10^{-2}$$