Carbo-Chlorination of Silica: Thermodynamic Simulation and Experimental Study

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Carbo-chlorination of silica represents an interesting route to prepare $SiCl_4$, which is an important precursor used in the chemical industry and microelectronic industry. Chlorination of several silica-containing materials in the presence of carbon was studied at atmospheric pressure in an isothermal reactor at laboratory scale, with continuous and stable gas flow. The influencing factors such as temperature, C/SiO_2 mole ratio and binder content in the mixture were studied. The experimental results showed that diatomite is the optimal material for carbo-chlorination to prepare $SiCl_4$. The conversion ratio of silicon dioxide increases with C/SiO_2 mole ratio, decreases with binder content increased in the mixture. $SiO_2 + 2Cl_2 + 2C = SiCl_4 + 2CO$ to be the dominant reaction above 800 °C according to the thermodynamic calculation. Based on the results, a probable procedures of the carbo-chlorination is proposed.

Keywords: Carbo-chlorination, Silica, Silicon tetrachloride.

INTRODUCTION

Silicon tetrachloride ($SiCl_4$) is an important inorganic compound used as silicon source materials for the production of organo silicates, silicon esters, organo silicon halides, silicone polymers[1-3], *etc*. Meanwhile, $SiCl_4$ is one of the most important precursors for the manufacturing of silica nano-particle[4,5], spherical silica particle[6], fumed silica[7], poly-silicon[8] which includes metallurgical-grade silicon, solar-grade silicon[9], electronic-grade silicon and optical fiber[10].

Several routes for silicon tetrachloride production have been reported in literatures, such as (i) preparing $SiCl_4$ by reaction of silicon with chlorine and under irradiation with ultra-violet light[11] and (ii) producing $SiCl_4$ by reaction of silicon carbide with hydrogen chloride[12]. Iwei *et al.*[13] conducted a process to produce silicon tetrachloride by the reaction between a silicon dioxide containing substance and boron trichloride. The generated di-boron trioxide was reduced and chlorinated to boron trichloride. Rice husk (a by-product of rice processing constituted mainly of silica and carbon) have also been used to prepare silicon compounds[14-16]. In the industry, $SiCl_4$ is produced as a by-product along with other chlorides[17], specially the poly-crystalline silicon through the chemical vapor deposition process[18], also, almost 50 % silicide in electric arc furnace slag bearing high titania converted into $SiCl_4$ by chlorination process, the generated $SiCl_4$ can be separated from $TiCl_4$ by fractional distillation after condensed, or $SiCl_4$ was produced by the direct chlorination of ferrosilicon or SiO_2/C mixture with chlorine[19].

This article describes a chlorination way to prepare $SiCl_4$ using different silicas. In the process, the solid silicon dioxide reacts with chlorine in the presence of C to form chlorides. The generated products in gaseous phase are carried away by the chlorine gas stream and cooled outside the reactor, then $SiCl_4$ can be further processed after distillation. Based on the thermodynamic simulation, some experiments were conducted to judge which material is the optimal one for carbo-chlorination. After the optimal material determined, the influence of parameters, such as temperature, C/SiO_2 ratio, binder content in the mixture was studied.

EXPERIMENTAL

Thermodynamic simulation: The main chlorination reactions of SiO_2 in the presence of Cl_2 and Cl_2 with C/CO as reductant are given by eqn. 1 to 4. The standard free energy changes of these reactions are given in Fig. 1. All of the thermo-dynamic data mentioned in this article were obtained from Factsage 6.2. From Fig.1 it can be deduced that the chlorination of SiO_2 in the presence of C/CO (according to reaction [1]-[3]) is thermodynamically feasible in random cases while reaction [4] is not thermodynamically favorable in the investigated temperature range at standard atmosphere. As the vertical dotted line shows, reaction 1 has greater negative free energy values than reaction 2 and 3 at temperature above 700 °C. This thermo-dynamic calculation proves that CO and $SiCl_4$ are expected to be the main gas phases when the temperature exceeds 700 °C when sufficient carbon is used as the reducing agent.
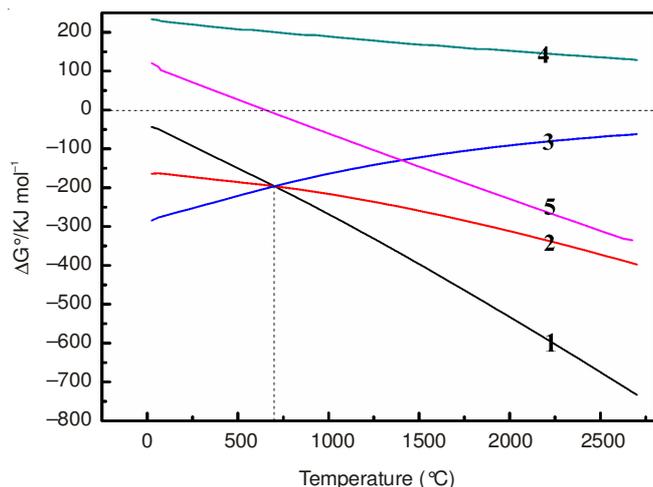
Fig. 1. Standard free energy change with different temperature of several reactions

$$SiO_2 (s) + 2Cl_2 (g) + 2C (s) \rightarrow SiCl_4 (g) + 2CO (g) \quad [1]$$
$$SiO_2 (s) + 2Cl_2 (g) + C (s) \rightarrow SiCl_4 (g) + CO_2 (g) \quad [2]$$
$$SiO_2 (s) + 2Cl_2 (g) + 2CO (s) \rightarrow SiCl_4 (g) + 2CO_2 (g) \quad [3]$$
$$SiO_2 (s) + 2Cl_2 (g) \rightarrow SiCl_4 (g) + O_2 (g) \quad [4]$$
$$C (s) + CO_2 (g) \rightarrow 2CO (g) \quad [5]$$
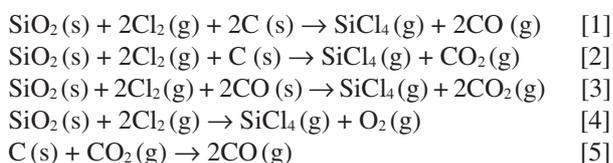
As for the reductants, other possible reactions in the reaction systems are insignificant, especially in the temperature range of 800-1000 °C.

$$CO (g) + Cl_2 (g) \rightarrow COCl_2(g) \quad [6]$$
$$C (g) + 2Cl_2 (g) \rightarrow CCl_4(g) \quad [7]$$
$$Cl_2 (g) \rightarrow 2Cl \quad [8]$$

Based on the above discussion, thermodynamic simulations of $SiO_2/Cl_2/CO$ and $SiO_2/Cl_2/C$ reaction systems are performed for calculating equilibrium.

The initial amounts of the reactants were chosen to be (i) $SiO_2 = 1$ mol, $Cl_2 = 6$ mol, CO = 10 mol and (ii) $SiO_2 = 1$ mol, $Cl_2 = 6$ mol, C = 4 mol. Excess chlorine and reductant were chosen to allow the reactions to go to completion[20]. Chemical equilibrium compositions of these reaction systems at different reaction temperatures and normal pressure were obtained and are plotted in Figs. 2 and 3.
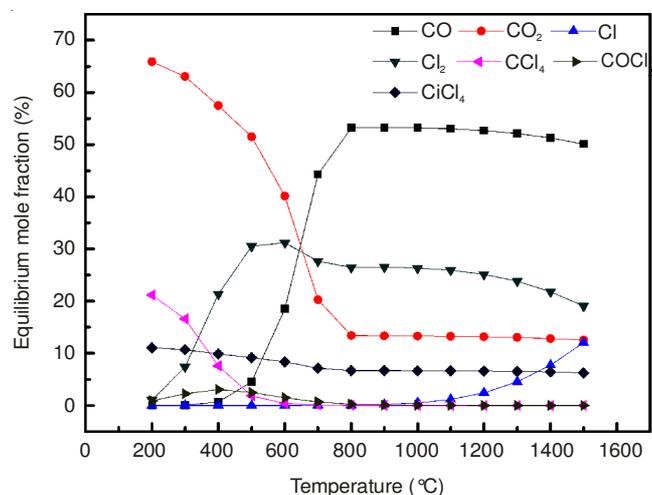
Fig. 2. Chemical equilibrium compositions for reactants: $SiO_2 = 1$ mol, $Cl_2 = 6$ mol, CO = 10 mol
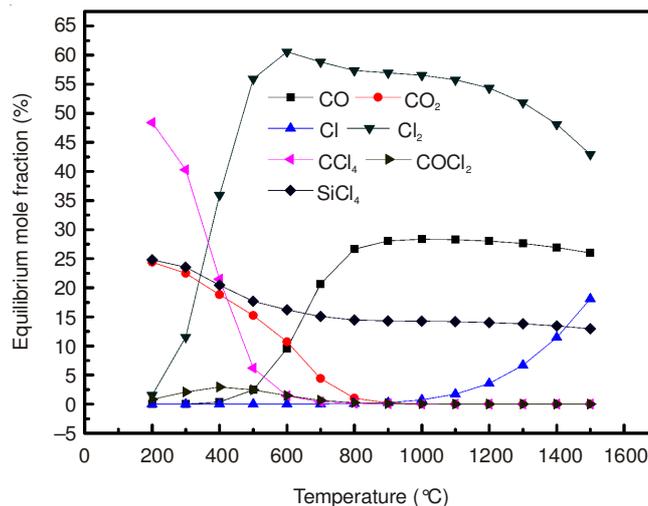
Fig. 3. Chemical equilibrium compositions for reactants: $SiO_2 = 1$ mol, $Cl_2 = 6$ mol, C = 4 mol

From the results reported in Figs. 2 and 3, the following conclusions can be drawn for the carbo-chlorination of SiO_2 with CO/C as reductant: (1) SiO_2 can be converted completely at all temperature considered (200-1500 °C) as the formation reaction of $SiCl_4$ can proceed spontaneously in terms of thermodynamics. (2) $SiCl_4$ is the most stable product of the chlorination process in the temperature range considered, regardless of whether the reductant is C or CO. (3) CCl_4 is produced only when the temperature is below 600 °C and its mole fraction is decreasing with temperature increased. (4) $COCl_2$ concentration is always low at all temperature. The Cl radical was observed at temperatures higher than 1000 °C. (5) for $SiO_2/Cl_2/C$ reaction systems, low temperature favors the formation of CO_2, at temperatures higher than 800 °C CO becomes dominant.

Fig. 4. shows a schematic representation of the experimental set-up employed in the carbo-chlorination of SiO_2. Chlorine and argon were supplied from cylinders. The argon was used as an inert diluent and carrier gas. The flow of the gases was regulated by metering valves and flow meters.

The reactor consisted of analundum tube (length 840 mm, OD 51 mm, wall thickness 6 mm), with a cover and a base which were made of steel. The joints between the alundum tube and the cover and base were fixed by steel rings to ensure gas tightness. The tube was placed vertically inside a furnace which was heated by $MoSi_2$ heating elements. There were three ports in the steel cover, one was for the thermocouple in order to measure the temperature in the reaction zone, one was for the vacuum pump and the third was for the gas outlet. There were two ports in the steel base, one was for a thermocouple and the other was for the gas inlet. The solid pellets were held in a graphite crucible (OD 44 mm, wall thickness 2 mm, length 112 mm) in which there were some holes to allow good contact with the gas, distributed equably.

The $SiCl_4$ reaction product was collected in a ring like condenser, where the generated gaseous phases are cooled and a sealed glass prepared for the condensed products. Finally, a two-stage scrubber using saturated caustic soda solution was used to absorb the chlorine and the generated CO was burned in the air to CO_2.
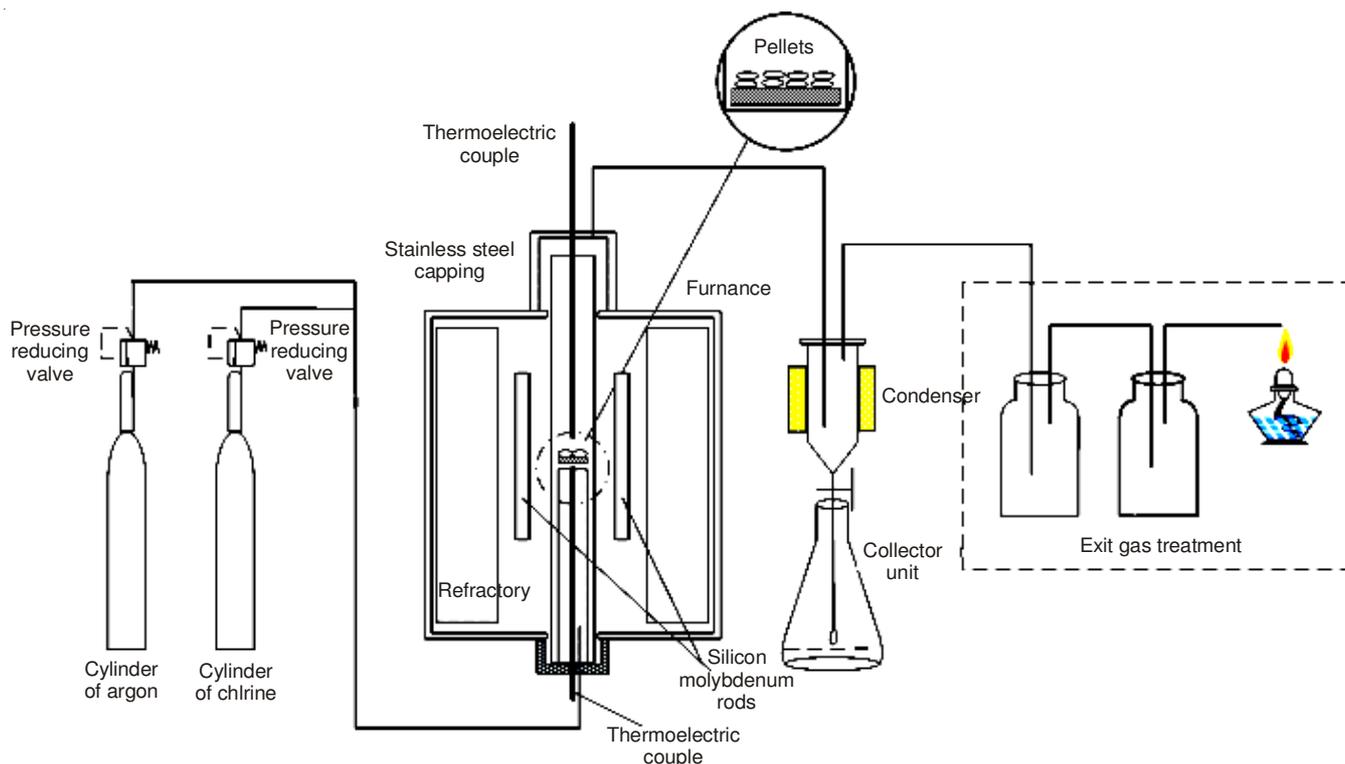
Fig. 4. Schematic representation of the experimental setup

Supporting equipments: An analytical balance was used for the measurement of the samples mass before and after carbo-chlorination. The balance has a maximum sensitivity of 0.0001 g. Chemical analysis was used to determine the mass per cent of silicon containing materials. X-Ray Diffraction (Rigaku CuK_α radiation ($\lambda = 0.154$ nm)) is used to observe the phases present before and after carbo-chlorination. A thermogravimetric analyzer (Model NETZSCHSTA449F3-temperature ranging from 33 to 1400 °C) was used to determine the content of unreacted carbon in the carbo-chlorination sample.

Characterization: Dinas rock, quartz sand, silicon dioxide and diatomite are chosen as the silica-bearing raw materials in this study. Dinas rock and carbon was crushed and milled through a 200-mesh sieve and the rest materials were analytic reagent. The content of SiO_2 in the four raw materials is shown in Table-1. The industrial analysis of the carbon used as reducing agent is shown in Table-2.

TABLE-1
CONTENT OF SiO_2 IN FOUR RAW MATERIALS

Silicon oxide	Dinas rock	Quartz sand	Diatomite
99.20	97.90	92.90	89.66

TABLE-2
INDUSTRIAL ANALYSIS OF CARBON

	S	Moisture	C	ash	volatiles
Content (%)	0.44	6.71	65.41	16.86	11.01

X-ray patterns of the four raw materials are presented in Fig. 5. It is noticed that crystal phase such as quartz, silicon oxide, formed in silicon dioxide, dinas rock, quartz sand, while cristobalite was found in diatomite and the intensity of the peaks was lower than the other materials. The results of

XRD patterns show that the diatomite was poorly crystallized. Diatomite, mainly consists of amorphous silica ($SiO_2 \cdot nH_2O$) derived from opalescent frustules of diatoms, is a fine-grained, low-density, soft, light weight biogenic sediment. Owing to its high surface area and amorphous structure, an improvement of the chlorination ratio was obtained by previous workers[21-23].

Experimental procedure: The silicas, carbon and binder ($Na_2SiO_3 \cdot 9H_2O$) were weighed accurately and mixed together, then pressed pellets at 20 Mpa.

The graphite crucible containing the samples was placedin the middle of the reactor and argon was introduced to purge the system. The reaction temperature was set and the furnace was switched on. The heating rate was controlled at 10 °C/min to prevent the samples from cracking as a result of thermal shock. The system was evacuated after the required temperature reached. Chlorine was then fed into the reactor to make the system to be filled and the flow rate of supplying chlorine was kept at 300 mL/min. After the specified chlorination time elapsed, chlorine is replaced by argon to purge the system. Then, the furnace gets switched off and cooled. When the reactor is cooled to room temperature, argon is interrupted and the samples are taken out from the furnace and weighed.

To obtain the mass per cent of SiO_2 in the unreacted samples exactly, the samples after carbo-chlorination were roasted in a muffle furnace at 1000 °C for 3 h. Then, the powder sample is identified by chemical analysis.

RESULTS AND DISCUSSION

According to the calculation by Factsage 6.2, it was shown earlier that there will be little or no $SiCl_4$ generated by reaction between SiO_2 and Cl_2. Since the formation of heat of $SiCl_4$ from Cl_2, SiO_2 and C is -161 kJ/mol, so it is clear that $SiCl_4$ can
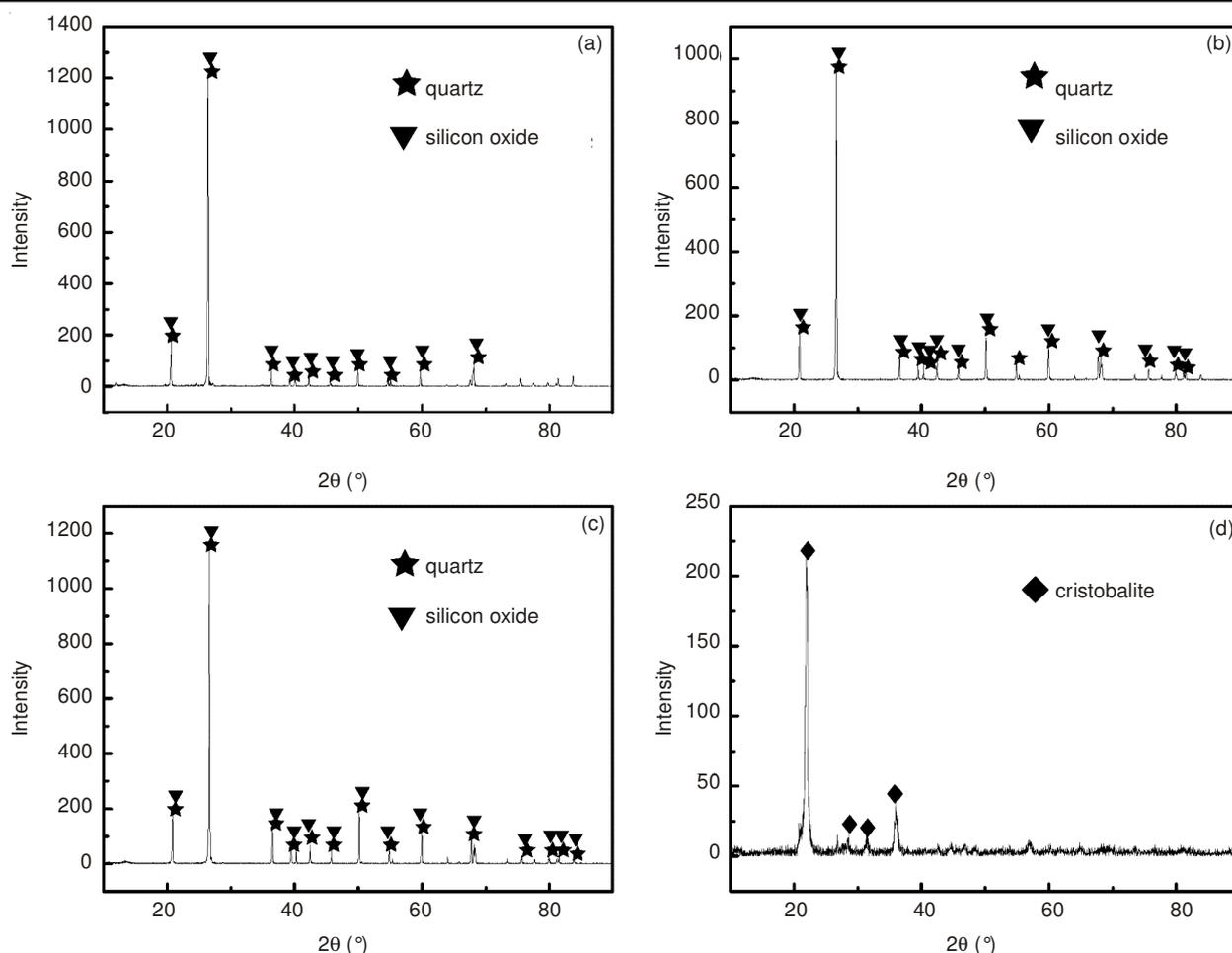
Fig. 5. X-ray patterns of the four raw materials, (a. dinas rock, b. quartz sand, c. silicon dioxide, d. diatomite)

be generated easily when carbon exists in the system. Factsage 6.2 was used to calculate the optimal generation of $SiCl_4$ with different temperature and carbon addition. The result is that the optimal C/SiO_2 mole ratios are 1.2, 1.4, 1.6, 1.8 at 900, 1000, 1100 and 1200 °C, respectively.

The degree of conversion of SiO_2 is defined as:

$$\eta = \frac{M_{SiO_2}^0 - M_{SiO_2}}{M_{SiO_2}^0}$$ [9]

where $M_{SiO_2}^0$ is the initial mass of SiO_2 in the starting material powder and M_{SiO_2} is the mass of SiO_2 in the powder after a specific reaction.

Several experiments were made with the four silicas mentioned above according to the calculations with a chlorine flow rate of 500 mL/min. The experiment result shown in Fig. 6.

From Fig. 6, it can be obtained that the conversion ratio of several silica materials increased with temperature raised. At the same temperature, the conversion ratio of diatomite was the highest among all the materials. Actually, silica can be found in more than one state-crystalline as in a quartz crystal, which is quite common in nature and amorphous as in the remains from a diatom[24].

Because of its amorphous structure and porosity, so it is feasible for diatomite to react with Cl_2 at a lower temperature than any other silicon-bearing ores. Moreover, the lower price
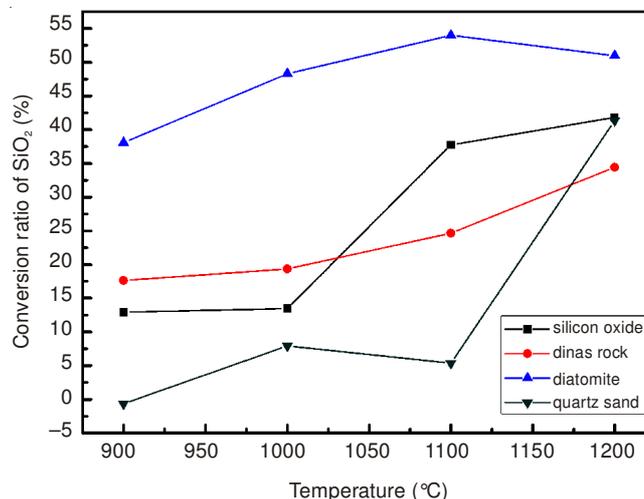
Fig. 6. Conversion ratio of different silicas at different temperature

of diatomite, small quantity of by-product $FeCl_3$ and rich storage make it a suitable raw material for the preparation of $SiCl_4$ by carbo-chlorination.

Subsequently, a series of experiments were made through the change of mass carbon to study the effect of C/SiO_2 mole ratio on the conversion of SiO_2. The result showed that the conversion ratio increased with carbon increases in Fig. 7.

At 1100 °C, the optimal C/SiO_2 mole ratio of the chlorination was 1.6 according to thermodynamics calculation.
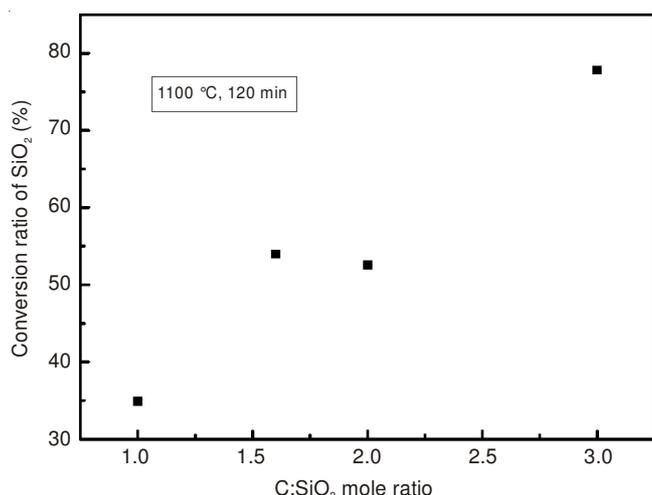
Fig. 7. Conversion of SiO₂ in diatomite with different C/SiO₂ mole ratio

However, Fig. 7 indicated that the conversion ratio of SiO_2 is the highest when C/SiO_2 mole ratio is equal to 3. It accounts for that the equilibrium module of thermodynamics calculated the conditions for the chlorination under a large range of constraints and it regarded all the carbon as reductant. Actually, a part of carbon would turn into some chlorides such as CCl_4 and carbon offer reaction areas for the formation of intermediates. To make SiO_2 convert into $SiCl_4$ in vast, excessive carbon should be added. Besides, some experiments are made by changing the mass of bind to study the relation between porosity and conversion ratio, the result indicates that conversion of SiO_2 decreased with binder increasing.

Procedures of the carbo-chlorination of SiO₂: The thermodynamic analysis presented earlier showed that CO is dominant in gaseous phase at high temperature, provided that enough carbon is present in the feed. Besides, as chlorine is inlet into the reactor without interrupt, CO is removed from the surface of the particles as long as it generated, so eqn. [3] is unfavorable. Therefore, we suppose eqn. [1] to be the global reaction, which in accordance with some researches[25]. According to eqn. [1], this is a gas-solid reaction system in which two solid reactants (SiO_2 and C) and one gaseous reactant (chlorine) are involved. The products are gaseous at reaction temperature.

Several routes were used to extract metal from some metallic oxide such as carbo-thermic reduction[26], electrolysis from molten salt for some active metals[27] and carbo-chlorination. As it was thermodynamically favorable for the formation of chlorides, Ilic *et al.*[28] discussed the chlorination of nickel oxides and nickel ferrites with or without additives and found that the chlorination degree of Ni, Fe, Cr increased with the increase in the quantity of coal. Some reporters considered that there is no necessary for carbon and oxides to contact, directly. And proposed that carbo-chlorination occurs by means of gaseous intermediates such as $COCl_2$, Cl atom and respective oxychlorides[29,30].

Amorebieta[31] studied the decomposition of chlorine over pyrolytic carbon surfaces and found that chlorine dissociated with a activation energy about a half of its bond energy. It is noted that chlorine was easy to dissociate on the carbon surface, so here chlorine atoms are suggested to be the active inter-

mediates formed by Cl_2 dissociation in the C-Cl_2 interaction. Chlorine atoms are formed on the carbon surface, so carbon surface is involved in the formation of intermediates. With carbon increasing, the activated chlorine atoms increased. The reaction between activated chlorine atom and SiO_2 is carried out more fully. In this system, carbon plays two important role: (a) the catalytic, activating the chlorine to obtaining activated chlorine atom. (b) the reductant, capturing oxygen from silicon dioxide.

The procedures of carbo-chlorination of SiO_2 is suggested to be as that chlorine decomposed into activated chlorine atoms in the presence of C, subsequently the bond of Si-O-Si is interrupted by actived chlorine atom and CO, then CO_2 releases. The procedures diagram (Fig. 8) of carbo-chlorination of SiO_2 and equations expressed as following:
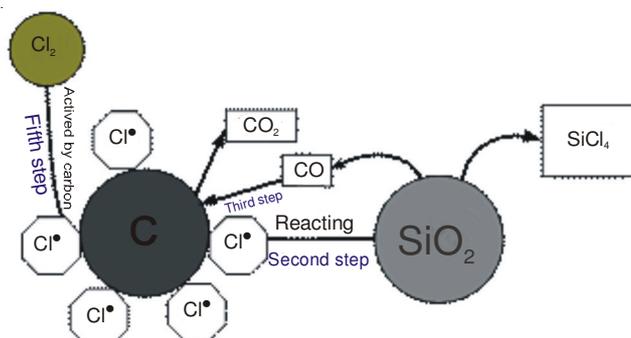
Fig. 8. Procedures diagram of carbochlorination of SiO₂

$$Cl_2 + C \rightarrow 2Cl^\bullet + C \qquad [10]$$
$$2CO + SiO_2 + 4Cl^\bullet \rightarrow SiCl_4 + 2CO_2 \quad [11]$$
$$CO_2 + C \rightarrow 2CO \qquad [12]$$
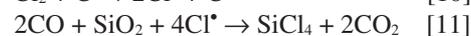
Conclusion

It is possible for SiO_2 to be converted to $SiCl_4$ by carbo-chlorination process. Here, carbon is the catalyst and the reductant. is thought to be the global reaction during preparation of $SiCl_4$, when sufficient carbon is present.

Due to its structure of amorphous silica and its properties of porosity and high surface area, diatomite is the best raw material to produce $SiCl_4$. At 1100 °C, the conversion ratio of SiO_2 increased with C/SiO_2 mole ratio.

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