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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Mechanically Activated Synthesis of Monosilane by the Reaction of Calcium Hydride with Silicon Tetrafluoride

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Abstract—Possibility of performing a mechanically activated synthesis of pure monosilane by the reaction of calcium hydride with silicon tetrafluoride in a rotating flow-through reactor containing milling bodies was analyzed. A number of operation parameters of the grinding reactor were theoretically evaluated and experimentally determined.

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High-purity silicon is frequently obtained by using the hydride method, which consists in synthesis of monosilane SiH₄, followed by purification and thermal decomposition of this compound [1]. One of techniques for production of the starting monosilane is based on the heterogeneous reaction of silicon trifluoride with calcium hydride CaH_2 in a flowthrough reactor:

$$SiF_4 + 2CaH_2 \rightarrow SiH_4 + 2CaF_2. \tag{1}$$

This method has been successfully used to obtain isotope-enriched monosilanes [2, 3]. The process is characterized by a high yield relative to SiF₄ (90– 97%), but the conversion of CaH₂ in the flow-through reactor does not exceed 14.5% because of the formation of a layer of a solid-phase product (CaF₂) on the surface of calcium hydride [4].

To raise the conversion of calcium hydride, the synthesis of SiH₄ by the reaction of SiF₄ with CaH₂ was performed under the static conditions. By keeping the reactants for 24 h under a SiF₄ pressure of no less than 30 atm at a temperature of 200°C, the conversion of CaH₂ was raised to 20% [5]. The disadvantages of the technique consist in its long duration, required elevated pressure, and need to regenerate or utilize solid-phase reaction products containing a considerable amount of calcium hydride.

Performing the synthesis of monosilane by reaction (1) in a salt melt makes it possible to achieve a high

(>90%) yield of monosilane in terms of SiF₄ and CaH₂ [6]. Implementation of the method is complicated by the high synthesis temperature (\sim 400°C) and the necessity for carrying out additional procedures for regeneration of the salt melt.

In view of the aforesaid, it is a topical task to improve methods for synthesis of monosilane and raise their efficiency.

A known way to stimulate heterogeneous chemical reactions is their mechanical activation [7]. In addition to activating the reactants, an intense mechanical treatment causes formation and renewal of the phase boundary surface, which is necessary for a chemical interaction to occur [8]. The mechanical activation is used for synthesis of volatile boron hydrides [9] and ammonia [10]. A flow-through vibrational installation for synthesis of monosilane, with counter flows of lithium hydride and silicon tetrachloride, has been reported [11] without any data on the efficiency of the activator of this type.

The aim of the present study was to perform a mechanically activated synthesis of monosilane by the reaction of silicon tetrafluoride and calcium hydride and to determined the conversion of calcium hydride.

EXPERIMENTAL

In activators used for gas-solid systems, the mechanical activation occurs in parallel with grinding

985

n, min ⁻¹	φ, %	$V_{\rm GB}$: $V_{\rm MG}$	Relative content of indicated fractions, mm, upon grinding, %						
			-1.6+1.0	-1.0+0.63	-0.63+0.4	-0.4+0.2	-0.2+0.1	< 0.1	
100	40	1:1	12.8	22.1	14.0	24.4	21.9	4.8	
125	40	1:1	0.1	0.4	0.5	5.0	25.7	68.3	
150	40	1:1	50.7	30.1	7.0	8.6	2.0	1.6	
125	30	1:1	13.1	22.6	8.9	17.8	6.9	30.7	
125	40	1:1	0.1	0.4	0.5	5.0	25.7	68.3	
125	50	1:1	1.1	1.9	2.8	9.1	29.2	55.9	
125	40	2:1	0	0	0.1	1.5	19.9	78.5	
125	40	1:1	0.1	0.4	0.5	5.0	25.7	68.3	
125	40	1:2	2.5	4.7	9.3	30.2	22.8	30.5	

Table 1. Input data and results of experiments performed for determining the optimal grinding conditions. Grinding duration 60 min

of the solid phase [12]. The following requirements to an activator for synthesis of monosilane can be formulated: leak tightness, safety, simplicity of design and maintenance, and possibility of control over, and variation of temperature. These requirements are satisfied by a tumbling or tubular mill in which a flowthrough mode is possible and high output capacity can be provided. The grinding efficiency in apparatus of this type depends on its dimensions and design, drum rotation frequency n, mill-filling coefficient ϕ , physicomechanical properties of a material being ground, and a number of other factors [13].

To provide effective grinding and renewal of the CaH₂ surface, a number of operation parameters were theoretically evaluated and experimentally determined. The experiments were performed using a flange reactor made of 12Kh18N10T stainless steel, with an inner diameter of 66 mm, length of 70 cm, and useful volume of 2350 cm³. The following calculated values of the optimal operating parameters were obtained for the given reactor: rotation frequency n = 124 rpm, reactor-filling coefficient $\varphi = 39\%$, minimum grinding body weight q = 0.015 N. To calculate q, it is necessary to know the minimum disintegration onset energy E_0 of particles of the material. E_0 was experimentally determined by the method described in [13]; for CaH₂ particles 1 mm in size, E_0 was 2×10^{-3} J.

Calcium hydride is a hygroscopic substance whose hydrolysis yields fine CaO and Ca(OH)₂ particles capable of distorting results obtained in grinding experiments. Therefore, commercial common salt was

used as a model material to be ground in these experiments. The experimental value of E_0 for 1-mm particles of this substance was 3×10^{-3} J, which is comparable with E_0 for CaH₂ particles of this size.

As grinding bodies served steel cylinders with a diameter of 10 mm and height of 10 mm because of their simpler fabrication and more effective grinding, compared with balls, via abrasion. The experimental procedure was as follows. The reactor was charged with a weighed portion of sodium chloride and grinding bodies in a certain volume ration; the reactor was closed, mounted on support bearings, connected to the gearbox shaft via a pulley, and the required rotation frequency of the reactor was set. The ground material was periodically subjected to a sieve analysis; the mass of fractions of the ground material was determined on a VL E134 electronic laboratory balance with an accuracy of ± 0.1 g. The experimental data obtained in a study of how the rotation frequency n, filling coefficient ϕ , and volume ratio between the grinding bodies and the material being ground, V_{GB} : V_{MG} affect the grinding efficiency are listed in Table 1.

It can be seen in Table 1 that the grinding is more effective at a rotation frequency of 125 rpm and reactor-filling coefficient of 40%, in agreement with the calculated data. It is noteworthy that an increase in the number of grinding bodies makes the grinding efficiency higher. However, the amount of calcium hydride charged into the reactor should be lowered in this case, which may impair the output capacity of the technique.



Fig. 1. Schematic of a setup for mechanically activated synthesis of monosilane. (1) Cylinder with SiF₄, (2) cylinder with H₂, (3) vacuum gage, (4) gas flow control valve, (5) junction unit (pivot), (6) supporting bearing, (7) flange reactor, (8) electric motor with a gearbox, (9) Petryanov filter, (10) cryogenic condenser, (11) receiving cylinder, and (12) rheometer.

The results obtained were used when performing a mechanochemical synthesis of monosilane by the reaction of SiF_4 with CaH_2 . The experiments were carried out on a setup shown schematically in Fig. 1. The basic units of the setup were cylinders with SiF_4 and H_2 , Bronkhorst Hi Tech gas flow control valves, above-described flange reactor with a resistive heater,

Flamont	CaH ₂ content, ppm				
Element	starting	upon synthesis			
В	<0.05	0.2			
С	≤1700	≤680			
Ν	≤400	≤13			
Ο	≤56000	25000			
F	61	>20 at %			
Mg	130	138			
Si	30	15000			
S	9.5	14			
Cr	17	13			
Mn	21	22			
Fe	29	50			
Ni	3.8	6.5			
Cu	17	67			
Sr	93	98			

Table 2. Results of a laser mass-spectrometric analysis of calcium hydride samples

condenser consisting of three in-series connected traps, and receiving cylinder. Silicon tetrafluoride was produced by thermal decomposition of Na₂SiF₆ [14]; CaF₂ was synthesized from shavings of distilled calcium and purified hydrogen [15]; on being synthesized, calcium hydride was ground in a box with dried atmosphere. The -1.0 + 0.63 mm fraction was used in the experiments.

The experimental procedure included the following stages: charging of calcium hydride and grinding bodies into the reactor, evacuation and heating of the reactor to 180–190°C, and delivery of a mixture of silicon tetrafluoride and hydrogen (50 : 50 vol %) into the rotating reactor. Gaseous reaction products were frozen-out in the condenser cooled with liquid nitrogen and, after an experiment was complete, were loaded into the receiving cylinder. The mass of consumed SiF₄ and gaseous reaction products was periodically determined by weighing cylinders with gases on an SP-30 electronic balance with an accuracy of ± 2 g. The experiments were continued until gaseous monosilane ceased to be released, as indicated by gravimetry and gas chromatography.

Figures 2 and 3 show how the content of SiH₄ in the gaseous reaction products and the conversion of CaH₂ depend on the duration of mechanical activation. It can be seen that, after approximately 30% of calcium hydride is consumed, the content of monosilane in the gaseous reaction products decreases and that of SiF₄ increases. After about 60% of calcium hydride is consumed, monosilane almost ceases to be formed. A possible reason why the reactant conversion decreases



Fig. 2. Content c of SiH₄ in gaseous reaction products vs. the duration τ of mechanical activation. $m(CaH_2) = 500$ g; volumetric flow rate of SiF₄, $10 \ h^{-1}$; $\varphi = 40\%$; $n = 125 \pm 2$ rpm; $V_{GB} : V_{MG} = 1 : 1$; the same for Fig. 3.

is that the limiting grinding of calcium hydride particles is reached [16], with the result that the surface renewal and the reaction of calcium hydride with silicon tetrafluoride almost cease. This assumption is confirmed by the presence of a considerable amount of calcium hydride in the solid phase, determined by its dissolution in water. The reaction of spent calcium hydride in water has an induction period (3–4 s), whereas the starting substance reacts with water almost instantaneously.

The particle size of the solid reagent was evaluated upon the synthesis by optical microscopy on a Zeiss Axioplan 2 imaging instrument. It was found that the main part of particles or their agglomerates have sizes of the order of $n \times 10^{-6}$ m.

It is noteworthy that the coloration of the solid phase changes upon synthesis from light gray to brown. A possible reason for the coloration change is that amorphous silicon is formed via reduction of silicon (Si^{IV} \rightarrow Si⁰) or thermal decomposition of monosilane. This assumption is confirmed by the results of a laser mass-spectrometric analysis of the starting CaH₂ and solid-phase reaction products (Table 2). According to the data in Table 2, the content of fluorine and silicon in the solid phase substantially increases. It should be noted that the reaction of SiF₄ with CaF₂ to give CaSiF₆ is possible; however, the equilibrium of this reaction is almost completely shifted to the left at a temperature of 195°C [17]. The high content of the oxygen impurity is due to the interaction of CaH₂ with water vapor in sample preparation. The content of gasforming elements, such as carbon and nitrogen, in



Fig. 3. Conversion *x* of CaH₂ vs. the duration τ of mechanical activation.

spent CaH₂ decreases. Pres-umably, this is due to the formation of volatile com-pounds of these elements with hydrogen and washing-out of these compounds from calcium hydride.

The monosilane sample obtained was analyzed for the content of C_1 – C_4 hydrocarbon impurities by the method described in [18]. The results obtained are listed in Table 3. It can be seen that the total content of C_1 – C_4 hydrocarbon impurities in monosilane does not exceed 3 × 10⁻³ mol %, which is comparable with the content of these impurities in monosilane produced from SiF₄ and CaH₂ by other methods without mechanical activation [3, 6].

In conclusion, the following can be noted. The mechanically activated synthesis of monosilane from silicon tetrafluoride and calcium hydride does not require any additional reagents (solvents and salt melts), which makes unnecessary their regeneration. The technique is comparatively simple methodolo-

Table 3. Content of C_1 – C_4 hydrocarbon impurities in monosilane according to gas-chromatographic data

Impurity	Content, mol %
CH ₄	$(2.5\pm0.3)\times10^{-3}$
C_2H_4	(1.3±0.1)×10 ⁻⁴
C_2H_6	$(2.6\pm0.3)\times10^{-4}$
C_3H_8	$(4.0\pm0.5)\times10^{-5}$
n-C ₄ H ₁₀	$(1.8\pm0.2)\times10^{-5}$
iso-C ₄ H ₁₀	$(3.7\pm0.7)\times10^{-6}$

gically and instrumentally and can substantially raise the conversion of calcium hydride. A promising way to improve the output capacity is to successively perform synthesis of calcium hydride, its grinding, and synthesis of monosilane in the same reactor or to organize a continuous process. The mechanical treatment of calcium hydride in synthesis of monosilane yields fine particles, and, therefore, it is necessary to take measures to preclude carry-over of these particles from the reactor and to remove inhomogeneous impurities from the monosilane obtained.

CONCLUSIONS

(1) A mechanically activated synthesis of monosilane by the reaction of silicon tetrafluoride with calcium hydride was performed in a flow-through reactor. It was found that the conversion of calcium hydride reaches a value of 60%.

(2) The conversion of calcium hydride is 30% at a nearly complete conversion of silicon tetrafluoride in mechanically activated synthesis.

(3) The total content of C_1-C_4 hydrocarbon (CH₄, C_2H_4 , C_2H_6 , C_3H_8 , $n-C_4H_{10}$, *iso*-C₄H₁₀) impurities in the resulting monosilane does not exceed 3×10^{-3} mol % according to gas-chromatographic data.

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