

INORGANIC SYNTHESIS  
AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of High-Purity Calcium Hydride

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**Abstract**—A procedure for synthesizing high-purity calcium hydride in high yield was suggested. The admixture composition of the resulting  $\text{CaH}_2$  was determined by laser mass spectrometry.

$\text{CaH}_2$  is used in laboratory practice as a desiccant that can take away water from crystal hydrates [1]. It is highly efficient in drying of hydrocarbons, ethers, and other solvents. Calcium hydride has found wide application as a reducing agent in preparing powders of certain metals (Ti, Zr, Nb, Ta, Mo, and W) from their oxides and halides [2, 3]. A method is known for converting silicon halide compounds (silicon tetrachloride, trichlorosilane, and silicon tetrafluoride) into silane by their reaction with  $\text{CaH}_2$  [4]. In this case, admixtures of  $\text{F}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{AsH}_3$ , and  $\text{PH}_3$  are removed from  $\text{SiH}_4$  via their adsorption on a metal hydride [5]. In [6], calcium hydride was used as a reducing agent to obtain high-purity hydrides of monoisotopic silicon ( $^{28}\text{SiH}_4$ ,  $^{29}\text{SiH}_4$ , and  $^{30}\text{SiH}_4$ ) from monoisotopic  $\text{SiF}_4$  by the reaction



The choice of  $\text{CaH}_2$  was determined by the fact that, unlike  $\text{NaF}$  in the reaction with  $\text{NaH}$ ,  $\text{CaF}_2$  does not react with monoisotopic  $\text{SiF}_4$  to give  $\text{CaSiF}_6$  in synthesis of silane [7, 8]. Moreover,  $\text{CaF}_2$  reacts with a  $\text{BF}_3$  admixture in silicon fluoride to give a stable  $\text{Ca}(\text{BF}_4)_2$  complex [4], which favors purification of the resulting  $\text{SiH}_4$  to remove boron-containing admixtures. At the same time,  $\text{CaH}_2$  is the safest in handling, compared with other hydrides and metal aluminum hydrides.

The compound  $\text{CaH}_2$  is a light gray crystalline substance that does not react with oxygen up to 400–500°C [9] and reacts with water to give  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ , and hydrogen [10]. In synthesizing  $\text{SiH}_4$  from  $\text{SiF}_4$ , the reactions of  $\text{SiF}_4$  with the products of  $\text{CaH}_2$  hydrolysis are thermodynamically allowed [11]. It has been established experimentally that presence of several percent  $\text{CaO}$  in calcium hydride substantially

decreases the yield of  $\text{SiH}_4$ , and, therefore, there is no point in using commercial-grade  $\text{CaH}_2$ . Moreover, an admixture of metal calcium in  $\text{CaH}_2$  may result in thermal reduction of  $\text{SiF}_4$  to give monoisotopic elementary silicon [12]. Therefore, development of a procedure for synthesizing active  $\text{CaH}_2$  in high yield is a matter of current interest.

The reaction of Ca with  $\text{H}_2$  becomes noticeable at 170–250°C [10],  $\Delta H_f^{298}(\text{CaH}_2) = -45.1 \text{ kcal mol}^{-1}$  [13]. For practical use, temperatures in the range from 250 to 700°C are recommended [14]. The hydrogenation of solid Ca to give a solid product is a topochemical process. Kinetic studies [15] revealed three stages of the reaction: formation of centers of  $\text{CaH}_2$  crystallization on the surface of a sample (induction period), formation of a  $\text{CaH}_2$  surface layer precluding a direct contact of  $\text{H}_2$  with Ca, and diffusion of  $\text{H}_2$  with the subsequent reaction at the Ca– $\text{CaH}_2$  interface (dissolution or formation of a chemical bond). The rate of Ca hydrogenation depends on temperature,  $\text{H}_2$  pressure, linear dimensions of a sample, internal structure of the metal, and admixtures present in calcium and hydrogen [15–17].

The admixtures of  $\text{O}_2$  and  $\text{H}_2\text{O}$  in hydrogen decrease the hydrogenation rate, because  $\text{CaO}$  formed on the surface of calcium hinders the diffusion of  $\text{H}_2$ . It was shown in [18] that 0.5% oxygen decelerates the reaction by a factor of 2.5, and 0.5%  $\text{H}_2\text{O}$ , by a factor of 6.

#### EXPERIMENTAL

To obtain high-purity  $\text{CaH}_2$ , we used distilled Ca in the form of 1.5-mm-thick shavings [TU (Technical Specifications) 95.768–80, manufactured by Mashinostroitel'nyi zavod Open Joint-Stock Company (Elekt-

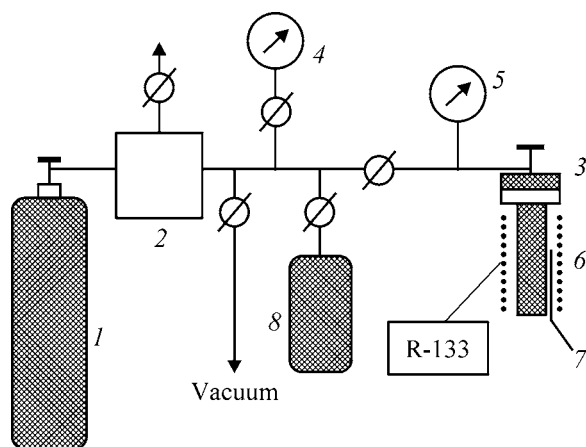
## Results of analysis by laser mass-spectrometry

Element	Content, at. %	
	Ca	CaH <sub>2</sub>
B	$<8 \times 10^{-6}$	$<1 \times 10^{-4}$
C	$<3 \times 10^{-2}$	$\leq 8 \times 10^{-2}$
P	$<1 \times 10^{-5}$	$1 \times 10^{-4}$
F	$7 \times 10^{-3}$	$\leq 1 \times 10^{-3}$
Mg	$1 \times 10^{-3}$	$1 \times 10^{-3}$
Al	$5 \times 10^{-5}$	$4 \times 10^{-5}$
Si	$2 \times 10^{-3}$	$2 \times 10^{-4}$
Cl	0.12	$2 \times 10^{-2}$
Fe	$1 \times 10^{-3}$	$5 \times 10^{-4}$
Mn	$1 \times 10^{-3}$	$7 \times 10^{-4}$
Cu	$6 \times 10^{-4}$	$3 \times 10^{-3}$
Zn	$2 \times 10^{-4}$	$<1 \times 10^{-4}$
Sr	$3 \times 10^{-2}$	$5 \times 10^{-3}$
S	$1 \times 10^{-3}$	$3 \times 10^{-4}$

rosta]) and H<sub>2</sub> purified by diffusion across a palladium membrane. The content of admixtures in calcium, as determined by laser mass spectrometry, is listed in the table.

The content of O<sub>2</sub> and H<sub>2</sub>O admixtures in purified hydrogen does not exceed 10<sup>-4</sup> mol %.

We synthesized CaH<sub>2</sub> on an installation shown schematically in the figure. The main units of the installation are a cylinder with H<sub>2</sub> 1, a H<sub>2</sub> purification unit 2, and a flange reactor 3. We controlled the pressure of H<sub>2</sub> during the process with vacuum gages 4 and 5. The temperature of the resistance furnace 6 was set with an R-133 temperature control unit and monitored with a Chromel-Copel thermocouple 7.



Schematic of the installation for synthesis of CaH<sub>2</sub>. (1–7) For explanations, see text; (8) receiver.

We synthesized CaH<sub>2</sub> by the following procedure. A stainless-steel flange reactor was charged with 350–400 g of Ca, connected it to the installation, evacuated to 10<sup>-1</sup> mm Hg, and heated to 360°C within 0.5 h. According to [16], melted Ca in the form of shavings starts to react with H<sub>2</sub> at 400°C; hence, we hydrogenated Ca in the temperature range 400–450°C. We filled the reactor with purified H<sub>2</sub> to a pressure of 5 atm and kept it for about 5 min. During this time, the pressure of H<sub>2</sub> in the reactor decreased first gradually and then abruptly to 0.05–0.1 atm. The increase in the rate of H<sub>2</sub> absorption is accounted for by the high rate of the hydrogenation reaction on the surface of Ca. In this stage of hydrogenation, we controlled the flow of H<sub>2</sub> into the reactor in such a manner that the pressure of H<sub>2</sub> in the reactor did not exceed 1 atm, since an elevated pressure of H<sub>2</sub> results in a rise in temperature.

A rise in temperature may lead to caking of CaH<sub>2</sub>, which impedes its withdrawal from the reactor. After a layer of CaH<sub>2</sub> is formed on the surface of Ca, diffusion of H<sub>2</sub> to the Ca–CaH<sub>2</sub> interface begins, and the rate of H<sub>2</sub> absorption decreases. To complete the hydrogenation, we raised the H<sub>2</sub> pressure in the reactor to 10 atm, and the temperature to 480°C. We judged the completion of the hydrogenation reaction from the cessation of the H<sub>2</sub> absorption.

The yield of CaH<sub>2</sub> was calculated as the ratio of the weight of CaH<sub>2</sub> obtained in the experiment to its theoretical value. The yield of CaH<sub>2</sub> was 99.6 ± 0.1%, i.e., the synthesis procedure results in an almost complete hydrogenation of Ca. The output capacity of the pilot installation for CaH<sub>2</sub> synthesis is 150 g of CaH<sub>2</sub> per hour.

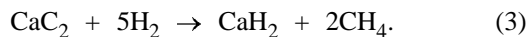
The resulting CaH<sub>2</sub> was analyzed by laser mass spectrometry for the content of admixtures. The results obtained are listed in the table. It can be seen that the main admixtures in CaH<sub>2</sub> are C and Cl, whereas the content of metal admixtures is at the level of 10<sup>-3</sup> at. %.

After the process was complete, we placed the cooled reactor in a box purged with dried nitrogen and then ground the CaH<sub>2</sub> obtained to powder with particle size of less than 0.6 mm. The powdered CaH<sub>2</sub> was charged into the reactor in a flow of purified H<sub>2</sub> in order to obtain silane.

An effective procedure for removal of carbon from metals [19] is their “washing” with purified H<sub>2</sub>. The admixtures of hydrocarbons can be formed in the reaction of H<sub>2</sub> with admixtures of metal carbides present in calcium:



In [20], CaH<sub>2</sub> was obtained in the reaction of calcium carbide with H<sub>2</sub> at 100–1000°C under an elevated pressure (up to 100 atm):



Therefore, side reactions of hydrogenation of carbon and its compounds to give hydrocarbons can occur under the conditions of CaH<sub>2</sub> synthesis.

In this study, we blew CaH<sub>2</sub> with a flow of purified H<sub>2</sub> at 250°C for 8 h in order to diminish the content of carbon admixtures. It was shown that, after contact with CaH<sub>2</sub>, the content of hydrocarbon admixtures in H<sub>2</sub> increases by two orders of magnitude, which allowed us to diminish the content of the most difficultly removable admixture of ethylene in silane by an order of magnitude.

### CONCLUSIONS

(1) High-purity calcium hydride was obtained by hydrogenation of distilled metallic calcium with purified hydrogen.

(2) The main admixtures in CaH<sub>2</sub> are C and Cl, whereas the content of metal admixtures is at the level of 10<sup>-3</sup> at.%. The procedure of "washing" of CaH<sub>2</sub> was used to decrease the content of carbon admixture in it.

### ACKNOWLEDGMENTS

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