Mechanochemical method of producing triethoxysilane*

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A mechanochemical method for synthesis of triethoxysilane from silicon-copper contact mass and ethyl alcohol in the developed vibration reactor is presented. It is shown that the process of a direct alkoxysilane synthesis in the vibro-boiling layer is affected by a series of control parameters such as the ratio between the contact mass and the mass of grinding bodies, the grinding body sizes and their ratios in a polydisperse mixture, power density. Optimization of these parameters allowed us to obtain $HSi(OEt)_3$ with a selectivity of 50% at a silicon conversion of 90% without the use of promoters.

Key words: triethoxysilane, direct synthesis, alkoxysilanes, mechanochemistry, mechanochemical activation, vibro-boiling layer.

Polyorganosiloxanes (POSs) represent one of the most demanded classes of organometallic polymers. Because of their thermal stabilities, a wide range of operating temperatures, hydrophobicity, permeability to gases, bioinertness, and high dielectric characteristics, they have found wide application both in everyday life and in high-tech developments.

The demand for products of POSs is increasing every year. However, their manufacturing is limited by a number of economic and environmental factors. It is necessary to note that the major part of organosilicon polymers is produced by hydrolysis of organochlorosilanes. In addition to the negative impact on the environment, the further disadvantage of this approach consists in the need to carry out this process in the same enterprise where the monomers are produced. Otherwise the starting chlorosilane should be transported, and this imposes certain risks because of instability of these compounds in the air.

The search for alternative raw materials for the synthesis of POSs has been conducted for a long time. The use of alkoxysilanes proved to be the most successful choice.[1—11] In this regard, the development of methods for the synthesis of alkoxysilanes is of great importance.

One of the most promising methods for production of alkoxysilanes is the direct synthesis. This heterogeneous process was discovered already in the middle of the last century.[12] However in contrast to the direct synthesis of chlorosilanes, it was not aimed at preparation of the most valuable derivatives. Therefore, chlorosilanes remain the most widely used monomers in the modern industry.[13—15]

Of the available direct synthesis procedures, the most promising is the passing of alcohol vapor through a layer of silicon powder with a catalyst. It results in the formation of $HSi(OAlk)_3$ and $Si(OAlk)_4$ as products. The reactor for implementing this method is called a fixed-bed reactor.[16—18] This synthetic approach is characterized by high efficiency and simplicity of instrumentation. High conversion and selectivity in respect to $HSi(OMe)_3$ can be achieved when using silicon powder with grains of <60 μm[19] or some CuCl precursors.[18,20] For instance, triethoxysilane was obtained recently[21] with a high selectivity (97%) at a silicon conversion of 64%, however, the process duration was about 30 h for a 5 g silicon loading.

In our previous study[16] with the use of a fixed-bed reactor, the silicon conversion did not exceed 40%, and the reaction proceeded only with MeOH as an alcohol and was displaced towards formation of $Si(OMe)_4$. The process selectivity could be controlled by addition of MeCl. It was also shown[22] that double promoting using the HF/EtCl pair can be applied to increase conversion and selectivity with respect to hydrosilane. However, the use of MeCl, EtCl and HF is unwanted since scaling of the process on going from laboratory to industrial level requires the use of large amounts of these toxic compounds.

As a rule, the principal parameters for controlling the process in a fixed-bed reactor are the temperature, concentration and type of a catalyst, the rate of introduc-

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tion of an alcohol and the addition of a halogen-containing promoters.

A fundamentally new method for synthesis of alkoxysilanes has been developed in the Institute of Organoelement Compounds of Russian Academy of Sciences. It consists in the interaction of metallic silicon with aliphatic alcohol in the presence of a catalyst at 200—300 °C in a vibro-boiling layer of grinding bodies at a vibrational acceleration above 26.6 m s^{-2}.[23]

To implement the proposed method, a reactor for the production of alkoxysilanes from silicon and alcohols by the direct synthesis was created. The reactor consists of a working chamber, which is equipped with grinding bodies, an electric heater, and process tubing and installed on a vibrodrive. Both the working chamber and grinding bodies are made of brass, a copper alloy.[24] The efficiency of this method was demonstrated for the synthesis of tetraethoxy- and tetramethoxysilanes,[25] which were obtained in high yields without the use of high-temperature heat carriers, as well as without a number of preliminary stages of preparation. However, a selective preparation of trialkoxysilanes using this method was not reported so far. At the same time, triethoxysilane is a practically important product, which has found its use in the production of semiconductor silicon and a series of organosilicon monomers such as APTES, triethoxyvinylsilane, 3-(triethoxysilyl)propyl methacrylate, *etc.*

In this regard, the purpose of this work is to study and optimize the factors affecting the yield of thriethoxysilane in the reaction of silicon-copper contact mass with ethanol in a vibro-boiling layer.

Results and Discussion

The reactions shown in Scheme 1 occur during the interaction of ethanol with silicon in the presence of copper.

Scheme 1

$$\mathrm{Si + ROH \xrightarrow[-H_2]{Cu,\ 200—300\ ^\circ C} HSi(OR)_3} \qquad (1)$$

$$\mathrm{HSi(OR)_3 \xrightarrow[-H_2]{Cu,\ ROH} Si(OR)_4} \qquad (2)$$

R = Me, Et

In this case, copper is in an active state, most likely, in the form of the intermetallic phase Cu_3Si. It is assumed that this inermetallic compound participates in the Cl atom transfer from copper to silicon (Scheme 2), producing active centers —($SiCl_n$)—.[26,27] The main chlorine source in the direct synthesis of organochlorosilanes is an organic halide (RCl). Pyrolysis of the latter results in an elimination of Cl and its interaction with Cu. Thus, Cu_3Si is regenerated, and the active reaction centers are formed.

Scheme 2

$$\mathrm{Cu_3Si + RCl \xrightarrow[-R_2,\ RH,\ H_2,\ C]{} CuCl + Si \longrightarrow}$$

$$\mathrm{\longrightarrow Cu_3Si + —(SiCl_{\mathit{n}})—}$$

In the case of the direct synthesis of alkoxysilanes, the copper regeneration does not take place. This determines the formation of Cu^0 clusters in the course of the process. Copper in this form catalyzes the reaction (see Scheme 1, equation 2).[17] As can be seen from Scheme 1, produced triethoxysilane interacts with ethanol. In addition, a gradual decrease in the active copper content results in the deactivation of the contact mass.[22] It explains the fact that introduction of little amounts of allyl chloride or chlorine-containing metal salts increases the yield of $HSi(OR)_3$. These compounds make up the lack of Cl, which is required for formation of CuCl in the system (see Scheme 2).

Carrying out the direct synthesis in a vibro-boiling layer makes it possible to avoid the use of compounds of this type. The dependences of the concentrations of reaction products and ethanol on the reaction time for a typical experiment in a vibration reactor are depicted in Fig. 1.

As follows from the data presented, the first stage of the reaction is characterized by a low ethanol conversion and a low concentration of triethoxysilane, *i.e.*, there is an induction period (see Fig. 1, period I). Apparently, it is associated with the formation of active centers and the increase in the specific surface of the contact mass in the grinding process. During the induction period, a little

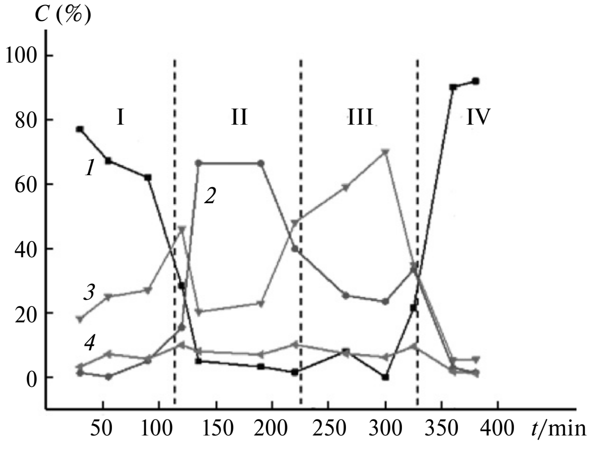

Fig. 1. Dependences of concentrations of starting ethanol (*1*), $HSi(OEt)_3$ (*2*), $Si(OEt)_4$ (*3*) and condensation products (*4*) on the reaction time (see Table 1, run *2*).

amount of $Si(OEt)_4$ is formed. Evidently, it is due to the presence of Cu^0 which catalyzes conversion of $HSi(OEt)_3$ into $Si(OEt)_4$ (see Scheme 1, equation 2), in the contact mass at the beginning of the synthesis, The peak of the reaction falls on period II (see Fig. 1), for which the maximum concentration of $HSi(OR)_3$ is observed, indicating the minimum content of inactive copper during this period. At stages II and III, the ethanol content in the distilled mixture approaches 0%. However, tetraethoxysilane becomes a predominant product over time. It is because of accumulation of deactivated Cu^0. In period IV, the reaction stops as it follows from the increase in the ethanol concentration to 100%. The concentration of condensation products remains invariable during the whole process since their formation, obviously, does not depend on the contact mass activity in different periods of the reaction.

Thus, the developed method for preparation of alkoxysilanes ensures high efficiency of the direct synthesis with ethanol, as evidenced by practically complete conversion of the alcohol at stages II and III of the process. It should be emphasized that under the used conditions, $HSi(OEt)_3$ is formed without addition of alkyl chlorides or HF during the process.

Performed trial evaluative experiments showed that the process of the mechanochemical synthesis of alkoxysilane can be controlled through a series of parameters, which determine rate, efficiency and completeness of transformations in the course of mechanoactivation. The following parameters can be attributed to the control parameters: the volume ratio of silicon and grinding bodies, total mass of the grinding bodies, dispersion of the grinding bodies, the ratios between the grinding bodies of different sizes in their polydisperse mixture, and the supplied energy, which is associated with the acceleration created at different frequencies and amplitudes of vibrations.

Experiments showed (Table 1, runs *1—4*) that an increase in contact mass loading (i.e., the change in the ratio between volumes of the silicon under the treatment and grinding bodies) from 12 to 60 g did not resulted in a significant reduction in the silicon conversion and selectivity with respect to triethoxysilane. The experiment duration increased in proportion to the load and amounted to 12 h. A further increase in the mass of the initial components to 120 g led to the reduction in the silicon conversion to 40% and selectivity to 17%.

In the course of further optimization carried out by varying the control parameters listed above, it was found that the selectivity of the process and the silicon conversion are affected by the dispersion of grinding bodies (see Table 1, runs *1* and *5*). As seen from the data of Table 1, the selectivity with respect to $HSi(OEt)_3$ increased from 36 to 54% when 1000 balls of 5 mm in diameter (see Table 1, run *5*) were used instead of two larger grinding balls of 40 mm in diameter (run *1*). Simultaneously, silicon conversion also increased. Perhaps, this effect is related to an increase in the number of points of contact (the number of contacts) between grinding bodies. Since mechanoactivation takes place at these points, its efficiency rises with the increase in their number.

The best result was obtained by the increase in the vibration acceleration (see Table 1, run *6*). In this case, almost complete conversion of silicon was achieved while maintaining the same high selectivity with respect to triethoxysilane. The reaction time was reduced to 4 h. The possible reason of this effect is that the increase in acceleration determines the larger number of collisions between grinding bodies per unit time.

The proposed by us mechanochemical method for the direct synthesis of alkoxysilanes enlarges the number of control parameters affecting the process rate, silicon conversion, and selectivity with respect to $HSi(OEt)_3$. For a full assessment of the influence of the control parameters on the nature and completeness of the process, it is necessary to know what are the characteristics, including dispersion, of silicon grains, with which alcohol preferably reacts at any time during the process. In future, we plan to study kinetics of dry (without an addition of alcohol) grinding, *i.e.*, mechanoactivation, to obtain granulometric composition of mechanically activated silicon with an interval of 5—10 minutes in a wide amplitude-frequency range at different ratios of masses of silicon and grinding bodies with the use of mono- and polydisperse grinding bodies at different degrees of filling the working chamber. This will establish

Table 1. Effects of control parameters on the production of triethoxysilane at $T = 250$ °C

Run	Vibrational acceleration, *g*	Loading Si/CuCl /g	Diameters and amounts of grinding bodies*, mm (pcs.)	Conversion of Si (%)	Selectivity to $HSi(OEt)_3$ /$Si(OEt)_4$ (%)	Time of reaction /h
1	7.5	10/2	10(500)+40(2)	65	36/64	5
2	7.5	20/4	10(500)+40(2)	63	38/62	6
3	7.5	50/10	10(500)+40(2)	50	41/59	12
4	7.5	100/20	10(500)+40(2)	40	17/83	17
5	7.5	10/2	5(1000)+10(500)	77	54/46	5
6	19	10/2	5(1000)+10(500)	90	50/50	4

a causal relationship between the control parameters and the final result of the mechanochemical synthesis.

Thus, we proposed a mechanochemical method for realization of the direct synthesis of alkoxysilanes in a vibro-boiling layer. It has been shown that the process of the direct synthesis of alkoxysilanes is affected by a number of control parameters such as the ratio between the contact mass and the mass of grinding bodies, the sizes of grinding bodies and their ratios in their polydisperse mixtures, and energy supply. The performed optimization of these parameters made it possible to obtain $HSi(OEt)_3$ with the 50% selectivity at the 90% silicon conversion without the use of promoters.

Experimental

Triethoxysilane (97%) and tetraethoxysilane (>97%) were employed as standards for GLC. These compounds and CuCl («Acros», >97%) were used without additional purification. Silicon KR-1 (98%; impurities: 0.7% Fe, 0.7% Al, 0.6% Ca; characteristic size is 140 μm) was subjected to a preliminary treatment with an aqueous solution of HF to remove the oxide layer. Ethanol was dried before the use over CaH_2 and kept over 3 Å molecular sieves; the final water content was less than 200 ppm.

The reactor for the synthesis of alkoxysilanes[24,28] consisted of a cylindrical working chamber installed on a vibrodrive. Hermetic working chamber of 1l in volume was made of pipe brass L59. It was filled by 70% with spherical grinding brass bodies of 5, 10 and 40 mm in diameter taken in different ratios with total mass of 2850 g. The working chamber was equipped with a heater, thermocouple, inlet and outlet pipes.

Product analysis. Samples were analyzed on a Crystal Lux-4000M chromatograph equipped with a catarometer at 50—280 °C, 20 degree min^{-1}, column (2 mm×2 m) with 5% SE-30 on Chromaton-N-AW-HMDS as a stationary phase. Helium (30 ml min^{-1}) was used as a carrier gas. The data were processed using the NetChrom 2.0 program.

NMR spectra were recorded using BrukerAvance III HD 400 NMR spectrometer (Germany), operating frequencies are 400 and 79 MHz for ^1H and ^{29}Si nuclei, respectively. Tetramethylsilane was used as an internal standard, $CDCl_3$ was used as a solvent. Spectra were processed with the use of the Mestrenova program.

Experiment conducting. A specified amount of the contact mass prepared by the reaction between Si and CuCl at 300 °C was loaded in the working chamber. The reactor was heated to 250 °C. Then vibrodrive was turned on, and ethanol was supplied into the chamber by a high pressure pump at a rate within 0.4—0.7 ml min^{-1} at a given vibrational acceleration in the range from 7.5 to 19*g*. The formed products of the reaction between silicon and ethanol were passed through a condenser to a receiver. Sampling and analysis of the samples of volatile products were carried out every 30 min. Conversion (*K*) and selectivity (*S*) were calculated by the following formulas:

$$K_{Si}(\%) = (n/n_{Si}) \cdot 100,$$

$$S(\%) = (n_{Si\text{-}prod}/n_{Si}) \cdot 100,$$

where n is the amount of the reaction products (mol), n_{Si} is the amount of used silicon (mol), $n_{Si\text{-}prod}$ is the amount of the silicon-containing product (mol).

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