Supplementary information

Mechanochemistry – a new powerful green approach to direct synthesis of alkoxysilanes

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1. Materials.

Technical-grade silicon KR – 1 (1000 – 2000 μ m, purity >98 %, impurities Fe < 0.7 %, Al < 0.7, Ca < 0.6 %) was used. Ethanol and methanol were purified by distillation over CaH₂ and then stored over molecular sieves, 3 Å. The water of the alcohols was less than 200 ppm. The reactor and grinding bodies were made of Brass L-59 (composition: Fe <0.3%, P < 0.01%, Cu 57 – 60%, As <0.01%, Pb <0.5%, Zn 39.1 – 43%, Sb <0.01%, Bi <0.003%, Sn <0.2%)

2. Methods and Analysis.

GC analysis was performed on a chromatograph (Crystallux 4000, Russia) at 50-280 °C, 20°/min; detector – katharometer, columns ($2 \text{ mm} \times 2 \text{ m}$) with 5 % SE-30 stationary phase deposited onto Chromaton-N-AW-HMDS, helium as a carrier gas (60mL/min). Data were detected and processed using the «NetChrom 2.0» program packages (Crystallux, Russia).

Scanning Electron Microscope - Energy-dispersive X-ray spectroscopy (SEM-EDX). Target-oriented approach was utilized for the optimization of analytic measurements.¹ Samples were mounted on a 25 mm aluminum specimen stub and fixed by graphite adhesive tape before measurements. Metal coating with a thin film (20 nm) of platinum was performed using magnetron sputtering method as described

earlier.² The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 2-10 kV accelerating voltage and at working distance 8-10 mm. The morphology of the samples was studied taking into account possible influence of metal coating on the surface.² EDX-SEM studies were carried out using Oxford Instruments X-max 80 EDX system.

X-ray powder diffraction (PXRD) was measured using Bruker D8 Advance $(\lambda(CuK\alpha) = 1.5418 \text{ Å}, \text{ Ni filter, Bragg-Brentano geometry)}$ diffractometer. The patterns were Rietveld refined using TOPAS 5 software. The crystalline size was calculated from broadening of the Lorentzian component of the peak profile.

X-ray photoelectron spectroscopy (XPS). The XPS spectra were measured on an Axis Ultra DLD spectrometer (Kratos Analytical) using a monochromatic AlK α source (1486.6 eV, 150 W). The spectrometer was operated in fixed analysis energy mode, with a pass energy of 20 eV for high resolution spectra and 160 eV for survey spectra. The photoelectron spectra were recorded with a step of 0.1 eV. The size of the analyzed area was about 300x700 µm². The energy scale of spectrometer was calibrated according to the standard procedure with respect to Au 4f_{7/2}, Ag 3d_{5/2}, and Cu 2p_{3/2} photoelectron peaks of pure metals at 83.96, 368.21 and 932.62 eV, respectively. The surface charging effect in the spectra was compensated against the C–H state in the C 1s spectra with the energy assumed to be 285.0 eV. The measurements were carried out at a pressure of 10⁻⁸ Torr at room temperature. Quantitative surface chemical analyses were calculated from the high-resolution core-level spectra, following the removal of a non-linear Shirley background.

NMR spectra were recorded on a Bruker AvanceTM 600 spectrometer (Germany) operating at 600.22, 150.93 and 119.26 MHz for ¹H, ¹³C and ²⁹Si respectively and Bruker Avance-III HD 400 spectrometer (Germany) operating at 400, 101 and 79 MHz for ¹H, ¹³C and ²⁹Si respectively. Spectra were recorded a spectrometer using chloroform-d. The chemical shifts for ¹H and ¹³C were indirectly referenced TMS via the solvent signals. The chemical shifts for ²⁹Si were measured with TMS as an external standard.

3. Experimental

Description of the reactor. The laboratory version of the developed vibrational reactor is shown in **Figure-s1**. It consists of a cylindrical working chamber-1, equipped with an electric heater-2, a thermocouple-3, a thermal sensor-4, an input-5 and output - 6. The hermetically working chamber volume - 1 liter chamber is made of brass of grade L59 and is filled with 70% brass grinding bodies of spherical shape with a dispersion of 5 mm (1000 pcs.) - 7 and 10 mm (500 pcs.) - 8, the total mass of 2850 g. It was mounted horizontally on the frame vibratory drive - 9.

The design of the eccentric self-centering vibrational drive of the apparatus excludes the transfer of dynamic loads to the foundation, provides the possibility of working in a wide amplitude-frequency range with adjustable parameters of oscillations of the working element that are adjustable and independent of the mass to be attached.





Description of experiment. An amount of 10 g (0.36 mol) of silicon was loaded in the reactor 1. Then the reactor was heated to 250 °C. Before the reaction, the silicon mass was grinded at 7.5 g, during 1 h. After that alcohol was added in the reactor by high-pressure pump 10 at flow rate 0.4 ml/min. The volatile products were condensed in condenser 11, and were collected in collector 12. The necessary acceleration was provided by the vibro-drive unit. During the process, at certain time intervals samples were taken through the sampler 13. Observation of the course of the experiment was performed by GC. The process was stopped when the production of silicon containing products in the samples was undetectable.

Silicon conversion and selectivity were estimated as follows:

Silicon conversion (%) =
$$\left[\frac{\text{Amount of product (mol)}}{\text{Sum of amount of silicon containing products (mol)}}\right] \times 100$$

Selectivity (%) = $\left[\frac{\text{Sum of amount of silicon containing products (mol)}}{\text{Amount of silicon charged into the reactor (mol)}}\right] \times 100$

4. PXRD – data



Figure s2. The experimental (blue line) and calculated (red line) powder patterns for *spent mass* and their difference (grey curve). Small ticks indicate calculated positions of the peaks.



Figure s3. The experimental (blue line) and calculated (red line) powder patterns for *initial silicon* and their difference (grey curve). Small ticks indicate calculated positions of the peaks.





Figure s4. Survey spectrum of the *initial silicon*.



Figure s5. Survey spectrum of the *spent mass* after reaction.

 Table s1. Samples composition determined from the survey spectra.

Sample	Cu, at.%	Zn, at.%	C, at.%	O, at.%	Ca, at.%	Si, at.%
Initial silicon	0.14	0.25	23.82	47.82	0.26	27.72
Spent mass after reaction	1.25	5.66	37.87	42.60	0.08	12.55

Table s2. Samples composition determined from the high-resolution spectra.

Sample	Cu, at.%	Zn, at.%	C, at.%	O, at.%	Si, at.%
Initial silicon	0.13	0.24	22.90	42.82	33.92
Spent mass after reaction	1.18	6.35	37.70	40.62	14.14

Fig. s6 shows the C 1s and Si 2p photoelectron spectra of the samples investigated. The spectra noticeably differ in line shapes that reflects different relative contribution of carbon-containing groups and chemical states of Si atoms.



Figure s6. The C 1s and Si 2p photoelectron spectra of the samples investigated.

In order to determine the relative amounts of carbon-containing groups and the chemical states of Si atoms curve-fitting procedure based on chemical shifts measured by Beamson and Holliger were used.^{3,4} **Figures 7-10** show fitting the C 1s and Si 2p with some Gaussian profiles and **Table s3** presents their characteristics.

Table s3. Binding energies and relative concentrations of the carbon-containing groups and silicon states.

		C-Si	C-	C-O-	C=O	C(O)	Si ⁰ ,	Si ⁰ ,	Si ⁺	Si ³⁺	Si ⁴⁺
			С/С-Н	C		0	Si2p _{3/}	Si2p _{3/2}			
				/C-			2				
				OH							
Initial	BE	285.0	286.5	288.0	289.4	98.95	99.56	100.8	102.5	I _{rel}	I _{rel}
silicon	,	0	5	3	9			2	7		
	eV										
	I _{rel}		0.74	0.18	0.05	0.03	0.57	0.28	0.06	0.09	15000
Spent	BE	284.0	285.0	286.5	288.0	289.2	98.71	99.32	100.5	101.1	103.1
mass		5	0	8	3	0			6	1	4
after											
reactio											
n											
	Irel	0.11	0.57	0.27	0.03	0.03	0.21	0.10	0.12	0.56	14500



Figure s7. Fitting the C 1s spectrum of the *initial silicon*.



Figure s8. Fitting the C 1s spectrum of the *spent mass* after reaction.



Figure s9. Fitting the Si 2p spectrum of the *initial silicon*.



Figure s10. Fitting the Si 2p spectrum of the spent mass after reaction.

Figure s11 shows the Cu 2p photoelectron spectra, which differ in both line shapes and positions of the main peaks.

The satellite at binding energy of ~943 eV in the spectrum of initial silicon is an indicator of Cu²⁺ state. In order to determine its relative content we used the Cu 2p spectrum of CuO, normalized by the satellite intensity as shown in **Figure s12**. The relative area under Cu²⁺ state in the Cu 2p spectrum is 0.36 and the binding energy of the Cu $2p_{3/2}$ is 934.48 eV. This binding energy is more than those presented in **Table s4** for CuO and may be assigned both size effect in photoelectron spectra and CuSiO₃ phase.⁴



Figure s11. The Cu 2p photoelectron spectra of the samples investigated.



Figure s12. Evaluation of Cu²⁺ state content in the Cu 2p *initial silicon*.

Comparative analysis of the Cu $2p_{3/2}$ line shape of spent mass after reaction shows that the spectrum may be fitted with three peaks at binding energies of 932.36, 933.00, 934.25 eV with intensity ratio of 0.79/0.05/0.15. As in case of sample initial silicon, the binding energies 934.25 and 934.42 eV should be assigned to CuO. The peak at 933.00 eV, may be assigned either to Cu nanoparticles because of positive chemical shift by 0.33 eV or, on the other hand, to Cu-Zn alloy. At low Cu content in Cu-Zn alloy the shift of Cu $2p_{3/2}$ peak may be as large as +0.8 eV and it is not broadened as in the case of size effect. The related shift of the Zn $2p_{3/2}$ is -0.3 eV. Zn–Cu alloy formation induces increase in the binding energy of Cu core-level and valence electrons and decrease in the binding energy of Zn.⁴ In our case, according to the quantification data for the spent mass after reaction, the Cu/Zn ratio is 0.19 and Zn $2p_{3/2}$ peak is shifted to lower binding energy region. Therefore, the hypothesis on formation of Zn–Cu alloy is more preferable.



Figure s13. Fitting the Cu $2p_{3/2}$ spectrum of the *spent mass* after reaction.

Fig. s14 displays the Zn $2p_{3/2}$ photoelectron spectra of initial silicon and spent mass after reaction. The spectra have similar line shapes but different binding energies of the Zn $2p_{3/2}$ peaks - 1022.27 and 1021.96 eV, respectively. The binding energies presented above can be assigned to ZnO. ^{5–7}



Figure s14. The Zn $2p_{3/2}$ photoelectron spectra of the samples investigated.

However, it is well known that Zn 2p peaks are not very sensitive to chemical state of zinc atoms,⁸ while LMM Auger peaks are more sensitive to the chemical environments. **Fig. 15** shows the LMM Auger spectrum of the sample studied.

The detailed analysis shows that two states are presented in the Auger spectra. For the spent mass after reaction the binding energies of the Auger peaks are 499.47 and 496.31 eV. Related modified Auger parameters are 2009.13 and 2011.79 eV. The first value 2009.13 eV can be assigned to ZnO (see Table 4), while the second one doesn't correspond to Zn⁰ nor to a possible CuZn alloy (Auger parameter is 2014.30 eV) and can be assigned to ZnO_x.^{5,6} The relative content of ZnO component in the Auger spectra is 0.64.



Figure s15. Fitting the Zn LMM Auger spectrum of *spent mass* after reaction with Gaussian components.

	Cu	Cu	Cu AP,	Zn 2p _{3/2}	Zn	Zn AP,	Ref.
	$2p_{3/2}$	LMM,		eV	LMM,		
	eV	eV	eV		eV	eV	
ZnO						2009.50-	5
						2011	
				1021.75	988.5	2010.25	9
				1021.9	988.3	2010.2	7
Zn ⁰						2013.40-	5
						2014.40	
				1021.8	992.1	2013.9	9
				1021.89	992.1	2013.99	9
Cu64Zn36	932.6	918.6	1851.20	1021.60	992.7	2014.30	9
Cu53Zn47	932.7	918.9	1851.6	1022.0	992.2	2014.2	10
Cu75Zn25	932.7	918.9	1851.6	1022.0	992.2	2014.2	10
CuO						1851.45	5
	933.7	918.3				1852.0	9
	933.75	918.3				1852.05	11
	934.1	917.7				1851.8	12
	933.7	917.8				1851.5	10
Cu ₂ O						1848.6-	5
						1849.6	
	932.5	916.6				1849.1	12
	932.5	916.0				1848.5	10
	932.5	916.2				1848.7	9
	932.5	916.6				1849.1	9
	932.7	916.2				1848.9	13
	932.8	915.9				1848.7	14
	932.9	916.3				1849.2	15
Cu ⁰						1850.7-	5
						1851.4	
	932.6	918.6				1851.2	9
	932.6	918.7				1851.3	9
	932.7	918.6				1851.3	9
	932.7	918.2				1850.9	13
	933.1	917.5				1850.6	11

Table s4. Characteristics of Сии Zn photoelectron and Auger spectra.

 $Cu AP = Cu 2p_{3/2} + Cu LMM$, $Zn AP = Zn 2p_{3/2} + Zn LMM$

Alternatively the data may be presented in terms of the Auger parameter α , which is defined as

 α = BE Cu 2p_{3/2} + KE ~Cu L₃M_{4,5}M_{4,5}

Size effect¹⁶



Figure s16. ¹H NMR (400 MHz, CDCl₃) spectrum of mixes products of reaction silicon with MeOH



Figure s17. ¹³C NMR (101 MHz, CDCl₃) spectrum of mixes products of reaction silicon with MeOH



Figure s19. ¹H NMR (600.22 MHz, CDCl₃) spectrum of mixes products of reaction silicon with EtOH



Figure s21.²⁹Si NMR (119.26 MHz, CDCl₃) spectrum of mixes products of reaction silicon with EtOH

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