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Production of Amorphous Silicon Dioxide Derived from Aluminum Fluoride Industrial Waste and Consideration of the Possibility of Its Use as Al₂O₃-SiO₂ Catalyst Supports

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Abstract: This paper presents the results of the study on the development of a methodology for the production of pure amorphous silicon dioxide containing up to 99.8 wt.% of SiO₂. As a starting material, a silica gel with a moisture content of up to 55 wt.% and an SiO₂/AlF₃ ratio of 4 was used. The silica gel was purified using alkaline and acidic solutions in concentrations ranging from 0.1 to 25 wt.%. The analysis of the experimental data allowed to identify the most suitable purification parameters of the starting material. The initial silica gel and the reaction products were studied using the methods of X-ray fluorescence, X-ray phase analysis, electron scanning microscopy, EDS microanalysis, and particle-size analysis. Amorphous silicon dioxide obtained according to the methodology developed by the authors forms agglomerates of spherical silicon dioxide particles up to 1 µm in size. Amorphous silicon dioxide was involved in the preparation of catalyst supports in order to consider the possibility of replacing part of the expensive raw material in the form of aluminum hydroxide. In the work, the characteristics of the addition of this amorphous silicon dioxide and the supports obtained from the traditionally used raw materials were evaluated.

Keywords: silica gel; amorphous silicon dioxide; aluminum fluoride; electron scanning microscopy

1. Introduction

Silicon dioxide or silica, existing today both as a natural and synthetic material, is required in many industries which are given further [1–3]. Materials that contain silicon dioxide are classified according to their SiO₂ content and production method. Low-grade stock, mainly sand, containing 45–80 wt.% of SiO₂, is used on a large scale in the construction of road pavement and in cement [4]. Other demanded materials, containing more than 95 wt.% of SiO₂ are classified into four main categories [5].

Precipitated silicon dioxide with a content of SiO₂ ranging from 60 to 90 wt.%, obtained by precipitation of a sodium silicate solution with mineral acids [6–8], with the possible addition of surfactants [9,10]. It is mainly used in the production of automotive tires [11], cosmetics and hygiene products, beer, and in the paint and varnish industry [12,13].

Pyrogenic (fumed) silica, containing about 99.5 wt.% of SiO₂ and obtained by vapor-phase hydrolysis of SiCl₄ [14,15] in a hydrogen/air flame at 1150–1200 °C. It has remarkable adsorption properties [7] and a wide scope of application in the construction (production of silicates, sealants, varnishes, and insulating materials) [16], pharmaceutical (manufacture of tablets and aerosols), and cosmetic (manufacture of lotions, creams, and

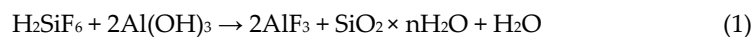
powders) sectors. The global production of pyrogenic silica amounted to 661 thousand tonnes in 2019 with the forecast for 2025 of 927 thousand tonnes [17].

Silica gels are hydrated nanoporous systems [18,19], mainly used as adsorbents in the purification and drying of industrial gases and liquids, removal of high polymer resinous substances from oil, gas chromatography, and as cat litter box fillers.

Silica fume (microsilica) is a by-product from the production of silicon. Silica fume is used mainly as an admixture to concrete.

High-purity silicon dioxide is also used for the production of specific materials, such as fused silica, which is the main material in the manufacture of optical fibers and specialized dishes for processing semiconductors and solar cells [20]. Amorphous silica is used as a sorbent and rarely as a component of supports or catalysts. The total volume of world exports of silica exceeds 2.5 billion U.S. dollars (according to data from 88 countries). The world leaders in the export of silicon dioxide are China, Germany, and the European Union. Hence, considering a high demand in various industry segments, silica is a valuable raw material and is currently produced using different technologies that depend on the field of application [21,22].

On the other hand, it is known that, at present, a by-product (waste) from the production of aluminum fluoride [23,24] and the processing of fluorapatite raw materials is silica gel [6,25–27]. The production of aluminum fluoride is based on the reaction of fluorosilicic acid (H_2SiF_6) with aluminum hydroxide according to the following chemical equation:



As a result of the reaction, a supersaturated solution of aluminum fluoride and a precipitate of hydrated silicon dioxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), called silica gel, are formed. The supersaturated solution of aluminum fluoride is relatively stable, which makes it possible to separate it from the silica gel on a filter until the moment when crystals of aluminum fluoride trihydrate ($\text{AlF}_3 \times 3\text{H}_2\text{O}$) begin to precipitate from it. According to regulations, the moisture content of silica gel concentration should be no more than 55 wt.%. Additionally, silica gel should contain no more than 0.8 wt.% of free silicofluoric acid.

At present, this waste is not being recycled and is accumulating in dumps [28]. Each year, the production of aluminum fluoride results in 40 thousand tonnes of silica gel (0.36 tonnes of pure SiO_2 per 1 tonne of aluminum fluoride) [29]. Silica gel industrial use until now has been poorly understood. It has been proposed to use silica gel for the production of sodium silicate solution, ceramics [30], zeolite NaA [31–33], calcium silicate [26], admixtures for cement [34,35], and clay [36]. However, amorphous silicon dioxide itself is of particular value. All the available studies do not pay attention to the initial state of silicon dioxide in silica gel. In this field, there are no data on the methods of obtaining pure silicon dioxide from this raw material, which could be used in many industries. At the time of obtaining materials such as zeolite or liquid glass from silica gel by methods that are known today, no special attention is paid to the issue of purification of silica gel, and the synthesis is carried out in the presence of all impurities.

In the conventional production processes for materials like zeolite or liquid glass from silica gel, the purification of silica gel is not taken into account, and the synthesis is carried out with a high amount of impurities. Therefore, this work is devoted to two tasks.

The first part of the work is to study the initial waste from the production of aluminum fluoride, namely silica gel, and the consideration of options for its treatment with acidic and alkaline agents. The chosen purification method was based on previously known studies. For example, in [35], by means of acid treatment of ferrosilicon, not the silicon dioxide, but pure silicon with an increased Si content was obtained (from 83.95 wt% to 99.999 wt%).

The second part of the work was to consider the possibility of using amorphous silicon dioxide obtained from silica gel as a raw material for $\text{Al}_2\text{O}_3\text{-SiO}_2$ type catalyst supports' production. Currently, there is not a single study describing the use of treated or

untreated waste from the production of aluminum fluoride as a catalyst or support component. However, it is known that certain wastes containing large amounts of silica and alumina are now considered in the preparation of catalyst supports. Thus, in [37], a broad review of the proposed types of waste was carried out. The main sources of these wastes are metallurgical enterprises, drill cuttings, glasses of various production, construction waste, ash from various technological processes, as well as spent catalysts from oil refining and petrochemistry.

Therefore, the second part of the work, which is the capability assessment of using amorphous silicon dioxide obtained from production waste as a raw material for the production of catalyst supports, is a very interesting issue from the catalysis point of view. Of greatest interest in this area is the assessment of the paste formability at various SiO_2 contents in the initial batch mixtures, as well as the consideration of the main operational properties of the obtained supports.

2. Materials and Methods

2.1. Materials

A silica gel with a 55 wt.% moisture content, obtained from an aluminum fluoride production enterprise (Russia), was used. For the leaching solutions' production, the following chemically pure commercial reagents were used: hydrochloric acid (chemically pure), as per State All-Union standard 3118-77, with an HCl concentration of 36% wt.; sulfuric acid (chemically pure), as per State All-Union standard 4204-77, with a concentration of H_2SO_4 95% wt.; and the granules of sodium hydroxide (chemically pure), as per State All-Union standard-4328-77. Acid solutions for leaching were prepared in the concentration range from 0.1 to 1.0 wt.%, and sodium hydroxide solutions with concentrations from 0.5 to 25.0 wt.%.

2.2. Methods

The leaching operation was carried out using an HEL series reactor system with constant temperature and stirring speed control. The morphology of the obtained sediments was analyzed using a TESCAN Vega 3 scanning electron microscope. The images of the samples were obtained in the secondary electron mode using an SE detector. The accelerating potential was 20 kV and emission current was 120 μA . The acceleration potential used was 15 kV. The data on the specific surface area of the samples were obtained by the method of low-temperature adsorption of liquid nitrogen on a NOVA3200e specific surface area analyzer. For the phase analysis, a Shimadzu XRD-700 powder X-ray diffractometer with $\text{CuK}\alpha$ radiation was used. Horiba LA 950 laser analyzer was used for the particle size distribution analysis. The chemical composition of the obtained powder samples was carried out by X-ray fluorescence analysis on an ED-2000 Oxford EDS spectrometer. The leaching was carried out using an HEL series reactor system with constant temperature and stirring speed control. The supports samples were obtained by means of the conventional technology from solid pastes according to the industrial scheme of the following sequence stages: mixing the aluminum hydroxide (binding agent) with the resulting amorphous silicon dioxide and peptizer to obtain plastic pastes, molding them on a laboratory-scale plunger press (through dies with a 5.0 mm diameter) into pellets, followed by cutting into cylindrical granules, their drying in ambient conditions, and heat treatment at final temperatures from 500 to 1150 $^\circ\text{C}$.

3. Experimental

A-set samples. In this experiment, the starting silica gel was dried at 95 $^\circ\text{C}$. Placed in a reactor with a stirrer, a solution of hydrochloric acid with a 0.1 to 1.0 wt.% concentration at a liquid/solid ratio of 10 was fed in parallel. The pulp was cured for 1 h, then the solid phase was separated from the mother liquor using vacuum filtration. The solid phase was washed from the mother liquor using hot distilled water until a controlled pH value of

about 7 was reached. The resulting wet precipitate was dried in air for 48 h and at a temperature of 95 °C for 10 h.

B-set samples. In this experiment, the starting silica gel was dried at 95 °C. Placed in a reactor with a stirrer, a solution of sulfuric acid with a concentration from 0.1 to 1.0 wt.% at a liquid/solid ratio of 10 was fed in parallel. The pulp was cured for 1 h, then the solid phase was separated from the mother liquor using vacuum filtration. The solid phase was washed from the mother liquor using hot distilled water until a controlled pH value of about 7 was reached. The resulting wet precipitate was dried in air for 48 h and at a temperature of 95 °C for 10 h.

C-set samples. In this experiment, the starting silica gel was dried at 95 °C. Placed in a reactor with a stirrer, a sodium hydroxide solution with a 0.1 to 25 wt.% concentration at a liquid/solid ratio of 10 was fed in parallel. The pulp was cured for 1 h, then the solid phase was separated from the mother liquor using vacuum filtration. The solid phase was washed from the mother liquor using hot distilled water until a controlled pH value of about 7 was reached. The resulting wet precipitate was dried in air for 48 h and at a temperature of 95 °C for 10 h.

4. Results and Discussion

4.1. Silica Gel Purification

The starting dried silica gel was a white powder. The components' contents in dried silica gel are presented in Table 1.

Table 1. Chemical composition of dehydrated silica gel.

Component	SiO ₂	AlF ₃	H ₂ O	SO ₃	Cl ⁻	CaO	Fe ₂ O ₃	K ₂ O
Content, wt.%	76.35	20.50	3.00	0.08	0.02	0.03	0.01	0.01

Figure 1 shows the X-ray diffraction pattern of the starting silica gel; all peaks present on the X-ray diffraction pattern were attributed to aluminum fluoride. The X-ray diffraction pattern does not show peaks inherent in crystalline silicon dioxide and, therefore, all silicon dioxide present in the silica gel is X-ray amorphous, which indicates the value of this material for further use in catalysis when creating SiO₂-Al₂O₃ systems.

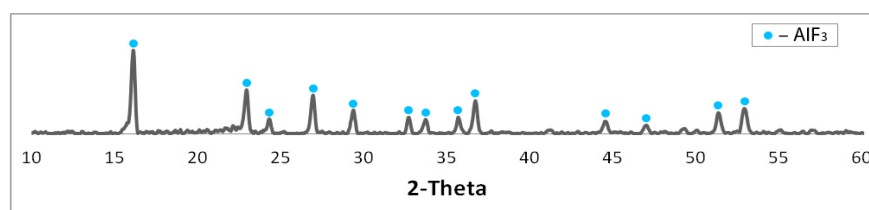


Figure 1. XRD of dried silica gel.

The results of morphological studies showed that the starting silica gel contained elongated aluminum fluoride particles up to 10 µm, whereas the silicon dioxide itself formed agglomerates of spherical particles up to 1 µm (Figure 2). The initial form of silicon dioxide particles is close to the morphology of silicon dioxide obtained by precipitation of sodium silicate with sulfuric acid.

To remove unwanted impurities, a series of experiments was carried out to purify the dried waste. Table 2 summarizes the leaching process parameters.

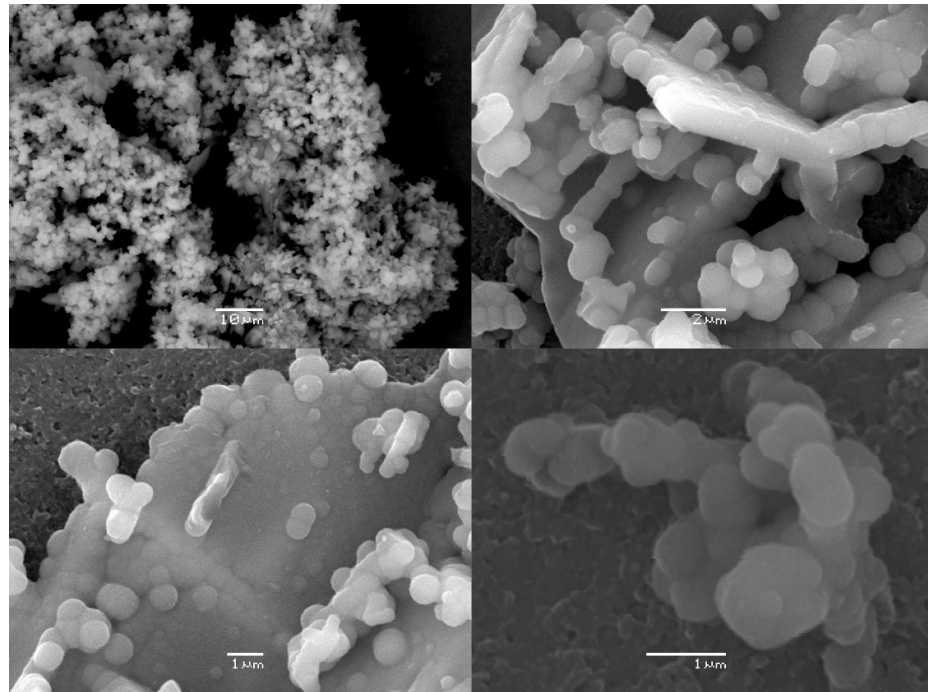


Figure 2. The morphology of the starting silica gel after drying.

Table 2. Parameters of the leaching process.

Sample Index	Change in Mass of the Solid Phase after Leaching, %	Reagent Name	Reagent Concentration, %	Liquid-to-Solid Ratio
1A	9	NaOH	0.5	10
2A	10		1.0	
3A	68		5.0	
4A	74		10.0	
5A	85		25.0	
1B	30	HCl	0.1	
2B	31		0.2	
3B	31		0.5	
4B	31		1.0	
1C	32	H ₂ SO ₄	0.1	
2C	32		0.3	
3C	32		0.5	
4C	32		1.0	

Leaching temperature—100 °C, Leaching time—1 h.

After the leaching, the removal of the main impurity elements led to a change in the mass of the solid phase. The dried product after leaching, on average, changed its weight from 9 to 32%. The use of low-concentration alkaline solutions of sodium hydroxide with a concentration of 0.5% did not allow to remove fluoride ions to a sufficient extent. Increasing the concentration to 1.0% gave better results; however, the sediments contained significant concentrations of sodium ions that are difficult to remove. Increasing the concentration above 1.0% led to significant solid phase losses during leaching, attributed to the transition of silicon into solution with the formation of a sodium silicate solution. The treatment of dried silica gel with the solutions of mineral acids gave better results. The analysis showed that, at a concentration of sulfuric acid starting from as low as 0.1 wt.%,

and a concentration of hydrochloric acid starting from 0.2 wt.%, the amounts of fluorine ions and aluminum compounds in the obtained samples decreased significantly. The data of X-ray fluorescence analysis of obtained samples are presented in Tables 3–5.

Table 3. Chemical composition of samples after treatment with sodium hydroxide.

Component	Content of Components in Silica Gel after Processing, %		
	1A (NaOH—0.5 wt.%)	2A (NaOH—1.0 wt.%)	3A (NaOH—5.0 wt.%)
SiO ₂	77.81	89.30	45.50
Al ₂ O ₃	7.25	6.99	22.42
F	11.86	-	-
Na ₂ O	3.08	3.71	15.00

Table 4. Chemical composition of samples after treatment with hydrochloric acid.

Component	Content of Components in Silica Gel after Processing, %			
	1B (HCl—0.1 wt.%)	2C (HCl—0.3 wt.%)	3C (HCl—0.5 wt.%)	4C (HCl—1.0 wt.%)
SiO ₂	97.35	98.85	99.23	99.61
Al ₂ O ₃	0.84	0.76	0.52	0.35
F	1.79	0.35	0.18	-
CaO	0.02	0.02	0.04	0.02
Fe ₂ O ₃	-	0.02	0.03	0.02

Table 5. Chemical composition of samples after treatment with sulfuric acid.

Component	Content of Components in Silica Gel after Processing, %			
	1C (H ₂ SO ₄ —0.1%)	2C (H ₂ SO ₄ —0.3%)	3C (H ₂ SO ₄ —0.5%)	4C (H ₂ SO ₄ —1.0%)
SiO ₂	98.35	98.73	99.78	99.88
Al ₂ O ₃	0.54	0.27	0.15	0.06
F	1.09	0.96	-	-
CaO	0.02	0.02	0.04	0.02
Fe ₂ O ₃	-	0.02	0.03	0.02

By means of titrimetry and photometry, impurities in the resulting liquid phase were determined. When treated with sulfuric acid, the mother liquor contained the following impurities: aluminum compounds (up to 67% of the total impurities), fluorine (up to 3.55% of the total impurities), silicon (up to 5% of the total impurities), and residual sulfuric acid 23% wt. (in terms of SO₃ from the total amount of impurities). According to the results, as mentioned above, during leaching with sulfuric acid, the aluminum compounds and SO₄²⁻ ions predominated in the mother liquor. The main part of fluoride ions was absent in the mother liquor, which indicates their transition to the gas phase during leaching. The next part of the research is the optimal disposal methods' development for the forming liquid and gaseous wastes in the proposed process.

For the most optimal sample of the amorphous silicon dioxide, the sample obtained in experiment 7 (H₂SO₄—0.1) was taken. This sample required a solution with the lowest concentration of mineral acid for leaching and containing more than 98%wt. of the SiO₂. These conditions with using a lower concentration sulfuric acid solution are environmentally and economically beneficial for mass production of the required purity silica. The product can be successfully implemented as a raw material for sorbents, liquid glass, and low-modulus zeolites. However, as this work was carried out in order to evaluate the use of the obtained amorphous silicon dioxide as a batch component for catalyst support production, a purer sample was used.

The dynamics of the morphological pattern changes during the leaching of silica gel with alkaline and acidic solutions can be traced in Figures 2 and 3.

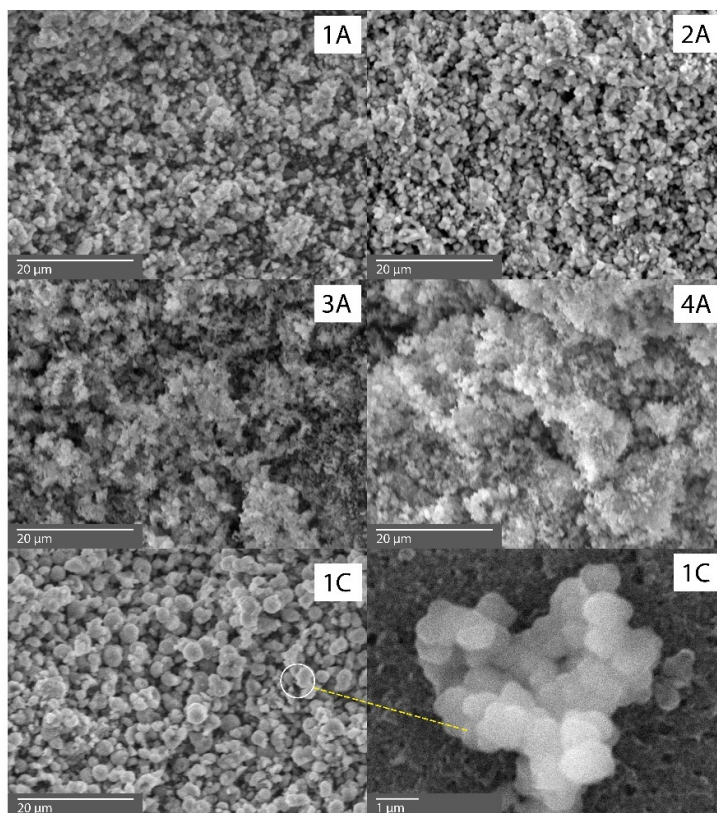


Figure 3. SEM of the samples after treatment of dried silica gel with alkaline (1A–4A) and acidic solutions (1C).

The results of the morphological analysis confirm the data of the microanalysis. In alkaline leaching, the breakdown of silica particles is observed, while inorganic acid leaching does not affect silica particles (Figure 3 (3A,1C)). The resulting silicon dioxide forms agglomerates up to 250 μm in size. A particle size of 2 to 52 μm accounted for the main fraction (Figure 4).

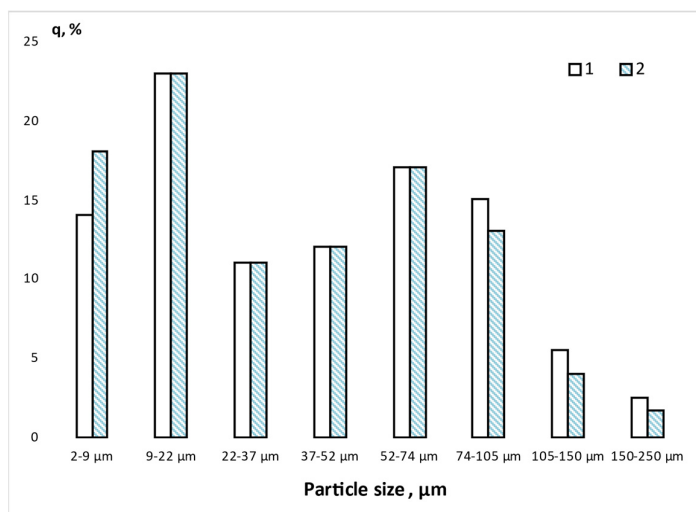


Figure 4. Particle size distribution: 1—starting dried waste (silica gel); 2—silicon dioxide (1C).

According to X-ray phase analysis (Figure 5), the X-ray diffraction patterns had only one broad peak at 23 °C, which corresponds to amorphous silicon dioxide [37]. Based on this, it was determined that the obtained silicon dioxide with up to 99.5% SiO₂ content was completely X-ray amorphous and retained its amorphous state up to the incineration temperature up to 1000 °C, despite that, at a temperature of 800 °C, an insignificant peak of unidentifiable crystalline phase appeared on the X-ray diffraction pattern at 38°, which disappeared again at a temperature of 1000 °C (Figure 5).

Figure 6 shows the characteristic infrared absorptions in the range from 550 to 4000 cm⁻¹. According to IR spectroscopy data, the obtained amorphous silicon dioxide was characterized by typical peaks at 1090 and 806–811 cm⁻¹, responsible for the fluctuations of the Si-O-Si bond. Absorption bands of stretching vibrations of the inner-OH group in the Si-OH bond centered at 460 cm⁻¹ [1,37,38], H-O-H vibrations in the 1500–2000 region, and stretching vibrations of the hydroxyl group of the water molecule in the 3200–3600 cm⁻¹ region were also observed.

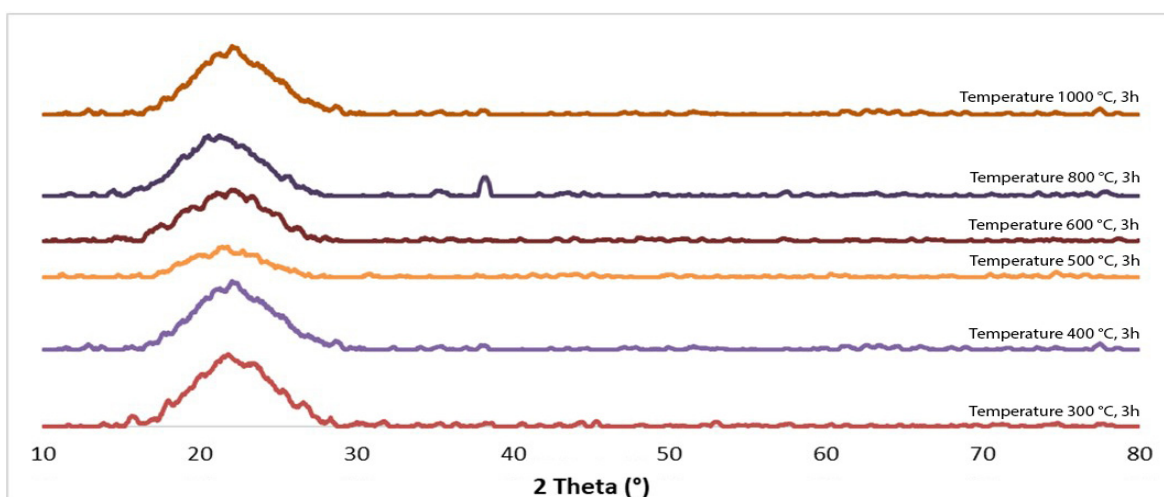


Figure 5. X-ray diffraction patterns of the obtained silicon dioxide (sample 1C) incinerated at temperatures of 300 to 1000 °C.

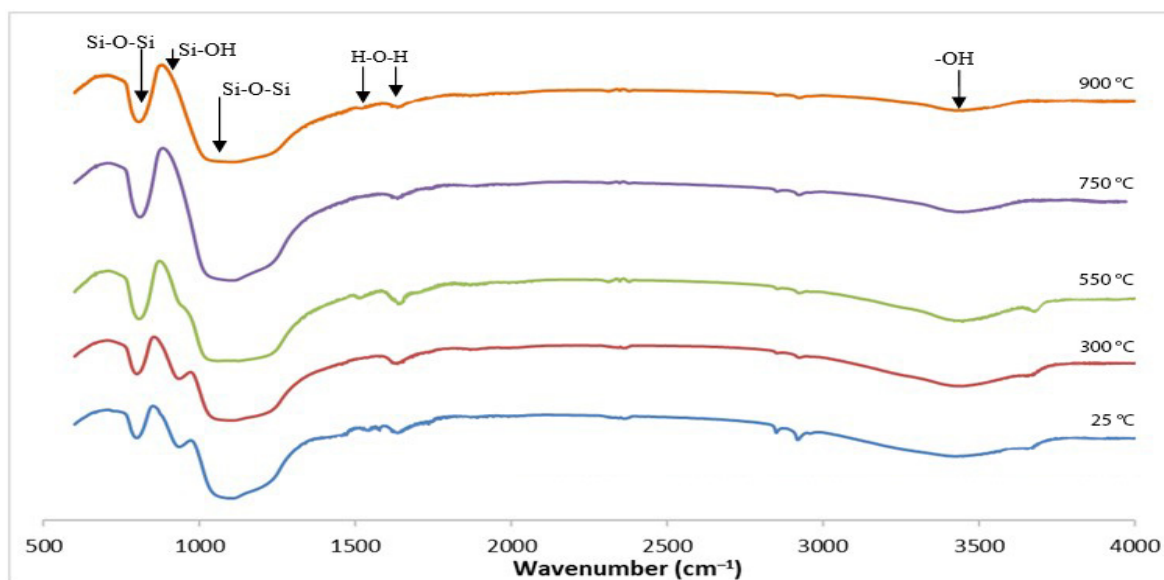


Figure 6. IR absorption spectra of the obtained silicon dioxide (sample 1C) incinerated at temperatures of 300 to 900 °C.

This suggests that the surfaces of the particles mainly contain silanol groups that adsorb water molecules. The presence of Si-OH groups definitely indicates that the obtained silicon dioxide is suitable for use in catalytic processes, as these groups act as Brønsted acid sites. Upon incineration of the samples to 900 °C, the intensity of all characteristic absorption bands decreased, except for the bands corresponding to Si-O-Si bonds.

4.2. Preparation of Catalyst Supports Based on Amorphous Silicon Dioxide

In further studies, a product obtained by purifying silica gel with a solution of sulfuric acid with a concentration of 1.0 wt.%, which is practically pure silicon dioxide with a SiO₂ content of about 99.8 wt.%, was selected. The work studied the possibility of obtaining granular catalyst supports based on a mixture of pseudoboehmite aluminum hydroxide (PAHO) and the resulting amorphous silicon dioxide. Moisture (W) of hydroxide was 14.57 wt.%, while loss on ignition (LOI) was 29.3 wt.%. Using extrusion molding, granules with a diameter of 5 mm were formed with a silicon content of 20 wt.% to 85 wt.%. The results of the preparation of Al₂O₃-SiO₂ supports are presented in Table 6. The main characteristics of the obtained supports are presented in Table 7.

Table 6. Technological table for the preparation of the Al₂O₃-SiO₂ supports.

Sample Number	The Composition of the Charge						Peptizer
	Binder			Filler			
	AHO Type	Content in the Charge, wt. %	d _{grains} , μm	Type	Content in the Charge, wt. %	d _{grains} , μm	
0 (Al ₂ O ₃ -100)	PAHO	100	Up to 40	SiO ₂	0	Up to 50	Nitric acid (HNO ₃)
1 (Al ₂ O ₃ -80:SiO ₂ -20)		80			20		
2 (Al ₂ O ₃ -60:SiO ₂ -40)		60			40		
3 (Al ₂ O ₃ -35:SiO ₂ -65)		35			65		
4 (Al ₂ O ₃ -20:SiO ₂ -80)		20			80		
5 (Al ₂ O ₃ -15:SiO ₂ -85)		15			85		

Table 7. Characteristics of heat-treated supports at temperatures from 550 to 1150 °C.

Sample Number	Strength of Samples	Granule Diameter after Heat, mm	The Total Degree of Shrinkage of Granules in Diameter after Heating, %	Moisture Capacity, cm ³ /g
	kg/cm ²			
Heat treatment at 550 °C				
0 (Al ₂ O ₃ -100)	90	1.6	20.0	0.46
1 (Al ₂ O ₃ -80:SiO ₂ -20)	60	3.46	30.8	0.46
2 (Al ₂ O ₃ -60:SiO ₂ -40)	88	3.50	30.0	0.47
3 (Al ₂ O ₃ -35:SiO ₂ -65)	68	3.63	27.4	0.50
4 (Al ₂ O ₃ -20:SiO ₂ -80)	62	3.35	33.0	0.56
5 (Al ₂ O ₃ -15:SiO ₂ -85)	50	3.66	26.8	0.58
Heat treatment at 750 °C				
0 (Al ₂ O ₃ -100)	95	3.23	35.4	0.50
1 (Al ₂ O ₃ -80:SiO ₂ -20)	85	3.40	32.0	0.50
2 (Al ₂ O ₃ -60:SiO ₂ -40)	73	3.50	30.0	0.48
3 (Al ₂ O ₃ -35:SiO ₂ -65)	65	3.67	26.6	0.53
5 (Al ₂ O ₃ -20:SiO ₂ -80)	65	3.33	33.4	0.55
Heat treatment at 900 °C				
0 (Al ₂ O ₃ -100)	95	3.21	35.8	0.42
1 (Al ₂ O ₃ -80:SiO ₂ -20)	89	3.35	33.0	0.43
2 (Al ₂ O ₃ -60:SiO ₂ -40)	84	3.40	32.0	0.45
3 (Al ₂ O ₃ -35:SiO ₂ -65)	81	3.59	28.2	0.46

5 (Al ₂ O ₃ -20:SiO ₂ -80)	57	3.38	32.4	0.49
Heat treatment at 1150 °C				
0 (Al ₂ O ₃ -100)	120	2.89	42.2	0.31
1 (Al ₂ O ₃ -80:SiO ₂ -20)	92	3.19	36.2	0.37
2 (Al ₂ O ₃ -60:SiO ₂ -40)	78	3.26	34.8	0.37
3 (Al ₂ O ₃ -35:SiO ₂ -65)	83	3.53	29.4	0.42
5 (Al ₂ O ₃ -20:SiO ₂ -80)	81	3.30	34.0	0.49

The results of determining the porosity of supports with a content of up to 60 wt.% Al₂O₃ and 40 wt.% SiO₂ heat-treated at temperatures from 550 to 1150 °C and samples 1–4 heat-treated at 550 °C are shown in Table 8 and Table 9, respectively.

Table 8. Porosity properties of sample 2 (Al₂O₃-60:SiO₂-40) at the temperature range of 550–1150 °C.

Name	Temperature							
	550 °C		750 °C		900 °C		1150 °C	
Pore Size, Å	Pore vol., cm ³ /g	Vol. Fraction, %	Pore Vol., cm ³ /g	Vol. Fraction, %	Pore Vol., cm ³ /g	Vol. fraction, %	Pore Vol., cm ³ /g	Vol. Fraction, %
0–40	0.014	3.00	0.001	0.27	0.000	0.00	0.0002	0.06
40–50	0.059	12.68	0.015	3.13	0.004	0.83	0.0013	0.38
50–60	0.031	6.75	0.017	3.65	0.005	1.21	0.0019	0.54
60–70	0.109	23.27	0.062	13.09	0.025	5.61	0.0155	4.33
70–100	0.084	17.95	0.169	35.47	0.114	25.31	0.0301	8.40
100–240	0.014	3.09	0.052	11.03	0.155	34.36	0.1027	28.63
240–380	0.004	0.90	0.005	0.97	0.010	2.11	0.0198	5.52
380–1000	0.005	1.00	0.007	1.56	0.005	1.15	0.0042	1.16
>1000	0.147	31.36	0.147	30.83	0.132	29.42	0.1830	50.98
Pore volume in H ₂ O, cm ³ /g	0.47		0.48		0.45		0.36	
Specific surface area (BJH method), m ² /g	190.7		148.5		107.5		50.1	

Table 9. Porosity properties of samples 1–4 heat-treated at 550 °C.

Name	Samples Heat-Treated at 550 °C							
	Al ₂ O ₃ -80:SiO ₂ -20		Al ₂ O ₃ -60:SiO ₂ -40		Al ₂ O ₃ -35:SiO ₂ -65		Al ₂ O ₃ -20:SiO ₂ -80	
Pore Size, Å	Pore Vol., cm ³ /g	Vol. Fraction, %	Pore Vol., cm ³ /g	Vol. Fraction, %	Pore Vol., cm ³ /g	Vol. Fraction, %	Pore Vol., cm ³ /g	Vol. Fraction, %
0–40	0.022	4.85	0.014	3.00	0.016	3.14	0.014	2.42
40–50	0.078	16.88	0.059	12.68	0.041	8.20	0.034	6.02
50–60	0.065	13.95	0.032	6.75	0.031	6.17	0.042	7.54
60–70	0.139	30.13	0.109	23.27	0.055	11.08	0.014	2.48
70–100	0.100	21.74	0.084	17.95	0.032	6.48	0.015	2.75
100–240	0.015	3.44	0.015	3.09	0.009	1.89	0.009	1.52
240–380	0.005	0.94	0.004	0.90	0.005	0.91	0.005	0.83
380–1000	0.003	0.64	0.005	1.00	0.003	0.68	0.005	0.88
>1000	0.034	7.41	0.147	31.36	0.308	61.45	0.423	75.56
Pore volume in H ₂ O, cm ³ /g	0.46		0.47		0.50		0.56	
Specific surface area (BJH method), m ² /g	260.9		190.7		119.4		86.8	

It is known that supports obtained on the basis of pseudoboehmite have the highest strength in comparison with all other industrially used aluminum hydroxides. So, for example, Table 10 shows the characteristics of the supports obtained using various binders. As a result of the work, it was found that supports based on PAHO with the addition of amorphous silicon dioxide up to 40 wt.% had a strength of about 88 kg/cm², comparable to supports obtained on the basis of pure aluminum hydroxide. It was also noted that the formation of the supports with the addition of silicon dioxide was better, as the paste itself was more plastic and did not stick to the extruder parts. These parameters indicate the possibility of replacing a part of the expensive aluminum hydroxide obtained by the waste ammonia-nitrate technology. Supports consisting of 80–85 wt.% silicon dioxide had a lower strength, about 50 kg/cm². However, even these values exceeded the strength indices of supports obtained from boehmite, with various degrees of crystallinity.

Table 10. Properties of Al₂O₃ supports based on various binders.

No.	Raw Material Type	g H ₂ O/g Al ₂ O ₃	Assessment of the Molded Paste	Properties of Cylindrical Granules after Heat Treatment at 550 °C		
				Specific Surface, m ² /g	Pore Vol., cm ³ /g	Mechanical Crushing Strength, kg/cm ²
1	PAHO (up to 87 wt.% pseudoboehmite).	1.06	Solid paste, highly plastic, excellent molding	320	0.63	84
2	Pural SB1 (up to 95 wt.% well-crystallized boehmite).	1.23	The paste is very dense, rubbery, translucent, good molding	230	0.48	24
3	AHO obtained by precipitation of sodium aluminate with nitric acid at 50 °C (up to 85 wt.% poorly crystallized boehmite).	1.38	Low-plasticity paste, thixotropic, difficult to mold	200	0.98	10
4	AHO mixture obtained by precipitation of sodium aluminate with nitric acid at 20 °C and at 100 °C (up to 80 wt.% well-crystallized boehmite).	0.95	Low-plasticity paste, soft, difficult to mold	-	0.70	14

The addition of silicon dioxide from 20 to 80 wt.% to the PAHO charge led to a decrease in the specific surface area of the support heat treated at 550 °C from 260 to 87 m²/g and, despite this, to an insignificant increase in the moisture capacity index from 0.46 to 0.58. The moisture content is an important indicator taken into account when preparing a catalyst by the impregnation method. Moreover, the advantage of the supports with the addition of amorphous silicon dioxide extracted from silica gel was a slight decrease in moisture capacity and specific surface area with an increase in the heat treatment temperature at 1150 °C. Usually, with these heat treatment parameters, the specific surface area of the support based on pure Al₂O₃ drops to 2–10 m²/g, depending on the type of initial binder.

5. Conclusions

The experimental results obtained in this study suggest that the silica gel, which is an industrial waste generated on a large scale and negatively impacting the environment, can be successfully used as a raw material for the production of pure amorphous silicon dioxide. The amorphous silicon dioxide with SiO₂ content up to 99.8% obtained according to the proposed method is in high demand in many industries and can successfully compete with products manufactured by existing technologies. It is especially worth noting

that, owing to its structure and the presence of active acid sites such silicon dioxide, it can be of particular interest as a promising material for creating catalyst supports with increased strength. So, on this basis, it is possible to develop formulations of supports with a predominance of macropores. Moreover, in the field of searching for a process applying these supports, and possibly catalysts $\text{Al}_2\text{O}_3\text{-SiO}_2$, perspective studies can be conducted. These studies are planned to be carried out by the authors of the article in the near future.

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