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THERMAL ANALYSIS OF MODIFIED POLYSILICIC ACID WITH AMINO ALCOHOLS

Abstract. The study examined the thermal analysis of polysilicic acid gels modified with solutions of different concentrations of ethanolamine in absolute ethanol. The effect of temperature on the sorption properties of these compounds at 30 °C, 50 °C and 80 °C was also analyzed thermally.

Keywords: polysilicic acid, ethanolamine, thermal analysis, sorption, desorption, carbon dioxide.

Introduction. Inorganic compounds of silicon – silicates are very common in the earth's crust and are present in almost all minerals. Polysilicic acids are mainly modified by silanol groups. There are basically two different methods used. In the first method, the organic matter is introduced into the polymerization reaction together with the substances forming polysilcates. Although the sol-gel method, which uses organosilicon compounds, is more efficient, mainly valuable monomers are used [1; 2].

The second method modifies existing polysilkates or aluminosilicates by adding organic matter. This process takes place with low yields and only on surfaces. Therefore, it can be widely used to obtain compounds that are mainly used in surface-based processes [3; 4].

The thermo gravimetrical method can be used to study the degree of modification of silicates with organic matter. It uses the decomposition of silicates at high temperatures. The added compounds are relatively easily broken down [5].

Silica gels have strong sorption properties and can be used for almost any substance. Various modifications are used to increase their sorption selectivity. At the same time, thermogravimetric methods are widely used in the study of sorption properties of gases and liquids [6].

Research methods. Thermal analysis was performed on a DTG-60 device manufactured by Shimadzu in Japan. Thermal stability analyzes were studied in the 40–60 °C range. Sorption properties were studied at 30 °C, 50 °C at 80 °C at a CO2 flow rate of 100 ml/min, and desorption at 110 °C at a flow rate of 100 ml/min argon gas.

Experimental part. Synthesis of sorbents. Gel of polysilicic acid was obtained by fine neutralization of sodium orthosilicate solution with 0.1 M solution of sulfuric acid. This gel is repeatedly washed in a solution of sulfuric acid with pH = 4 and then in distilled water and filtered. The precipitate is heated to 110 °C until a constant mass is obtained.

Technical ethanolamine was distilled at low pressure in an inert medium. A solution of ethanolamine in ethyl alcohol was prepared. Soak 10 ml of the solution in 5 g of polysilicic acid for 5 hours. It is then heated to 80 °C until the mass remains unchanged. Excess ethanolamine was isolated by low pressure driving. The process was performed separately with 10, 20, 30% solutions.

The decomposition rate and thermal stability of the obtained sorbents were studied at temperatures up to 600 °C.

Analysis of the obtained results. The thermal analysis of the samples at high temperatures is almost the same, with temperatures above 200 °C decreasing only due to the water released as a result of the decomposition of the water and silanol groups in the silica gel (Fig. 1).

The decomposition of the samples can logically be divided into 3 parts: up to 200 °C, 200–400 °C, and 400–600 °C. The decomposition rates of the samples at these stages are given in Table 1. The results are given in percentages as the starting materials are obtained in different masses during the experiments.

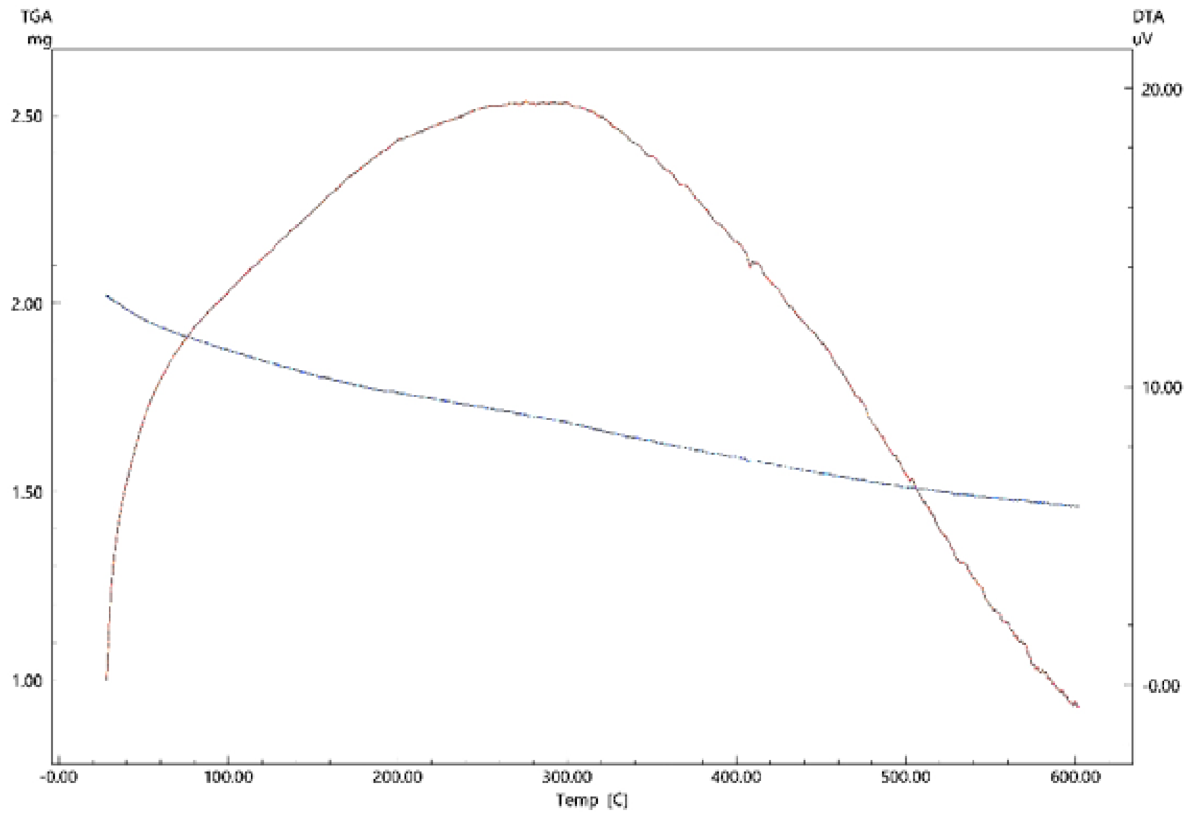

Figure 1. Thermogravimetric analysis of silica gel modified with 30% solution ethanolamine

Table 1.– The degree of decomposition of the obtained samples at different temperatures

№	Samples	Degradation rate,%			Toatl, %
		40–200 °C	200–400 °C	400–600 °C	
1	Modified with 10% solution	8.754%	8.612%	6.421%	23.787%
2	Modified with 20% solution	9.221%	8.584%	6.352%	24.157%
3	Modified with 30% solution	12.525%	8.663%	6.436%	27.624%
4	Unmodified	5.442%	8.278%	6.378%	20.098%

In the first decomposition stage, mainly the separation of sorption water and gases is observed. This is because non-organic modified polysilicic acid also decomposes in this range. It can also be assumed that the bulk of the organic layer and the sorbed solvent are also separated.

In the second decomposition stage, the decomposition of the remaining organic part along with water in the form of crystal hydrate is also observed. It can be seen from the difference from the fragmentation of the unmodified sample that it is around 5% of the total fragmentation.

Since the third decomposition stage is mainly due to the decomposition of the silanol groups, it proceeds to almost the same extent in all samples.

Due to the fact that the decomposition is carried out in an inert medium, the modified samples are black due to the presence of carbon in the final products. In unmodified silica gels, the final product is white SiO_2.

The table can be used to determine the degree of modification of polysilicic acid in solutions of different concentrations. In this case, the rate of increase in the mass of substances released during decomposition was used. According to him, 3.69% with 10% solution, 4.05% with 20% solution and 7.53% with 30% solution were found to contain modified organic compounds. This allows the samples to be used as sorbents due to the presence of nitrogen-containing functional groups in the compounds. The absorption properties of these sorbents from carbon dioxide were also studied thermogravimetrically.

The sorption properties of CO_2 gas of the obtained samples were also analyzed by thermogravimetric method.

The change in the maximum sorption capacity during the sorption / desorption cycle of thermogravimetrically modified sorbents was studied. Maximum sorption capacities at 30 °C for sorption and 80 °C for desorption were used (Figure 2). During the cyclic operation of the sorbent in 2 temperature ranges, a decrease of 7–10% was observed after 5 cycles. Such a decrease can be explained by the partial release of amino groups at high temperatures. This is because the sorption capacity of the unmodified sample is virtually unchanged. The optimum conditions for the desorption process are around 80 °C, and at higher temperatures the desorption is faster and more complete, resulting in a significant reduction in the number of processing cycles. After desorption at 100 °C, after 5 cycles of the modified sample with 30% solution, the maximum sorption capacity decreases by more than 30%.

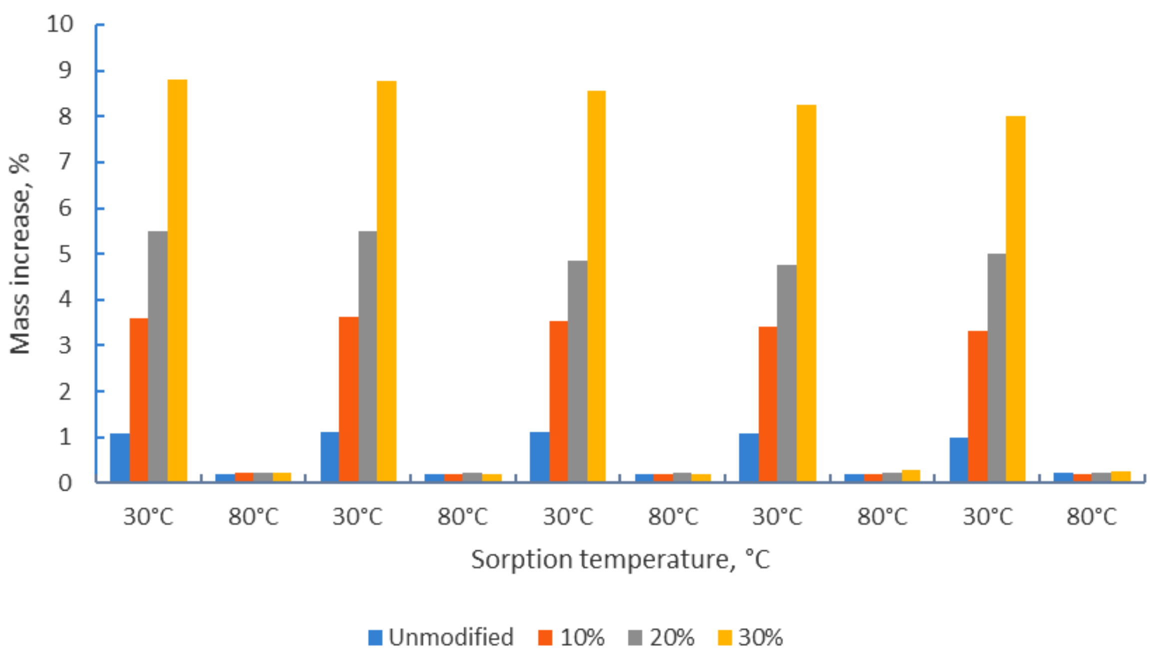

Figure 2. Cyclic performance of samples in the processes of sorption (30 °C) and desorption (80 °C) of carbon dioxide

Conclusion. The degree of modification of ethanolamine with solutions of different concentrations was determined thermally. The degree of modification was determined as the degree of fragmentation increased. The ability of sorbents to absorb carbon dioxide also explains the importance of organic functional groups in sorption, since the increase is directly proportional to the increase in the organic content included.

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