

Original Article

Effects of Different Factors on the Kinetics of Modification of Polysilicic Acids with Ethanolamine

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Abstract - The article discusses the effect of various factors on the modification rate of polysilicic acid. The reaction of polysilicic acid with ethanolamine is due to the polycondensation of the silanol and hydroxyl groups. The formation of the corresponding product as a result of the reaction has been confirmed by IR spectroscopy. The dependence of the reaction rate on temperature and the addition of tetraethyl orthosilicate has been studied. The optimum time for modification was shown to be 5 hours without tetraethyl orthosilicate and a temperature of 60°C, and 2 hours and 60°C in the presence of tetraethyl orthosilicate.

Keywords - Silicic acid, Ethanolamine, Tetraethyl orthosilicate, Temperature, Reaction kinetics.

1. Introduction

Polysilicic acid is one of the most common inorganic polymeric substances. Minerals such as silica and aluminosilicates are mainly based on polysilicate. The processes of modification of various polymers of the substance by the Sol-gel method are widely studied [1]. Including functional groups by modifying different silicates with organic amines increases their applicability in different fields. To activate styrene-ethylene copolymers, the modification process, first with maleic anhydride and then with ethanolamine, was studied [2]. In addition, 2-amino-2-methyl-1-propanol, modified with glycerine, has also increased thermal stability [3].

The specific properties of the compounds obtained by the sol-gel method are obvious. It also allows the synthesis of selective specific catalysts, especially for catalytic processes [4]. To increase the efficiency of metal catalysts, adding metal ions to modified functional groups on the surface of polymers is also used [5]. Sol-gel also allows the polycondensation of silanol groups and the formation of special porous compounds by applying various alcohols in the drying process at supercritical pressure. [6].

Trimethoxysilane was used to obtain styrene and methacrylate copolymers obtained from maleic anhydride by the sol-gel method, in which colloidal silicon oxide was attached to the surface. [7]. Modifying silica surfaces by polymerising silanes in organic solvents with silica nanoparticles is also presented [8].

Welding alkyl chains can also change the surface of silicates. In this case, mainly polycondensation of silanol groups is used [9].

The surface of silicates can also be modified by spraying silicon-containing compounds. This method is effective for larger bodies, such as building concrete [10].

Silica gels modified with organic amines can be used for carbon dioxide sorption. In this case, the sorption level allows the separation of carbon dioxide from methane [11]. Selective ion-exchange sorbents resistant to high temperatures were also obtained from the potassium-nickel hexacyanoferrate/silica composite's ethanol modification to separate active isotopes in nuclear waste [12].

Low molecular weight representatives of organic amines and amino alcohols form complexes in the form of sweater ions with carbon dioxide. It has been shown that sorbents can also be obtained by immobilizing such compounds in inorganic porous matrices [13].

The thermal stability of polyethylene polymers modified with silicon nanoparticles and changes in sorption capacity during adsorption-desorption processes have been studied [14-17]. The sol-gel method also used silica gel nanoparticles obtained from the liquid phase [18].

Carbon dioxide sorbents based on the modification of amines and polyamines based on various porous solids have been the most widely studied in recent years [19-22].



Amine-based solid sorbents have attracted the attention of researchers due to their high CO₂ sorption, low energy consumption, high stability, and low pollution properties. Liquid adsorbents have disadvantages such as high toxicity, foaming, decomposition and evaporation at high temperatures [23,24].

Adding silicon-organic compounds to the silanol groups on the silica gel surface also yielded more stable compound sorbents. However, organosilicon compounds are more expensive substances. Although low molecular weight compounds are considered to have a much higher reaction yield, the reaction yield of silicon organic compounds containing the amino group is much lower, and a smaller amount of silanol groups can be exchanged [25-27].

2. Materials and Methods

2.1. Chemicals

Commercial solution of sodium silicate, 1 M solution of hydrochloric acid (chemically pure), ethanolamine, absolute ethanol, tetraethyl orthosilicate.

2.2. Methods

2.2.1. IR spectroscopy

IR spectroscopic analyses were performed to determine the presence of relevant functional groups in the compounds' composition. IR spectra were performed on a 400-4000 cm⁻¹ IRTracer-100 instrument manufactured by Shimadzu in Japan.

2.2.2. X-ray phase measurement XRD

Measurements of the phase characteristics of the studied powders were carried out on a Panalytical Empyrean powder X-ray diffractometer. The measurements were carried out with a Cu tube ($K\alpha_1 = 1.5406 \text{ \AA}$), room temperature in the range of angles 2θ , in the range from 5° to 90° in the step-by-step scanning mode with a step of 0.013 degrees and a signal accumulation time at a point of 5 s.

2.2.3. Surface detection analysis

The surface area was determined on a Mac-Ben-Bacra scale based on sorption properties. Measurements were made by benzene sorption up to 1 atmospheric pressure. The calculations were performed on a computer based on BET theory.

3. Experimental part

3.1. Synthesis of polysilicic acid.

Polysilicic acid was obtained from a solution of sodium orthosilicate (liquid glass) by treatment with a 1M solution of hydrochloric acid. The resulting white precipitate was filtered, and the salt residue was washed with water. Dried at room temperature. It was ground and heat treated at 200 °C until the mass remained unchanged.

3.2 Modification with ethanolamine.

10 g of the obtained polysilicic acid was obtained and treated with a 10% solution of 30 g of freshly distilled monoethanolamine in ethanol in a 100 ml flask equipped with a refrigerant for 5 hours at 60°C.

The resulting product was filtered, and the solid residue was removed. It was dried at 80°C for one hour at a pressure of 0.02 bar. This product is designated as SIL-5-60.

3.3. Determining the optimal conditions.

Modifying polysilicic acid with monoethanolamine was performed at different temperatures and reaction times to determine the optimal conditions of the process. The number next to the reaction product SIL is marked with the time in hours and the last number with temperature. It was based on the increase in the mass of the final product relative to the initial mass in all reactions.

3.4. To determine the effect of tetraethyl orthosilicate on reaction time and temperature.

In the modification of polysilicic acid with monoethanolamine, all reactions were repeated with the addition of 1% tetraethyl orthosilicate to the total mass of starting materials. The samples obtained were marked in the form of SILT.

4. Results and Discussion

4.1. IR - spectral analysis.

IR spectra were obtained to determine the structure of the products obtained. The IR spectrum was obtained on an IR-100 instrument in the wavenumber range of 400–4000 cm⁻¹ (Fig. 1).

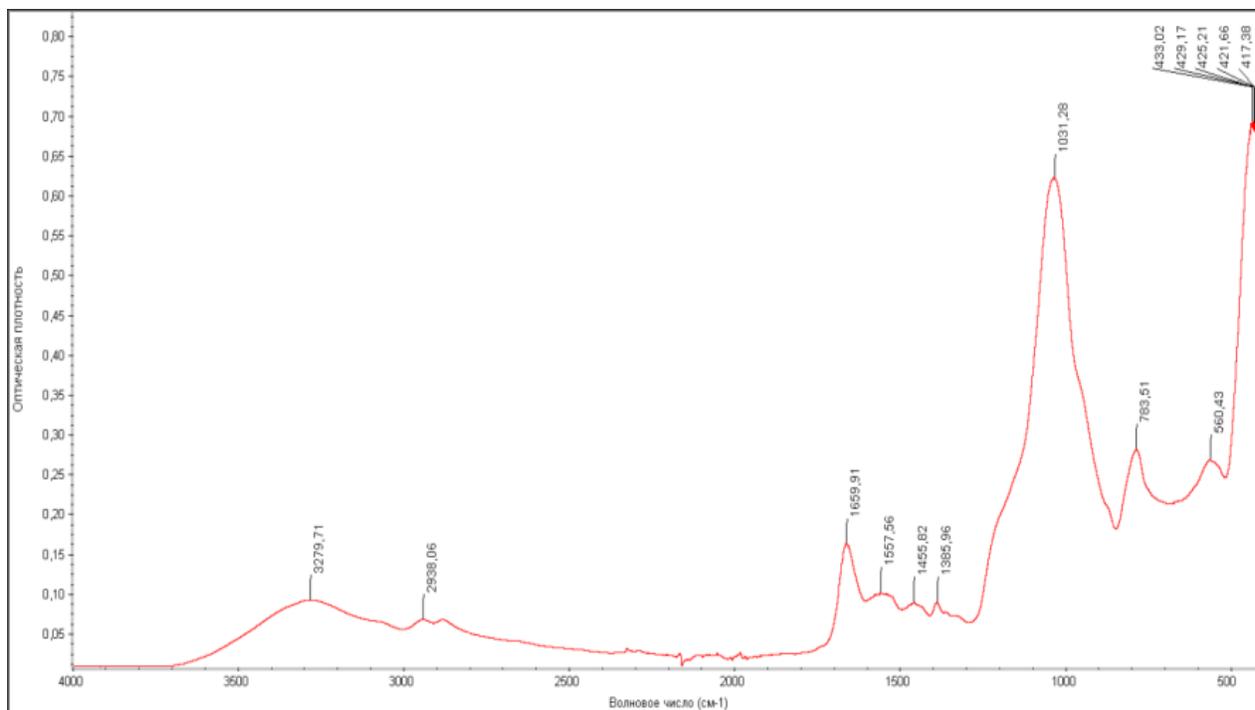


Fig. 1 IR spectrum of SIL-5-60 sample

The IR spectrum of the modified silicic acid showed wide oscillation frequencies of hydroxyl groups in the 3279 cm^{-1} regions. It indicates that the hydroxyl groups have not been fully modified. Observations of the valence oscillations of hydrogen atoms in methylene groups in the 2938 cm^{-1} area indicate the presence of a bonded organic fraction. In the area of 1031 cm^{-1} , intensive vibrations of Si-O-C bonds are observed. While there are deformation oscillations of the amine group at a frequency of 1659 cm^{-1} , the valence oscillations of the N = O and N-O bonds formed as a result of partial oxidation of the amine group are manifested in 1385, 1455, 1557 cm^{-1} regions.

4.2. Evaluation of the effect of temperature on the reaction rate.

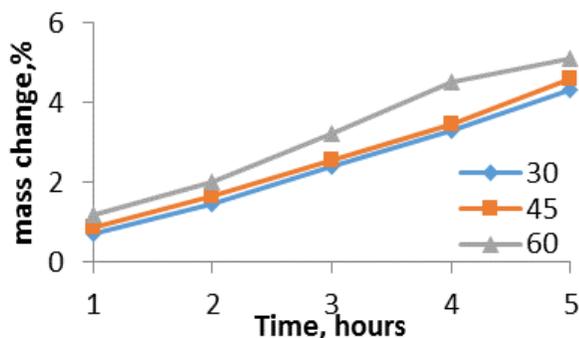


Fig. 2 The dependence of the reaction yield on time and temperature

An increase in temperature increases the rate of the reaction. At the same time, due to the faster evaporation of

ethyl alcohol, a solvent, the concentration of ethanolamine in the mixture increases. It leads to an increase in the reaction rate.

Increasing the reaction medium's temperature increases the reaction's yield, as shown in Figure 2. After 5 hours, the reaction rate does not change. However, it should be borne in mind that not all parts of polysilicic acid react. According to elemental analysis and IR spectroscopy results, modification with ethanolamine occurs only at the expense of silanol groups. These groups are present only on the surface of polysilicic acid, which has a lattice polymer structure [28].

4.3 Effect of tetraethyl orthosilicate effect on reaction rate.

Adding tetraethyl orthosilicate significantly increases the reaction rate (Fig. 3).

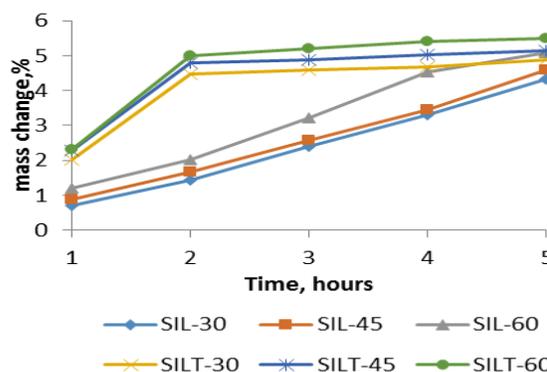


Fig. 3 Changes in the reaction rate in the presence of tetraethyl orthosilicate

In the polysilicic acid modification process, only the silanol groups on the surface are esterified. Tetraethyl orthosilicate, on the other hand, can form four silanol groups. As a result, the process is accelerated. However, due to the high stability of tetraethoxylated silicon-oxygen bonds, silicic acid rapidly covers the surface of the particles, and their cross-linking processes also proceed. However, an increase in the number of free silanol groups on the surface of the particles leads to an increase in the degree of esterification. However, the direct binding of tetraethyl orthosilicate to ethanolamine molecules is slow. Therefore, the reaction time is reduced; however, the degree of modification is not significantly increased.

4.4. X-ray phase analysis.

An X-ray diffractogram of silica gel modified with monoethanolamine is shown in Fig. 4.

The X-ray diffractogram shows that the presence of broad and high poles indicates that the atoms are in an amorphous form, with the main part of the sample arranged randomly.

It also appears that there are differences from the X-ray diffractogram of silica gel cited in the literature [29]. The analysis of the obtained diffractogram was performed using computer programs OriginLab and Profex.

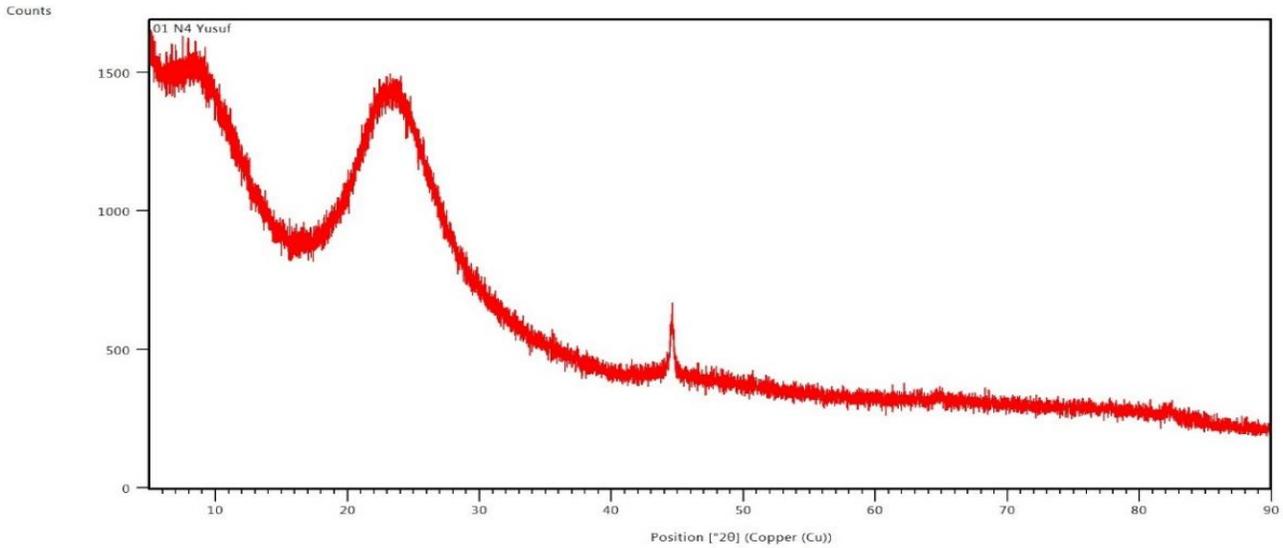


Fig. 4. X-ray diffractogram of polysilicic acid modified with ethanolamine (SIL-5-60 sample)

Table 1. Results of X-ray phase analysis of modified polysilicic acid

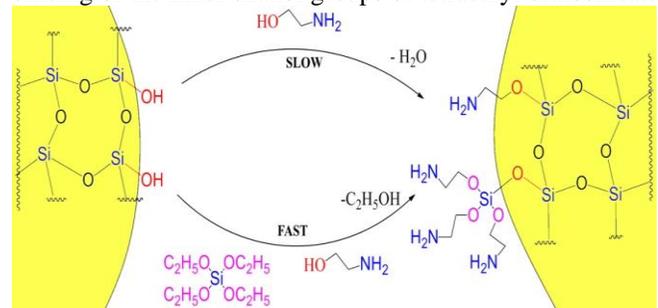
Profile area	Counts	Amount
Total area	35300,36	100.00 %
Diffraction peaks	10959,8	31.04 %
Amorphous phases	1840442	68.96 %
Degree of crystallinity (DOC) = 31.04 %		
Amorphous content (weight %) = 68.96 %		

In the process of identifying the constituents, peaks belonging to various minerals of silicon oxide and organic substances such as urea and acetates were detected. It proves the presence of organic modification in the sample composition.

4.5. Determining the surface area

In determining the surface area, measurements were made based on all samples' sorption of benzene vapor at low pressure. According to the results of isotherms at a maximum pressure of 1 atmosphere, the surface area is 10% less than in samples with different tetraethyl orthosilicates. It can be

thought of as a result of the pores being blocked by the binding of the inner silanol groups of tetraethyl orthosilicate.



5. Conclusion

The reaction of polysilicic acid with ethanolamine is due to the polycondensation of the silanol and hydroxyl groups. The dependence of the reaction rate on temperature and the addition of tetraethyl orthosilicate was studied. The optimum time for modification was shown to be 5 hours without tetraethyl orthosilicate and a temperature of 60°C, and 2 hours and 60°C in the presence of tetraethyl orthosilicate.

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