Derivatographic analysis of bentonite "navbahor" in the technology of obtaining a nanocatalyst

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Abstract. This study presents an experimentally identified derivatogram of bentonite from the Navbahor mine, the texture of bentonite, physical and chemical characteristics, chemical composition, and their analysis of the retaining substance used in the preparation of nanocatalysts based on Zol-gel technology.

1 Introduction

In the world, silica materials and compositions derived from them are widely used in various fields of industry due to their unique properties, including high chemical, thermal, and mechanical stability, low toxicity, sorption properties, and the manifestation of catalytic inertia. Mesoporous silica materials are of particular practical importance, and the applications of these materials, as well as their effectiveness, are characterized by their structure and surface morphology, which include comparative surface, porosity size, dependence on the average diameter, and high sorption properties. Porous nanomaterials with improved surface morphology and geometric characteristics are widely used in various fields of industry and production. In particular, the role of porous nanomaterials in the production of heat-protective coatings, in the production of alternative energy, in catalysis, as a preservative and sorbent in chromatography, in the separation of individual genes in genetic engineering, in the chromatographic analysis of drugs, in wastewater treatment from various pollutants, in construction, and in the production of chemical sensors is incomparable. The world is dedicated to the synthesis of porous materials and composites, as well as the management of their textural characteristics, and the number of published scientific papers is growing every year. Porous silica materials and their applications in composites formed by monomers of various functional groups, as well as metal oxides of variable valence, are determined by their textural characteristics, which depend on the methods of their extraction. This is based on the interest of controllers in creating new synthesis methods that allow

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purposefully controlling the laws of formation of silica materials and composites as well as texture characteristics. It is known that the direction of application of porous silica materials and compositions obtained on their basis, as well as their effect, are determined by the characteristics of such textile products as their comparative surface, porosity size, and porosity distribution. Therefore, the management of the characteristics of the mentioned texture, the production of porous silica materials and various compositions based on them, which demonstrate this property, is one of the urgent problems and is an important scientific direction. In recent years, Zol–gel technology has been conducting large-scale scientific and practical research on the synthesis of a mass of inorganic and organo-inorganic materials at low temperatures. It differs from other technologies because of a number of advantages, such as the simplicity of the equipment used in the technology, energy efficiency, environmental safety, efficiency, flexibility, etc. [1-8]. It is also distinguished by the fact that the initial precursors carry out a polycondensation reaction of hydrolytics under mild conditions and the possibility of introducing monomer oxides, polymers, or metals of variable valence with a functional group into the reaction system, using a single solvent for all reagents and the ability to control both the structure and the size of the final product [9]. In the Zol-gel process, organic and inorganic components can be mixed in the right proportions and into nanostructures. Under certain conditions, the first substances used in Zol-gel technology are polymerized or poly-dissolved groups, as well as compounds that can form micelles [10]. As a result of the hydrolysis of these compounds, sol is formed. The Zol measurement of the initial subcorsors in an aqueous solution formed as a result of hydrolysis under acidic or alkaline conditions is a stable suspension of particles ranging in size from 1 nm to 100 nm (10-9-10-7m) [11]. The particles may consist of amorphous or crystalline porous polymer structures. Agglomeration of subcolloid membranes is also observed in the halls in the case of aerosols in a highly dispersed liquid (lyosol) or gas medium. As a result of the polycondensation reaction, the first particle passes into an oligomer or polymer, the viscosity increases and turns into a gel [12]. The gel is a three-dimensional dispersing phase formed as a result of the interaction of primary colloidal particles. Depending on the nature of the solvent (water or alcohol) used in the transition of SOL to gel, various lyogels can be obtained [13]. The reason is that nanocatalysts exhibit high catalytic activity, intrinsic selectivity, stability, etc. The high efficiency of nanocatalysts is due to the processes of their charge, power, mass, amplification, and information transfer (transport). These processes occur in nanotubes as well as in chemical reactions in nanotubes. The practical application of such catalysts leads to an unprecedented improvement in the environmental characteristics of many processes and technologies in industry; a reduction of harmful emissions emitted into the atmosphere; the creation of environmentally friendly types of alternative energy sources; and new products and materials.

Based on the analysis of the literature [14], the prospect of using a nanoparticle-based catalyst in catalysis depends on the following two scientific aspects: Firstly, as the particle size decreases, a large percentage of atoms settle on the surface, so a catalyst consisting of nanoparticles will have a large surface area. The surface will be very active in reactions. Secondly, many properties of nanosystems depend on their size (size effect). Therefore, by changing the size of nanoparticles, it is possible to control not only their activity, but also their selectivity. When the size of the catalytic membrane decreases, the reaction rate increases dramatically. The high consumption of energy and raw materials for existing technologies with heterogeneous catalysts forces us to look for new ways to implement the registered processes. One of the ways to solve this problem is to carry out the process on nanocatalysts. Therefore, in the synthesis of inorganic oxide materials, the substance that conducts the Zol-gel process has the advantage of using bentonite compared to other materials, and the ultradispersity compound makes it possible to create unique structures with
high porosity, thereby reducing the microhomoogeneity of the resulting compounds and ensuring the uniformity of the distribution of components.

One of the main processes in the Zol-gel technology is the heat treatment of this material: drying and firing, and, as a result, obtaining catalytic sorbents with high-quality porosity. Therefore, thermogravimetric tracking of bentonite is considered a conductive substance, and the definition of its basic description is relevant.

2 Methods

The chemical composition of bentonite from the Navbahor deposit was determined by methods in accordance with the standards of the International Union of Theoretical and Applied Chemistry (IUPAC).

Also during the study, the texture and physico-chemical characteristics of the catalyst were determined by IR spectroscopy and thermography.

The elemental composition of the obtained materials was determined using X-ray spectrum microanalysis (RSMA) with the addition of JEOL-JED-6390 EDS in a JEOL-2200 scanning electron microscope.

The acidic properties of ammonia in the universal sorption gas analyzer USGA-101 were studied by thermodestered desorption.

Crystal 5000 chromatography with capillary colon and flame ionization detectors was used to determine the qualitative and quantitative composition of the reaction products. The amount of hydrogen and carbon oxides was carried out in the gas chromatography "Crystal-5000", which was equipped with a detector and a column for retaining the PropakQ phase by thermal conductivity.

The determination of the porous structure and comparable surface area of the catalysts was carried out in an automatic gas adsorption analyzer, TriStar II, by the method of Brunauer, Emmett, and Wyres (bet). The comparative surface area was calculated at 77 K using a nitrogen adsorption isotherm. The size and pore size of the catalysts were determined from data on desorption and adsorption isotherms, respectively, at a relative pressure of R/R0. Thermometric measurement of mass changes during studies is of great importance for qualitative analysis. This requires simultaneous application of differential thermal and thermographic methods (1, 4). Derivatography is a method that simultaneously measures the test product (T), temperature, weight change (tg), weight change rate, and enthalpy change (DTG) in a sample.
Derivatogram - non-isothermal kinetic data were collected in the derivatography Od-103. The figure depicts the derivatograph device and the scheme of actions, which includes a measure, a photographic device, a working camera and a control element, as well as a large registration drum. The test sample is heated in an oven in a specific container with a constant temperature. The light signal from the illuminated optical slit, which is situated on the balance lever, registers the slit's deviation from the scale in the form of a thermogravimetric curve on photo-intensive paper.

A coil with a large number of revolutions, suspended on a scale and moving in the same area as a permanent magnet, is used to quantify the rate of weight change. The magnet's force field creates a voltage in the moving coil, whose magnitude is proportional to the arm's deflection. In the photo-intensive paper, the light signal of the galvanometer attached to the coil terminals is defined in such a way that the primary curve is a derivative of tg, that is, a differential of the thermogravimetry curve (DTG).

A differential circuit for connecting thermocouples is also used to obtain the differential thermal analysis (DTA) curve line. All curved lines are copied to the

A differential method was used for kinetic analysis of the thermoanalytic curve obtained by thermogravimetry under non-isothermal conditions. [16]

3 Results and discussion

Bentonite in Navoi region, Navbakhor district, is a light gray powder, practically insoluble in odorless water and organic solvents, the pH value of the suspension is 7.1-8.7. The weak alkalinity of the suspension is explained by the presence of hydroxide soil and hydroxide metals in the clay. The combined meso-macroporous adsorbent in terms of adsorption properties is 54.5 m²/g, the surface area of which is comparable, the pore size is 0.065 cm³/g, the average porosity is 4.8 nm, the adsorption activity for blue methylene is 62.0 bentonite/g, this is confirmed by a number of literature data [22,23]. According to its technological properties, it is a fine powder of medium weight, having an average yield. For use in the chemical industry, standardization of bentonite clay is carried out.

Standardization of bentonite was carried out according to the following indicators: characteristics, pH value of the aqueous suspension, adsorption activity during drying, cation exchange ability, heavy metals (mishyak), comparative surface area, volume and average size of tampons.

Technological and adsorption standardized characteristics of bentonite clay "Navbahor" are presented in Table 1.

Table 1. Technological and adsorption characteristics of bentonite clay "Navbahor"

<table>
<thead>
<tr>
<th>№</th>
<th>Quality indicators of bentonite clay</th>
<th>Features of bentonite clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>characteristic</td>
<td>light gray powder, odorless, almost insoluble in water and organic solvents</td>
</tr>
<tr>
<td>2</td>
<td>Suspension of pH (5 in 100) in water</td>
<td>7.1-8.7</td>
</tr>
<tr>
<td>3</td>
<td>Weight loss during drying,%</td>
<td>Not more than 8%</td>
</tr>
<tr>
<td>4</td>
<td>Adsorption activity, bentonite/g</td>
<td>62.0±0.2</td>
</tr>
<tr>
<td>5</td>
<td>Cation exchange capacity of bentonite</td>
<td>19.4</td>
</tr>
<tr>
<td>6</td>
<td>Meringue</td>
<td>no</td>
</tr>
<tr>
<td>7</td>
<td>the ratio of elements Si⁴⁺ and Al³⁺</td>
<td>3:1</td>
</tr>
</tbody>
</table>
Specific surface area according to the five-point BET method, m²/g 54.5±2.0

P/V₀ = 0.98, cm³/g volume of porous pressure 0.065±0.005

Average pore size, in nm 4.8

Moisture content in bentonite clay, % 26 ±28

Moisture content in the dry bentonite layer, % 2-3

To find out its dependence on the heating heat of bentonite, it was specially heated in a crucible from 70 to 500 °C, and the main indicators of its textural characteristics were calculated: comparative surface - Sourt, m²/g; comparative volume - Vₛ, cm³/g and activation energy E₀, kJ/mol. Have been identified. The results obtained were included in Table 2.

Table 2. Textural descriptions of “Navbahor” bentonite depending on the heating temperature

<table>
<thead>
<tr>
<th>T°C</th>
<th>Sourt m²/g</th>
<th>Vₛ cm³/g</th>
<th>W₀ cm³/g</th>
<th>E₀ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>65</td>
<td>0.062</td>
<td>0.031</td>
<td>12.74</td>
</tr>
<tr>
<td>100</td>
<td>64</td>
<td>0.064</td>
<td>0.031</td>
<td>13.38</td>
</tr>
<tr>
<td>150</td>
<td>72</td>
<td>0.061</td>
<td>0.034</td>
<td>13.09</td>
</tr>
<tr>
<td>400</td>
<td>74</td>
<td>0.072</td>
<td>0.035</td>
<td>12.44</td>
</tr>
<tr>
<td>500</td>
<td>66</td>
<td>0.063</td>
<td>0.032</td>
<td>11.72</td>
</tr>
</tbody>
</table>

As can be seen from the example of Navbahor bentonite (Table 2), with an increase in the heating temperature of samples from 70 to 500 °C, their specific surface and porosity volume arise mainly during the heat treatment of bentonite clay under the influence of microporosity heat, resulting in the formation and stagnation of texture parameters.

In accordance with the standards of the International Union of Theoretical and Applied Chemistry, the chemical composition of “Navbahor” bentonite was determined, and the results obtained were presented in Table 3.

Table 3. Chemical composition of bentonite "Navbahor"

<table>
<thead>
<tr>
<th>Name</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>NaO</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline bentonite soil</td>
<td>57.91</td>
<td>0.35</td>
<td>13.69</td>
<td>5.10</td>
<td>1.84</td>
<td>0.48</td>
<td>1.53</td>
<td>1.75</td>
<td>0.43</td>
<td>0.75</td>
</tr>
<tr>
<td>Alkaline earth soil</td>
<td>56.23</td>
<td>0.61</td>
<td>13.56</td>
<td>6.50</td>
<td>3.76</td>
<td>0.69</td>
<td>0.98</td>
<td>2.20</td>
<td>0.92</td>
<td>0.49</td>
</tr>
</tbody>
</table>

A comparative analysis of the chemical composition of bentonite, which is considered alkaline bentonite and ground soil, showed that their chemical composition is not sharply different from each other, but: TiO₂, Fe₂O₃, MgO, K₂O, P₂O₅ the amount is slightly more in alkaline earth soil, and SiO₂, Na₂O, SO₃ the amount is more in alkaline bentonite soil.

Before acid activation of bentonite or kaolin, the sample was heated at 150 °C for 30 minutes to remove water. After acid activation, their mass became, %: SiO₂ – 70,17, Al₂O₃-9.49, Fe₂O₃-1.39, MgO-0.64, Na₂O-0.17, K₂O-1.27, CaO-0.20, TiO₂-1.63, MnO-0.01.

Analysis and calculation of the bentonite derivatogram. According to the results of non-isothermal thermogravimetric studies of bentonite, a derivatogram was obtained in which four curved lines were described: T, TG, DTG and DTA. Figure 2 shows the derivatogram of bentonite "Navbahor".
Fig. 2. Derivatogram of bentonite "Navbahor"

The lines of the derivatogram curve are intended for analysis and calculation of the quality of bentonite material, determination of kinetic constants along the lines of the TGA curve.

Qualitative analysis of the derivatogram makes it possible to determine the types of water connection in concrete with the material and the stages of its drying temperature.

From the considered properties of the colloidal-capillary-porous bentonite clay material, it follows that it is practically difficult to draw a boundary between the compounds of a particular type of water with a rigid frame of the material. Bentonite is also a complex system with its own structure, both by nature and has various moisture compounds, at different stages of dehydration of its flour, the moisture limit of one type or another plays an important role.

The classification of forms of moisture binding in colloidal capillary-porous materials, proposed by P.A. Rebinder [24-26], takes into account the formation of various forms and the energy of their binding to the material. According to him, all its forms of moisture are divided into three large groups: chemical (molecular), physico-chemical (absorption, osmotic humidity during storage (swelling and structural humidity), physico-mechanical (humidity in macro- and microcapillaries).

The quantitative description of the material's contact energy is crucial for practical purposes. P.A. Rebinder - the value of the free energy of isothermal dehydration - is the only criterion employed in the classification of contact forms with the material to determine this. We can deduce from this that when water is connected to a material, the pressure of water vapor on its surface lowers, and so the free energy reduces. The effort (in erg/mol) used on removing 1 mole of water from the material, or more accurately, on its separation, is computed as the energy of the connection traveling at a constant temperature:

$$-\Delta F = L = RT \ln \frac{P_u}{P_n} = -RT \ln \varphi$$

Here: $R$ – gas constant.
$P_u$ – pressure of steam saturated with free water
$P_n$ – $u$ moisture-resistant material balances the pressure of water vapor in the hole in an inert gas or vacuum:

$$\varphi = \frac{P_u}{P_n}$$

Chemical (molecular), physico-chemical (due to absorption, osmotic storage), and physico-mechanical (due to absorption, osmotic storage) are the three types of linked water (moisture) found in derivatogram DTA line bentonite (humidity of macro- and micro-capillaries). When heated from the DTA and tg lines, the physico-mechanical (moisture in macro- and micro-capillaries) moisture comes out first, then the physico-chemical (moisture due to suction, osmotic storage) moisture comes out second, then the destoruction begins to
occur evenly for 35-50 minutes, then it breaks down. In comparison, we can observe that the TG and DTA lines are both confirmed. When compared to the T temperature line, it is also feasible to establish which temperature range these processes have passed through.

From the derivatogram, the primary decomposition of bentonite began at a temperature of 70% and ended at 300%. Over the past 35 minutes, 80 bentonite was lost or 363.0 bentonite was 11% of the total mass. The damage occurred due to absorbed systemic water and other volatile compounds.

Methods for determining kinetic constants from these curved lines have recently become popular.

The most convenient techniques of computing the curve lines obtained by linear heating speed are tested. Non-isothermic Kinetics has the advantage of requiring less energy and allowing the qualitative and quantitative aspects of the process to be determined using short experiments. In this example, there are numerous independent methods for obtaining the reaction's kinetic constant.

Initial approximations of kinetic parameters are estimated by the method of small squares of weight

\[ \sum_{i=1}^{M} \omega_i (\alpha_i^a - \alpha_i^p)^2 \rightarrow \min \]  

Here: \( \alpha^a \) va \( \alpha^p \) - the level of experimental and accounting communication.

For weight coefficients, as a rule, the following form is used:

\[ \omega_i = \alpha_i^\beta \]  

For example: \( \omega_i = 1/\alpha_i \) on a statistical scale.

The change in the indicator in the weight formula is equal to the change in the degree of participation of various experimental points in the calculation of parameters. This change greatly affects the results of parameter estimation. Having seen the approbation of the least squares weight method with different values, it was shown that it is most optimal to install it

\[ \beta = -1 \]  

The resulting parameters are checked as follows: the selected synthetic equation is combined with the cadmium variable of the Euler method and used as a choice of the following functional optimal parameters:

\[ f(\alpha, E, m, n, p) = \int_{T_0}^{T_k} (\alpha^a - \alpha^p) \rightarrow \min \]  

Optimization is carried out by a modified Nelder-Mead method, which provides an approximation of the initial approximation with successful positioning.

To calculate the kinetic parameters of the process, we used the models of the thermochemical equation - Vakhuski - Voboril and Yerofeyev, which are modifications of the equation.

When using the first model, kinetic constants are calculated by the differential method along the lines of the TG curve. A modified Nelder-Mead method can be used for optimization.

It also takes into account the thermal effects of reactions associated with the deviation of the sample temperature from the set values corresponding to the linear law. It is based on the differential equation of thermal decomposition of a solid:
\[ \frac{d\alpha}{d\tau} = z \exp \left( -\frac{E}{RT} \right) (1 - \alpha)^n \]  

(5)

The logarithmic form of this equation:

\[ \ell n \frac{d\alpha}{d\tau} = \ell n z - \frac{E}{RT} + n \ell n(1 - \alpha) \]  

(6)

Here: \( \alpha \) - exchange rate, \( z \) - the exchange frequency coefficient, 1/c; \( E \) - activation energy, kcal/mol, \( N \) - reaction mode.

The solution of this linear equation can be obtained by the least squares method with further improvement of the Nelder-Mead method.

When describing the kinetics of thermal decomposition, the second method from the topochemical Yerofeyev equation is used, which has the form as shown above:

\[ \frac{d\alpha}{d\tau} = z \exp \left( -\frac{E}{RT} \right) (1 - \alpha) \left( -\ell n(1 - \alpha) \right)^{\frac{n-1}{n}} \]  

(7)

Thus, using the above equations, it is possible to simulate the kinetics of decomposition processes during high-temperature treatment of bentonite clay.

The calculations were carried out on an IBM PS/XT personal computer using the EUREKA data processing package (from Borland International), which includes the processing of static data by the least squares method and the iteration method. The results of the account are presented in Table 4.

<table>
<thead>
<tr>
<th>№</th>
<th>Name of the material</th>
<th>kinetic parameters</th>
<th>Variations of the Yerofeyev equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( z )</td>
<td>( E ) kcal/mol</td>
</tr>
<tr>
<td>1</td>
<td>Alkaline bentonite soil</td>
<td>13.90</td>
<td>18.2</td>
</tr>
<tr>
<td>2</td>
<td>Alkaline earth soil</td>
<td>12.80</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Because the kinetic characteristics of alkaline bentonite and bentonite from alkaline earth soil calculated using the topochemical model of the Yerofeyev equation are quite similar. For example, for alkaline bentonite soil, the obtained constants when incorporated in the Yerofeyev equation are:

\[ \frac{d\alpha}{d\tau} = 13.90 \exp \left( -\frac{18.2}{RT} \right) (1 - \alpha) \left( -\ell n(1 - \alpha) \right)^{\frac{1.21-1}{1.21}} \]  

(8)

For Alkaline earth soil:

\[ \frac{d\alpha}{d\tau} = 12.8 \exp \left( -\frac{17.4}{RT} \right) (1 - \alpha) \left( -\ell n(1 - \alpha) \right)^{\frac{1.36-1}{1.36}} \]  

(9)

takes shape.

4 Conclusion

Technological and adsorption standardized descriptions of bentonite clay "Navbahor" were compiled. Bentonite "Navbahor" with an increase in the heating temperature of samples from 70 to 500°C, their specific surface area and porosity volume arise mainly during the heat treatment of bentonite clay under the thermal action of microcircuits, resulting in the
formation and stagnation of texture parameters with the release of stratified water, and the porous structure.

A comparative analysis of the chemical composition of bentonite, which is considered alkaline bentonite and ground soil, showed that their chemical composition does not differ sharply from each other, but: the amount of TiO$_2$ is more than one fold, and the amount of SiO$_2$, Na$_2$O, SO$_3$ is greater than in alkaline bentonite soil. Kinetic parameters of alkaline bentonite and bentonite of alkaline earth soil were determined based on the results of the calculation of kinetic parameters based on the model of the topochemical Yerofeyev equation. For the practical application of the constants obtained in the Yerofeyev equation, the equations were obtained.

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