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CATALYTIC PROPERTIES OF ACID-MODIFIED ALUMINOSILICATES IN GLYCEROL KETALIZATION WITH ACETONE.

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The catalytic properties of natural aluminosilicates from Ukrainian deposits modified with sulfuric acid were studied in glycerol ketalization with acetone. Bentonite (Bent, Dashukivske deposit), clinoptilolite (Cli, Sokyrnytske deposit) and trepel (Tr, Konoplianske deposit) were treated with sulfuric acid to increase their acidity and improve catalytic performance. The influence of catalyst loading, reaction temperature and glycerol:acetone molar ratio on glycerol conversion and initial rate of its consumption was investigated. It was found that catalytic activity strongly depends on structural, adsorption and acidic characteristics of aluminosilicates. The highest catalytic activity was observed for sulfuric acid-modified bentonite (H-Bent), which provided a maximum glycerol conversion of 81% at 45 °C, catalyst loading of 3 wt.% and glycerol:acetone molar ratio 1:25. H-Tr and H-Cli exhibited lower activity, reaching 71% and 60% conversion, respectively, under the same conditions. The superior performance of H-Bent is associated with its higher specific surface area (243 m^2/g), developed mesoporous structure and higher concentration of Brønsted and Lewis acid sites. Nitrogen adsorption-desorption analysis showed that all investigated samples belong to type IV isotherms, characteristic of micro-mesoporous materials. H-Bent had the highest total pore volume and mesopore surface area, while H-Cli contained a noticeable fraction of micropores. Pyridine adsorption studies revealed that H-Bent contains both Brønsted and Lewis acid sites of medium and high strength, whereas H-Tr and H-Cli are characterized mainly by weak and medium-strength Brønsted sites. Kinetic analysis demonstrated that the reaction order with respect to glycerol is close to one for H-Bent and two for H-Tr, indicating differences in rate-limiting step and reaction mechanism. The pseudo-Michaelis constants and maximum reaction rates were also determined, confirming the significantly higher catalytic efficiency of H-Bent compared to other investigated samples. Furthermore, the obtained results demonstrate that sulfuric acid-modified bentonite is a promising low-cost and environmentally friendly catalyst for glycerol valorization into cyclic ketals, which can be considered valuable fuel additives and intermediates for chemical industry.

Keywords: glycerol, ketalization, natural aluminosilicates, acid modification, heterogeneous catalysis.

INTRODUCTION. Due to rapid growth of global biodiesel production, large amounts of glycerol are generated as the main by-product [1]. Currently, the global production of glycerol from biodiesel exceeds its demand, leading to market oversaturation and a decrease in its price. Under such conditions, the search for efficient ways to use excess glycerol to obtain value-added products becomes particularly relevant [2]. Therefore, the conversion of glycerol into other commercially valuable compounds is a promising approach to enhance the economic attractiveness of biodiesel production and to make the process more sustainable and environmentally friendly.

Among the possible routes for glycerol transformation, its acetalization and ketalization – reactions with aldehydes or ketones in presence of acid catalysts to form acetals or ketals have attracted considerable attention. The obtained compounds are characterized by a wide range of practical applications, including use as fuel components, solvents, lubricant additives and intermediates in organic synthesis. Of particular interest is glycerol ketalization with acetone to form solketal [3], a compound considered an effective fuel additive for improving the performance characteristics of motor fuels.

An important aspect of implementing such processes is development of accessible, efficient and stable heterogeneous catalysts. One possible solution is use of inexpensive and readily available natural aluminosilicates, whose structural and acid-base properties can be purposefully modified, in particular by acid treatment.

The aim of this work is to investigate the catalytic properties of natural aluminosilicates from Ukrainian deposits, namely bentonite (Bent, Dashukivske deposit), clinoptilolite (Cli, Sokyrnytske deposit) and trepel (Tr, Konoplianske deposit), modified with sulfuric acid (H), in glycerol ketalization with acetone, as well as to study the influence of nature of these aluminosilicates on glycerol conversion and catalyst stability during the process.

EXPERIMENTAL AND RESULTS DISCUSSION. The modification of natural aluminosilicates with sulfuric acid was carried out according to procedure described in [4] with some changes. A 50 g of natural Bent, Cli and Tr (fraction 1.0–2.0 mm) was placed into a 250 mL round-bottom flask equipped with a reflux condenser, followed by addition 100 mL of sulfuric acid (3 mol/L). The suspension was maintained in a water bath (~100 °C) under constant stirring for 2 h, then stirred for an additional 1 h without heating. The sulfuric acid was removed by decantation, the samples were washed with distilled water. The procedure was repeated until a negative test for sulfate ions was achieved (no white precipitate upon addition of $BaCl_2$). The samples were dried at 120 °C for 1 h, calcined at 500 °C for 5 h and ground in an agate mortar, obtaining particles of average size 0.05 mm (fraction 0–1.0 mm).

The acidic properties of prepared catalysts were studied using pyridine adsorption as a spectral probe. Tablets weighing 10 mg with a surface area of 64 cm^2 were obtained by pressing aluminosilicate powders without a binder. The tablets were activated at 350 °C under vacuum for 1 h. Pyridine adsorption was carried out at 150 °C for 30 min, after which physically adsorbed pyridine was removed by evacuation at the same temperature for 30 min. The samples were cooled and their IR spectra were recorded using a «Spectrum one» Fourier-IR spectrometer (Perkin-Elmer). The samples were then stepwise heated to 250 °C and 350 °C, held at each temperature for 30 min, cooled and corresponding IR spectra were recorded. The concentrations of Brønsted and Lewis acid sites were calculated according to method described in [5].

Nitrogen adsorption-desorption isotherms at 77 K were measured by volumetric method using an «AMI-Micro-300 Series analyzer (Altamira Instruments, Micro300C-02-Analysis Station 3)». The surface area was calculated in relative pressure range of $0.1 \leq p/p_o \leq 0.3$ using Brunauer – Emmett – Teller (BET) equation, while the mesopore size distribution was determined using Barrett – Joyner – Halenda method [6]. The micropore size distribution was determined by Saito – Foley method [7], the micropore volume was estimated using t-plot method [6].

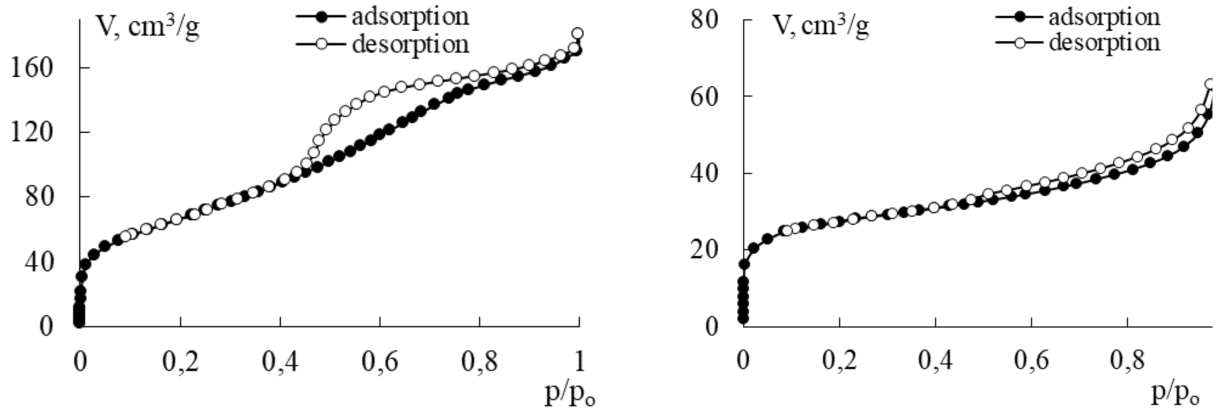
The catalytic activity of prepared catalysts was tested in a thermostated glass reactor (25 mL) equipped with a reflux condenser and a magnetic stirrer. Solutions with different glycerol:acetone ratios were prepared using 1.4-dioxane to adjust the volume. The reactants were placed in reactor, after reaching the desired temperature (25 °C, 35 °C, and 45 °C), catalyst was added and reaction time was recorded. Samples were taken whitin 2 h into centrifuge tubes (2 mL), cooled to room temperature to prevent further reaction and evaporation losses, centrifuged for 5 min using a mini centrifuge (IKA® mini G) to separate the catalyst from reaction mixture. Eight samples were taken, first after 5 min, then after 15 min and 30 min.

The samples were analyzed using a gas chromatograph (Shimadzu GC-2030, Japan) equipped with a flame ionization detector, a ZB-624 Plus capillary column (30 m × 0.32 mm × 1.80 μm). The initial column temperature was 80 °C (held for 4 min), followed by heating to 230 °C at a rate of 50 °C/6 min. The detector temperature was 350 °C, the injector temperature was 250 °C. The carrier gas (helium) flow rate was 35.5 cm^3/s, the split ratio was 100. The analysis was performed using the internal standard method with propanol as the standard. To 0.5 mL of sample, 0.03 mL of internal standard was added and 0.2 μL was injected into chromatograph.

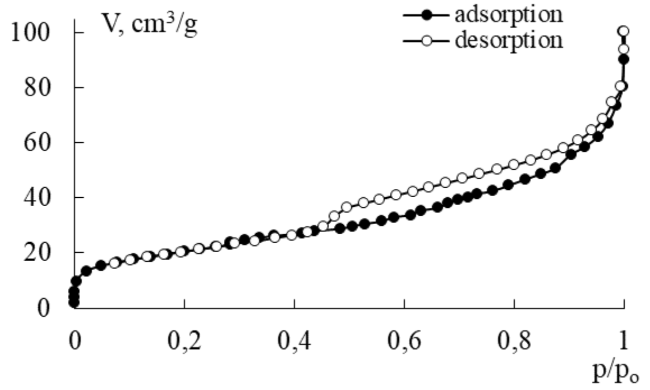
Glycerol conversion was determined after 2 h of reaction. The initial rate of its consumption was determined graphically as tangent of slope of concentration–time curve: $r = \mathrm{tg}\,\alpha/60$, $mol \cdot L^{-1} \cdot s^{-1}$.

Structural and adsorption characteristics of prepared catalysts. The structural and adsorption properties of acid-modified Bent, Cli and Tr were investigated. In particular, nitrogen adsorption-desorption isotherms were analyzed, the surface area was determined and the nature of acid sites was examined in order to evaluate the influence of these characteristics on catalytic activity. According to classical classification of adsorption-desorption isotherms (77 K), the obtained isotherms (Fig. 1) can be assigned to type IV [8], which is typical of micro- mesoporous materials. Type IV isotherms exhibit an initial uptake at low relative pressures, formally characteristic of adsorption in micropores, as well as a region at $p/p_o > 0.45$ corresponding to adsorption in mesopores accompanied by capillary condensation (i.e., condensation of vapor in pores and narrow channels of solid sorbents), as evidenced by presence of a hysteresis loop between adsorption-desorption branches.

The phenomenon of capillary condensation is associated with condensation of adsorbate vapor in pores of sample at pressures lower than saturation vapor pressure. The appearance of a hysteresis loop in adsorption-desorption isotherm is related to different mechanisms of pore filling and desorption. The presence or absence of micropores in type IV isotherms can be determined using the comparative t-plot method, since adsorption in initial region of isotherm may also occur in mesopores.



H-Bent H-Cli



H-Tr

Fig. 1. Nitrogen adsorption-desorption isotherms by samples of prepared catalysts.

The surface area values of prepared catalysts, determined using Brunauer – Emmett – Teller (BET) equation [8, 9], are presented in Table 1. Along with specific surface area, important characteristics include pore volume and pore size distribution. The micropore volume was determined using the t-plot method. The mesopore diameter was calculated using the adsorption branches of isotherms. This is due to peculiarity of adsorption-desorption hysteresis observed in nitrogen adsorption isotherms (77 K), which typically closes at relative pressures of 0.45–0.50 and corresponds to tensile strength limit of liquid adsorbate meniscus rather than to presence of mesopores of that size.

Table 1.

Structural and adsorption characteristics of prepared catalysts.

Characteristic	H-Bent	H-Cli	H-Tr
Total pore volume (adsorption at $p/p_o = 0.99$), cm^3/g	0.26	0.11	0.12
BET surface area, m^2/g	243	101	74
Micropore volume, cm^3/g	–	0.021	–
Mesopore diameter (dV/dlogD), from adsorption branch of isotherms, nm	5.0 –	5.0 ~60	5.8 ~60

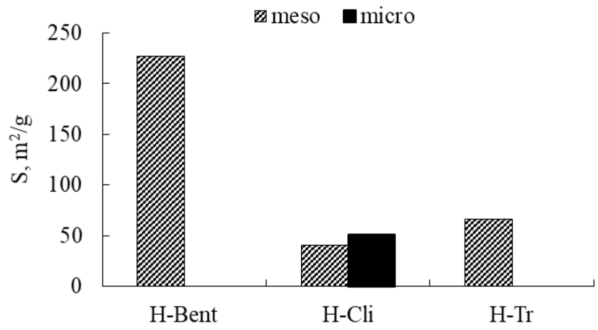
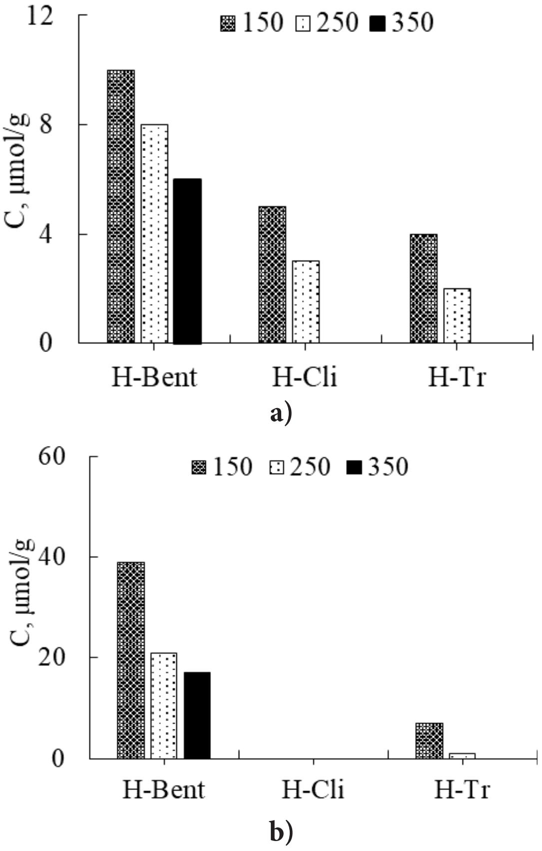


Fig. 2. Total pore area of investigated catalysts.

As can be seen, H-Bent exhibits a higher surface area ($S_{meso} + S_{external}$), which facilitates easier diffusion (accessibility) of reactants and reaction products to active sites. This, in turn, affects its catalytic properties, i.e., the larger surface area, the higher catalytic activity. Also, H-Bent, compared to H-Tr and H-Cli, has a larger mesopore surface area (Fig. 2), while micropores are absent and are present only for latter sample ($S_{micro} = 51$ m^2/g). In case of investigated samples (based on shape of isotherms), it is not possible to distinguish between adsorption in mesopores and on external surface ($S_{meso} + S_{external}$, $V_{meso} + V_{external}$). The total adsorption volume (cm^3/g) at $p/p_o = 0.99$ is 0.26 for H-Bent, 0.12 for H-Tr and 0.11 for H-Cli. For the latter, the micropore volume (cm^3/g) is 0.021. According to the isotherms analysis, the mesopores in the samples are heterogeneous in size, with distribution maxima at 5.0–5.8 and weak intensity at ~60 nm for the H-Tr and H-CLI samples (Table 1).

The concentrations of Brønsted and Lewis acid sites in prepared catalyst samples were determined using stepwise pyridine adsorption. Brønsted centers arise from protonation of surface hydroxyl groups (Si–OH–Al) after acid treatment, while Lewis centers are formed through the formation of coordinatively unsaturated aluminum atoms as a result of partial decationation and dealumination of the structure under the action of sulfuric acid. By analyzing the vibrational frequencies of pyridine, it is possible to distinguish absorption bands corresponding to coordinatively bound pyridine adsorbed on Lewis acid sites (1455 cm^{-1}) and pyridinium ions formed upon interaction of pyridine with Brønsted acid sites (1528 cm^{-1}) [10]. According to pyridine adsorption data obtained at 150 °C, 250 °C, and 350 °C, the concentration of Brønsted acid sites in H-Bent sample decreases by 2 μmol/g with each increase in temperature. For H-Cli and H-Tr samples, concentration also decreases, and at a pyridine desorption temperature of 350 °C, the absorption bands corresponding to pyridine adsorbed on Brønsted acid sites disappear. At the same time, for these samples at 150 °C and 250 °C, concentrations of acid sites are similar magnitude (Fig. 3). Based on obtained data, in particular the desorption of pyridine from Brønsted acid sites at relatively low temperatures (350 °C), it can be concluded that H-Cli and H-Tr samples contain only weak and medium-strength Brønsted acid sites.



a)

b)

Fig. 3. Distribution of Brønsted (**a**) and Lewis (**b**) acid centers.

At the same time, within the studied series of modified aluminosilicates, Lewis acid sites are absent in H-Cli, whereas for H-Tr their concentration does not exceed 10 μmol/g. For H-Bent, concentration is 40 μmol/g at 150 °C and decreases two fold with an increase in temperature to 250 °C, remaining practically unchanged upon further heating (250–350 °C). The H-Tr sample is characterized predominantly by weak and medium-strength Lewis acid sites, whereas H-Bent is distinguished by a significant fraction of strong Lewis and Brønsted acid sites. The higher concentration and strength of the acid centers (especially in the case of H-Bent) provides increased catalytic activity, which is consistent with experimental data on glycerol conversion and initial rates of its consumption.

Catalytic activity of prepared catalysts in glycerol ketalization with acetone. The effects of catalyst loading, reaction temperature and reactant molar ratio on glycerol conversion (*X*) and its initial consumption rate (*r*) were investigated. As shown in Fig. 4, for all three catalysts, an increase in catalyst loading (M_{cat}) leads to an increase in both *X* and *r*. H-Bent exhibits the highest activity: conversion increases from 21% to 81% and remains high even at lower catalyst loadings of 0.25–0.5 wt.%. In contrast, H-Tr is inactive at 0.25 wt.% and shows only 10% conversion at 0.5 wt.%; with further increase in M_{cat}, conversion reaches 71%. As for H-Cli, its activity becomes noticeable starting from 1 wt.%, with conversion increasing from 32% to 60%.

The initial rate of glycerol consumption in presence of H-Bent increases two fold at 0.25–0.5 wt.% and three fold at 0.5–1 wt.%. With a further increase in catalyst loading (2–3 wt.%), the rate remains practically unchanged (Fig. 4). In presence of H-Tr, the rate increases three fold at 0.5–1 wt.% and almost two fold at 1–2 wt.%, while further increases (2–3 wt.%) do not significantly affect the rate. For H-Cli, the rate increases two fold with each increase in catalyst loading (1–3 wt.%).

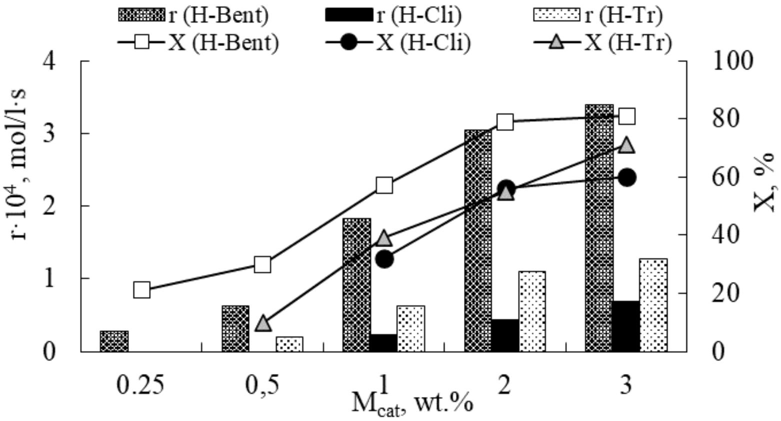


Fig. 4. Effect of catalyst mass fraction on glycerol conversion and initial rate of its consumption (glycerol: acetone = 1:25; 45 °C; 2 h).

The higher activity of H-Bent may be attributed to its layered structure, developed mesoporosity and higher specific surface area (Fig. 2, Table 1), which ensure better accessibility of active sites for reactant molecules. Acid treatment leads to formation of a significant number of Brønsted acid sites, which provides additional catalytic activity to H-Bent. Moreover, the presence of interlayer spaces promotes adsorption and diffusion of reactants, further enhancing catalytic performance.

With increasing reaction temperature, conversion increases as expected, reaching a maximum of 81% at 45 °C in presence of H-Bent. At 25 °C, H-Tr and H-Cli show no activity, while at 35 °C they exhibit similar conversions (35%). With a further increase in temperature, conversion rises to 71% for H-Tr and 60% for H-Cli. In presence of H-Bent, the initial rate remains almost unchanged between 25–35 °C and increases nearly three fold at 35–45 °C. The rate also increases approximately three fold in presence of H-Tr and nearly two fold in presence of H-Cli (Fig. 5).

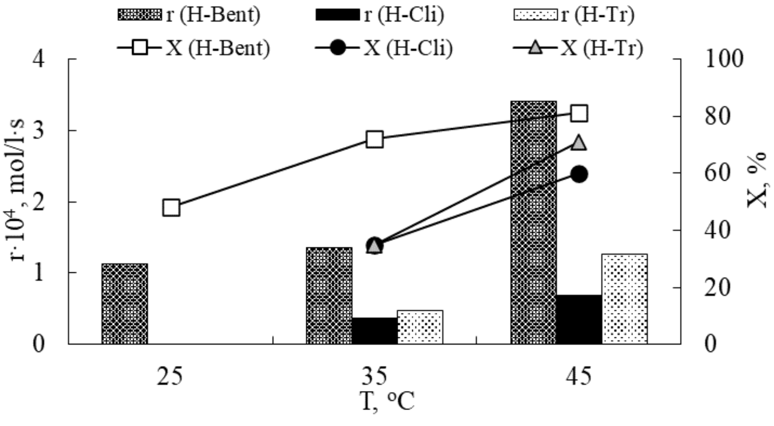


Fig. 5. Effect of reaction temperature on glycerol conversion and initial rate of its consumption (glycerol:acetone = 1:25; M_{cat} = 3 wt.%; 2 h).

In presence of H-Tr and H-Cli, at a glycerol:acetone molar ratio lower than 1:12, the activity of these catalysts is rather low. For H-Tr, conversion is 25%, while for H-Cli it is 14%. With an increase in molar ratio (1:25), conversion increases for both samples, reaching 71% for H-Tr and 60% for H-Cli. In contrast, H-Bent loses its activity only at a molar ratio of 1:1.3, where glycerol conversion is as low as 2%. At a ratio of 1:3, conversion increases significantly (38%) and continues to rise with a further increase of reactant ratio. The initial reaction rates also increase with an excess of acetone (Fig. 6). In presence of H-Tr, rate increases significantly by 5 times when the glycerol:acetone molar ratio increases from 1:12 to 1:25, while in presence of H-Cli it increases by nearly 2.5 times. All investigated catalysts withstand only two reaction cycles.

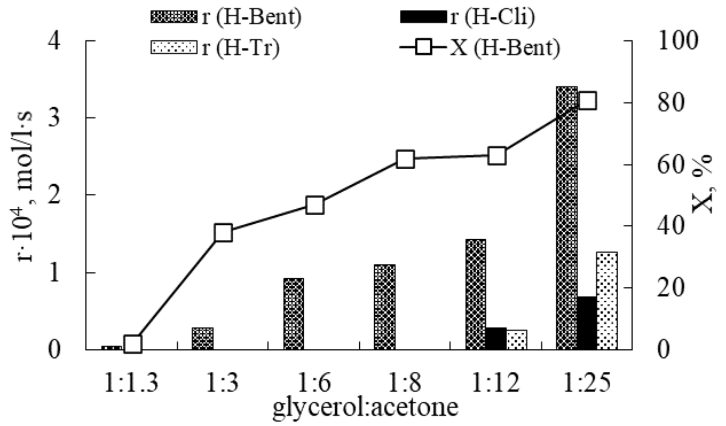


Fig. 6. Effect of glycerol:acetone molar ratio on glycerol conversion and initial rate of its consumption (45 °C; M_{cat} = 3 wt.%; 2 h).

The features of reaction between glycerol and acetone in presence of prepared catalysts were conditionally studied according to Michaelis-Menten model. Graphically, the Michaelis-Menten equation represents a hyperbola. It can be linearized using the method of double reciprocal values (Lineweaver – Burk method), i.e., by plotting 1/r versus 1/C, or by other methods. This approach allows determination of Michaelis constant (K_M) and the maximum reaction rates (r_{max}). By constructing such a plot, a straight line is obtained with a slope of K_M/r_{max} and an intercept on ordinate axis at $1/r_{max}$. As shown in Table 2, the pseudo K_M and r_{max} values are significantly higher for H-Bent. In this case, the formation of [acetone-catalyst] complex occurs at a higher rate, after which it interacts with glycerol. Subsequently, the [acetone-catalyst-glycerol] complex decomposes into reaction product, and the catalyst is regenerated.

Table 2.

Pseudo Michaelis constants and maximum reaction rates of glycerol with acetone (glycerol:acetone = 1:25; 45 °C; M_{cat} = 3 wt.%; 2 h).

Catalyst	**K_M**	**r_{max}**
H-Bent	1.65	12.3
H-Tr	0.54	0.32
H-Cli	–	–

In determining the concentration order of reaction with respect to glycerol (n_{GL}), it was found that H-Bent catalyzes the process stably over a wide range (five points) of glycerol concentrations (0.1–0.48 mol/L). In presence of H-Tr, this range covers three concentrations (0.2–0.55 mol/L), while for H-Cli it is limited to only two values – 0.24 mol/L and 0.6 mol/L. Therefore, determining the concentration order with respect to glycerol in presence of H-Cli is not appropriate. In contrast, the order is equal to one for H-Bent and two for H-Tr. The obtained values of concentration order indicate different mechanisms of interaction between glycerol and active sites of investigated catalysts. A first-order for glycerol in presence of H-Bent suggests that a single glycerol molecule participates in rate-limiting step, which may be associated with better accessibility of acid sites and effective adsorption of reactant on catalyst surface. The second-order dependence observed for H-Tr may indicate a more complex rate-limiting step, possibly involving two glycerol molecules, or a more significant role of adsorption effects on catalyst surface. For H-Cli, determination of concentration order is not reliable due to narrow range of studied concentrations and low catalytic activity, which may be attributed to a lower number of accessible active sites.

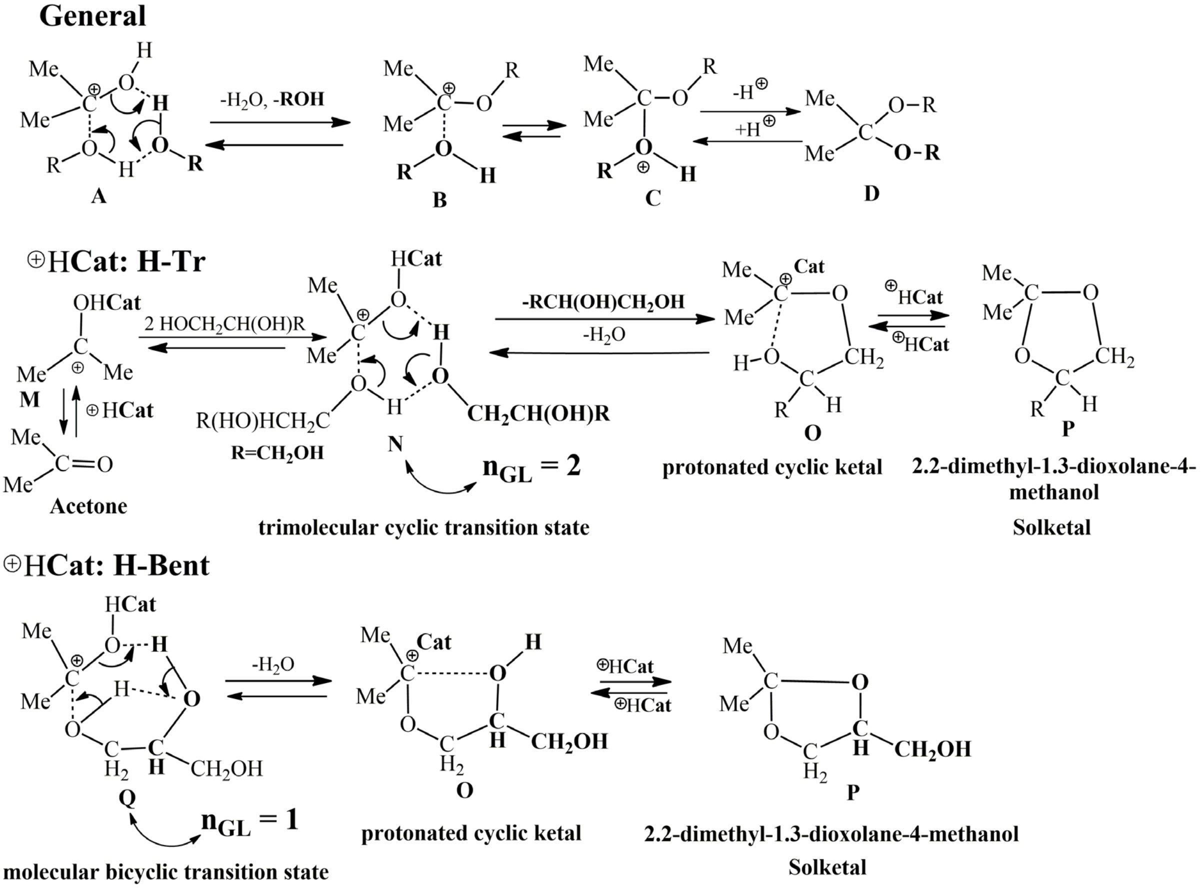


Fig. 7. Scheme of mechanism of glycerol ketalization with acetone.

Thus, it should be noted that in presence of investigated catalyst samples, the mechanism of reaction between glycerol and acetone is realized differently. Based on general scheme of ketal formation (**A**-**D**) under acid catalysis, a trimolecular cyclic transition state **A** is formed, in which the second alcohol molecule in rate-limiting step facilitates the removal of water, leading to formation of intermediate **C**. According to Michaelis-Menten model (Fig. 7), in presence of H-Tr, since the reaction order is equal to two, a trimolecular cyclic transition state **N** is realized, in which a second glycerol molecule promotes water elimination, forming intermediate **O**. In case of H-Bent, a similar role in molecular bicyclic transition state **Q** is played by secondary hydroxyl group of the same attacking glycerol molecule, which accounts for difference in reaction orders observed in presence of investigated acid catalysts.

It should be noted that the Brønsted acid centers are responsible for protonation of acetone carbonyl group, which is a key step in the glycerol ketalization mechanism and contributes to the formation of a reactive carbocationic intermediate. In turn, the Lewis acid centers act as electron-withdrawing centers capable of coordinating the oxygen-containing functional groups of the reagents, which facilitates the activation of molecules on the catalyst surface.

CONCLUSIONS. The catalytic properties of natural aluminosilicates modified with sulfuric acid (H-Bent, H-Cli, H-Tr) in glycerol ketalization with acetone were investigated. It was established that their activity is determined by structural-adsorption characteristics and the concentration of acid sites. H-Bent is characterized by highest specific surface area (243 m^2/g), a developed mesoporous structure and a higher concentration of Brønsted and Lewis acid sites, which ensures the maximum glycerol conversion of 81% at 45 °C, 3 wt.%, and a 1:25 molar ratio, as well as a higher initial glycerol consumption rate.

Kinetic analysis revealed differences in rate-limiting step and reaction mechanism: in presence of H-Bent, the reaction order with respect to glycerol is equal to one, whereas for H-Tr it is equal to two. Thus, acid-modified bentonite (H-Bent) is the most promising among the investigated aluminosilicates as an effective heterogeneous catalyst for glycerol ketalization with acetone.

AUTHOR CONTRIBUTIONS STATEMENT:

Davtian A. S.: Conceptualization, Data curation (literature analysis), Methodology and Investigation (conducting experimental research, modification of natural aluminosilicates with sulfuric acid), Writing – original draft.

Levchenko O. O.: Investigation (conducting experimental research), Writing – review & editing (discussing the results).

Yaremov P. S.: Methodology and Investigation (study of nitrogen adsorption-desorption by catalyst samples, determination of surface area, pore area).

Kurmach M. M.: Conceptualization, Methodology and Investigation (study of Brønsted and Lewis acid centers on catalysts surface).

Kamalov G. L.: Supervision, Funding acquisition.

All authors have read the results of the study and approved the final version of the manuscript.

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КАТАЛІТИЧНІ ВЛАСТИВОСТІ КИСЛОТНО-МОДИФІКОВАНИХ АЛЮМОСИЛІКАТІВ У КЕТАЛІЗАЦІЇ ГЛІЦЕРИНУ АЦЕТОНОМ

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Зазначено каталітичні властивості природних алюмосилікатів українських родовищ у кеталізації гліцерину ацетоном. З'ясовано вплив масової частки каталізатора, температури реакції та мольного співвідношення реагентів на конверсію гліцерину та початкову швидкість його витрати. Максимальну конверсію 81% досягнуто у присутності H-Bent за 45 °C, 3 мас.% каталізатора та співвідношенні гліцерин : ацетон = 1:25. Вивчено структурно-адсорбційні та кислотні характеристики каталізаторів (розмір пор, площа поверхні, концентрація та співвідношення Бренстедівських та Льюїсівських кислотних центрів) і співставлено вплив цих характеристик на їхні каталітичні властивості.

Ключові слова: гліцерин, кеталізація, природні алюмосилікати, кислотна модифікація, гетерогенний каталіз.

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