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THERMOCHEMICAL AND CATALYTIC PROPERTIES OF MODIFIED BENTONITES

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Thermochemical properties of bentonites, natural (from three Ukrainian deposits) and modified by physical and chemical methods have been investigated. The three-step mass loss process with two endothermic effects in the ranges of 130–150 °C and 500–600 °C was observed for all bentonite samples under study. These natural and modified bentonites were used as supports for obtaining palladium(II)-copper(II) catalysts for carbon monoxide oxidation. The activity of the catalysts has been found to depend on both the origin of bentonites and the techniques of their modification.

Keywords: bentonites, modification, thermochemical behavior, catalytic activity, carbon monoxide, oxidation

INTRODUCTION

Due to their unique structural and physicochemical properties, natural bentonites containing montmorillonite and α -quartz as major phases are commonly used in different fields of science and technology. In chemistry, they are predominantly used as catalysts for reactions with the participation of organic compounds [1].

Natural and modified bentonites as supports of metal-complex compounds catalyzing redox reactions of gaseous compounds such as CO, O₃, and SO₂ are little-studied. Our recent work [2] shows that the activity of natural material supported catalysts for environmental purposes significantly depends on the technique of support pretreatment. Various modification methods [3–8] are used for changing physicochemical properties of natural bentonites. They can be divided into three groups: (i) physical methods such as thermal or microwave treatment; (ii) chemical methods such as water or acid treatment, incorporation of metal ions or metal salts by ion exchange or impregnation, respectively, and intercalation of large stable ions such as hydroxo complexes of Al, Cr, Fe, Ti *etc.* into interlayer space; and (iii) methods combining physical and chemical techniques.

Generally, the modification of natural materials results in considerable changes in the ratio of major phases (for bentonites, the major phases are montmorillonite (Mont) and α -quartz), in specific

surface values, in the capability to adsorb water vapor and in some other physicochemical properties [4, 8–11].

Since the activity of supported copper-palladium complexes in the reaction of carbon monoxide oxidation with air oxygen [8] is the function of a great number of physicochemical properties of natural materials applied as supports, it can be useful to find some semiempirical relationships between the activity of a supported catalyst and certain properties of a support.

Though the thermochemical behavior of many natural bentonites has been studied [4, 12–14], there is a lack of the information about thermochemical properties of bentonites modified by different techniques. In particular, such data concerning bentonites modified with complex compounds of Pd(II) and Cu(II) catalyzing carbon monoxide oxidation with air oxygen are absent in literature.

The aim of the work was to elucidate how some methods of modification of natural bentonites affect their thermochemical properties and catalytic activity of copper-palladium complexes supported on them in the reaction of carbon monoxide oxidation with air oxygen.

EXPERIMENTAL

Bentonites from three Ukrainian deposits: Gorbskoye, Bent(G), (Technical Conditions TU U 26.8-05792908.005:2005), Dashukovskoye,

Bent(D) (TU U 14.2-00223941-006:2010), and Kirovogradskoye, Bent(K) (TU U 14.2-23231149-001-2002) were used as initial materials.

The major montmorillonite phase was identified in the three bentonite samples at the following values of angles of reflection, 2θ , and interplanar spacing (d , Å): 5.930° (14.90) – 19.820° (4.48) – 34.925° (2.56) – 54.905° (1.67) for

N-Bent(D); 6.180° (14.29) – 19.925° (4.46) – 35.165° (2.55) – 54.890° (1.67) for N-Bent(K); and 6.395° (13.82) – 20.015° (4.44) – 35.075° (2.56) for N-Bent(G) [15].

The description of modification techniques and conditions of their realization used in the work are presented in Table 1.

Table 1. Description of both natural and modified bentonites and techniques of their treatment

Notation conventions	Modification and treatment techniques
N-Bent(D, G, K)	Drying at 110 °C until constant weight
H-Bent(D, G, K)-1 and H-Bent(D)-6	Acid-thermal modification, <i>i.e.</i> boiling in 3M HNO ₃ for 1 and 6 h, respectively, followed by washing with distilled water until pH 5 and drying at 110 °C until constant weight
H ₂ O-Bent(G)	Hydrothermal modification, <i>i.e.</i> boiling in distilled water for 1 h followed by drying at 110 °C until constant weight
300-Bent(G)	Calcination at 300 °C for 3 h
Pd(II)-Cu(II)/Bent	An incipient wetness impregnation of both natural and preliminary modified bentonite samples (10 g) with 5 ml of aqueous solution containing certain amounts of K ₂ PdCl ₄ , Cu(NO ₃) ₂ , and KBr, aging of the moist samples obtained by such a chemical modification of bentonites for 24 h, and consequent drying at 110 °C until constant weight

The dried catalysts for carbon monoxide oxidation obtained as a result of chemical modification of natural and preliminary modified bentonites have the following chemical composition (in mol/g): K₂PdCl₄ – $2.72 \cdot 10^{-5}$, Cu(NO₃)₂ – $2.9 \cdot 10^{-5}$, and KBr – $1.02 \cdot 10^{-4}$.

Thermogravimetric measurements for natural and modified bentonite samples (0.25 g) were carried out with an accuracy of $\pm 5\%$ by a Paulik, Paulik and Erdey derivatograph at a heating rate of 10 °C/min and temperature ranging from 25 to 800 °C.

Kinetics of carbon monoxide oxidation with air oxygen over Pd(II)-Cu(II)/Bent catalysts was investigated using a gas flow setup with a fixed-bed reactor at 293 K, the fixed relative humidity of 76 %, the initial carbon monoxide concentration (C_{CO}^{in}) in a gas-air mixture (GAM) of 300 mg/m³, and the linear velocity of the GAM equal to 4.2 cm/s. CO oxidation was monitored by measuring the final carbon monoxide concentration (C_{CO}^f) using an electrochemical gas analyzer 621EKH04, with minimal detectable CO concentration of 2 mg/m³ and detection time of 45 s.

The reaction rate for CO oxidation was calculated by using the following equation:

$$W = \frac{w(C_{CO}^{in} - C_{CO}^f)}{m_{cat}}, \text{ mol}/(\text{g} \cdot \text{s}),$$

where $w = 1.67 \cdot 10^{-2}$ is the volume flow rate of GAM, L/s; C_{CO}^{in} , C_{CO}^f are, respectively, the initial and final CO concentrations, mol/L; m_{cat} is the weight of a catalyst sample, g.

The experimental amount of CO oxidized (Q_{exp}) was determined from the experimental function ΔC_{CO}^f vs. τ . The CO conversion under the steady-state conditions (η_{st}) and the number of catalytic cycles (n) per 1 mole of Pd(II) ($Q_{Pd(II)}$) were calculated at the experiment end point by using the following formulas:

$$\eta_{st} = \frac{(C_{CO}^{in} - C_{CO}^f)}{C_{CO}^{in}} \cdot 100, \%; \quad n = Q_{exp}/Q_{Pd(II)}.$$

RESULTS AND DISCUSSION

Fig. 1 shows TG, DTG, and DTA curves for samples of natural bentonites from three Ukrainian deposits at the temperature ranging from 25 to 800 °C.

Profiles of TG curves for natural bentonites demonstrate that a three-step process of surface

dehydration takes place. A similar change in TG curves (figure not given) occurs for all modified

bentonites. The data of thermogravimetric analysis are presented in Table 2.

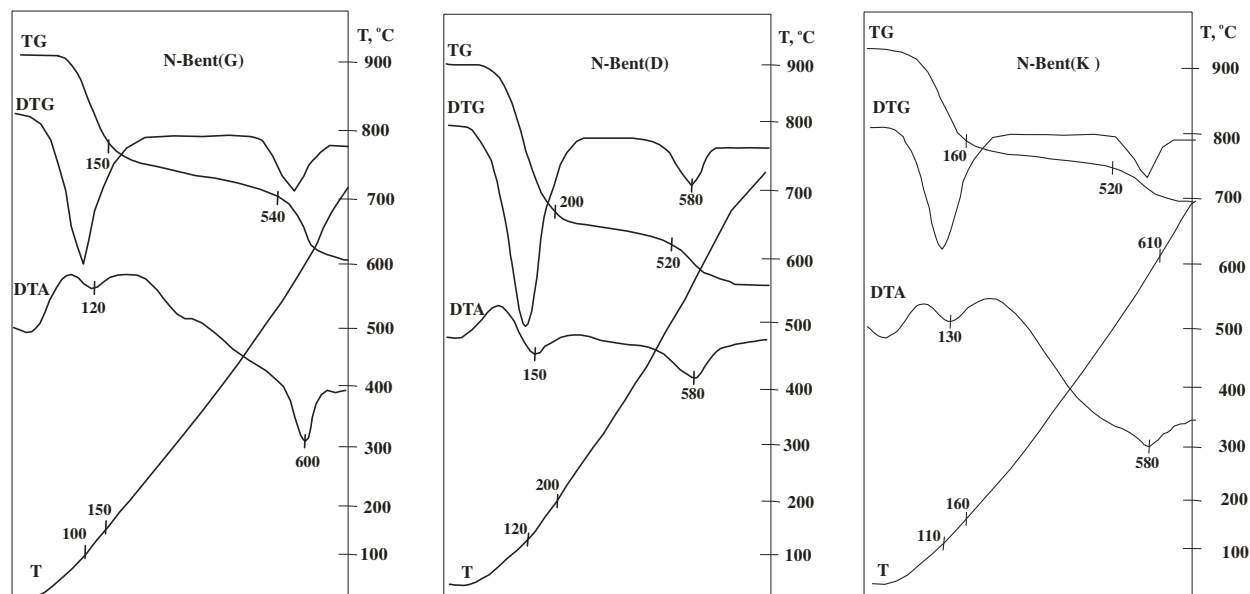


Fig. 1. TG, DTG, and DTA curves for samples of natural bentonites from three Ukrainian deposits

Table 2. The data of thermogravimetric analysis for both natural and chemically modified bentonites

Sample	Maximum temperatures of endothermic effects, °C		Weight loss, %, in temperature intervals, °C			m_{sp} , mmol/g	C_{OH} , mmol/g
	T_1	T_2	25-110	25-300	400-800		
N-Bent(D)	150	580	4.8	11.2	3.4	3.56	3.78
H-Bent(D)-1	140	580	4.4	10.8	3.6	3.56	4.00
Pd(II)-Cu(II)/H-Bent(D)-1	140	590	4.4	10.0	4.0	3.11	4.44
H-Bent(D)-6	140	570	2.8	8.0	5.6	2.89	3.89
Pd(II)-Cu(II)/H-Bent(D)-6	140	570	2.8	10.0	4.8	4.00	4.88
N-Bent(G)	120	590	4.0	7.8	6.0	2.11	6.66
H-Bent(G)-1	130	600	4.9	8.8	5.6	2.17	6.22
Pd(II)-Cu(II)/H-Bent(G)-1	110	600	3.2	6.0	5.6	1.56	6.22
H ₂ O-Bent(G)	140	590	2.4	7.6	6.8	2.89	6.66
Pd(II)-Cu(II)/H ₂ O-Bent(G)	110	590	3.2	5.6	6.0	1.33	6.66
300-Bent(G)	110	600	3.2	7.2	5.4	2.22	6.66
Pd(II)-Cu(II)/300-Bent(G)	120	590	3.6	6.4	6.0	1.56	6.66
N-Bent(K)	130	580	3.2	6.8	2.4	2.00	2.66
H-Bent(K)-1	120	580	3.2	6.4	2.2	1.78	2.44
Pd(II)-Cu(II)/H-Bent(K)-1	120	580	3.2	5.6	3.0	1.33	3.33

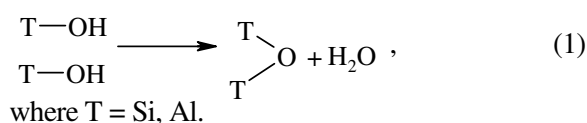
According to the concept of bentonite dehydration, the first step in the TG curves represents the loss of physically adsorbed water, the second step corresponds to the loss of interlayer water, and the third step shows the loss of water forming as a result of the surface dehydroxylation [4, 12–14]. DTA curves for natural bentonites demonstrate two

endothermic effects: the first one is in the range from 120 to 150 °C (the loss of adsorbed and interlayer water) and the second one is in the range from 580 to 600 °C (the surface dehydroxylation). The temperature values corresponding to the maximum of the first endothermic effect (T_1) decreases in the order N-Bent(D) > N-Bent(K) >

N-Bent(G) from 150 to 120 °C. The second endothermic effect has its maximum (T_2) at 590 °C in the case of N-Bent(G). T_2 values for other two natural bentonites decrease by 10 °C. Values of T_1 and T_2 change after the bentonite modifications. T_1 values for all modified samples of Bent(D) decrease by 10 °C compared with N-Bent(D) whereas T_2 values for modified samples of Bent(D) change irregularly in the range from 570 to 590 °C. T_1 values irregularly ranging from 110–140 °C and maximum T_1 value for H₂O-Bent(G) are observed for Bent(G) samples. T_2 values are the highest for 300-Bent(G), H-Bent(G)-1, and Pd(II)-Cu(II)/300-Bent(G) for Bent(G) samples. T_1 for modified Bent(K) samples decreases by 10 °C compared with N-Bent(K) but T_2 remains the same for all Bent(K) samples. For natural bentonites, the weight loss decreases in the order N-Bent(D) > N-Bent(G) > N-Bent(K) from 15.2 to 10 % in the temperature range from 25 to 800 °C. The weight loss for modified bentonite samples decreases by ca. 1 % compared with natural ones.

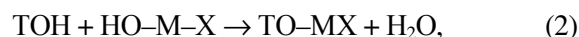
Our practice [8, 10, 11, 15] shows that temperature of 110 °C is optimal for catalyst drying in the process of obtaining metal-complex catalysts supported on natural materials. Taking into account that the water content in the catalyst composition takes a considerable part in achievement of its high catalytic activity in the case of CO oxidation [16] and there is a certain difference between thermochemical behavior of bentonites under study, it is important to quantify the specific amount of water (m_{sp}) residual in all bentonite samples after their drying at 110 °C. To this end, it is necessary to determine the weight losses in the temperature ranges of 25–110 °C and 25–300 °C (Table 2). The second of them corresponds to the loss of almost all water adsorbed on the outer and interlayer surface. It is evident that the specific amount of residual water in Bent(D) based samples is higher than that in others.

The data concerning the weight loss in the range from 400 to 800 °C are used for quantifying the surface OH group content (Table 2). For this purpose, it can be postulate that the reaction of dehydroxylation in the case of both natural and modified bentonites proceeds as follows



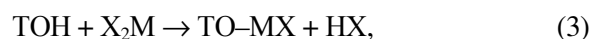
As can be seen from Table 2, N-Bent(G) has the highest content of surface OH groups that remains almost the same for its modified forms.

The catalysts based on H-Bent(D) and H-Bent(K) have the content of OH groups higher than initial bentonites. The equilibrium pH values for aqueous suspension of N-Bent(D) and N-Bent(K) are 8.75 and 6.27, respectively, whereas this magnitude for N-Bent(G) is only 3.96 [15]. Because of the high pH, Pd(II) and Cu(II) complexes on N-Bent(D) and N-Bent(K) can be in their hydrolyzed forms leading to an extra water loss by the following surface reaction



where M = Pd(II), Cu(II); X = Cl⁻, NO₃⁻.

At enhanced temperatures, unhydrolyzed acido complexes of Pd(II) and Cu(II) which formation is probable on N-Bent(G) can participate in other surface reactions



However, as far as C_{OH} values are practically invariant and the derivatograph used in the work does not indicate any difference in the recorded thermograms, it is arguable that those reactions contribute negligibly to the total thermochemical process.

Fig. 2 shows time dependence of C_{CO}^f in the course of carbon monoxide oxidation with air oxygen over the catalysts based on both natural and modified bentonite derived from Gorbskoye deposit.

The results of testing other catalysts are summarized in Table 3.

The reaction kinetics is characterized by attainment of a steady state when the reaction rate, W_{st} , and CO oxidation level, η_{st} , are constant in 25–30 min. It can be concluded that the activity of catalysts under study depends on both the bentonite origin and the technique of its modification. For the catalysts based on natural bentonites, their activity increased in the order N-Bent(D) << N-Bent(K) < N-Bent(G). For the latter two the process is steady-state, however, when η is constant, $C_{\text{CO}}^f > \text{MPC}_{\text{CO}}$. The acid modification of bentonites results in increasing the catalysts activity in the order H-Bent(K)-1 < H-Bent(D)-1 < H-Bent(G)-1. The dependence of the activity of Bent(G) based catalysts increases in the order N-Bent(G) <

$H_2O\text{-Bent(G)} < 300\text{-Bent(G)} < H\text{-Bent(G)}-1$. It should be noted that the high CO oxidation level at which $C_{CO}^f < MPC_{CO}$ is observed for the catalysts based on acid-modified Bent(D) and Bent(G) and on thermally modified Bent(G). The highest activ-

ity is demonstrated by Pd(II)-Cu(II)/H-Bent catalysts, however, the duration of acid modification for Bent(G) and Bent(D) is unequal, *i.e.* 1 and 6 h, respectively.

Table 3. Kinetic and stoichiometric parameters of the reaction of CO oxidation with air oxygen over natural and modified bentonite supported $K_2PdCl_4\text{-Cu(NO}_3)_2\text{-KBr-H}_2O\text{/Bent}$ catalysts

Support	$W \cdot 10^9, \text{ mol/(g}\cdot\text{s)}$		$C_{CO}^f, \text{ mg/m}^3$	$\eta_{st}, \%$	$Q_{exp} \cdot 10^4, \text{ moles of CO}$	n
	W_{in}	W_{st}				
N-Bent(D)	6.8	-	300	-	1.27	0.5
N-Bent(D)-1	12.8	15.1	48	84	12.8	4.7
H-Bent(D)-6	15.6	17.5	8	97	14.9	5.5
N-Bent(G)	14.8	15.7	38	87	13.4	4.9
H-Bent(G)-1	17.2	17.4	10	97	14.9	5.5
$H_2O\text{-Bent(G)}$	15.3	16.1	31	90	13.8	5.1
300-Bent(G)	16.5	17.2	14	95	14.7	5.4
N-Bent(K)	9.6	10.4	126	58	8.91	3.3
H-Bent(K)-1	11.4	13.2	80	73	11.2	4.1

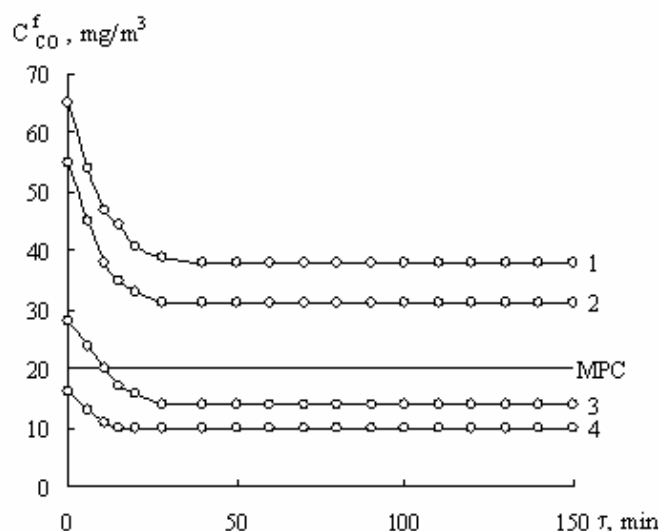


Fig. 2. Time dependence of C_{CO}^f for CO oxidation with air oxygen over $K_2PdCl_4\text{-Cu(NO}_3)_2\text{-KBr/Bent(G)}$ catalysts: 1–N-Bent(G), 2– $H_2O\text{-Bent(G)}$, 3–300-Bent(G), and 4–H-Bent(G)-1

The analysis of stoichiometric reaction parameters, Q_{exp} and n , summarized in Table 3 shows that $n > 1$ for all catalysts under study, except for N-Bent(D) based catalyst. This implies the repeated palladium(II) participation in the reaction of carbon monoxide oxidation with air oxygen.

Comparison of the obtained information about thermochemical properties of bentonites, both natural and modified, and about the activity of related catalysts shows that the highest catalytic ac-

tivity is demonstrated by Pd(II)-Cu(II) complexes supported on the modified forms of Bent(G) which specific amount of water residual after drying at 110 °C is the lowest, whereas the content of surface OH groups is the highest.

CONCLUSIONS

The data of thermogravimetric analysis show that the process of dehydration of bentonites, both natural and modified in a variety of ways, is three-

step, consisting of the loss of adsorbed and inter-layer water and the surface dehydroxylation. The former two steps have the endothermic effect at maximum temperature ranging from 120 to 150 °C whereas the surface dehydroxylation step has the endothermic effect at the maximum temperature ranging from 580 to 600 °C.

The most active catalysts for the reaction of carbon monoxide oxidation with air oxygen are those based on natural and variously modified bentonite originating from the Gorboskoye deposit and having the minimum specific water content (after drying at 110 °C) and the maximum amount of OH groups.

Термохімічні та каталітичні властивості модифікованих бентонітів

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Вивчені термохімічні властивості природних і модифікованих фізичними та хімічними методами бентонітів з трьох родовищ України. Для всіх зразків характерний тріступеневий процес втрати маси з проявом двох ендоефектів в області 120–150 °C і 580–600 °C. Природні та модифіковані бентоніти використовували як носії для отримання паладій(II)-купрум(II)-каталізаторів окиснення монооксиду вуглецю. Встановлено істотний вплив походження і способу модифікування бентонітів на активність каталізаторів.

Ключові слова: бентоніти, модифікування, термохімічні властивості, каталітична активність, монооксид вуглецю, окиснення

Термохимические и каталитические свойства модифицированных бентонитов

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Изучены термохимические свойства природных и модифицированных физическими и химическими методами бентонитов из трех месторождений Украины. Для всех образцов характерен трехступенчатый процесс потери массы с проявлением двух эндоефектов в области 120–150 °C и 580–600 °C. Природные и модифицированные бентониты использовали в качестве носителей для получения палладий(II)-медных(II)-каталитических окисления монооксида углерода. Установлено существенное влияние происхождения и способа модифицирования бентонитов на активность каталитических.

Ключевые слова: бентониты, модифицирование, термохимические свойства, каталитическая активность, монооксид углерода, окисление

REFERENCES

1. Centi G., Parathonor S. Catalysis by layered materials: A review. *Micropor. Mesopor. Mater.*, 107 (2008) 3.
2. Rakitskaya T.L., Kiose T.A., Oleksenko L.P. et al. The effect of water capacity on the activity of Pd(II)-Cu(II) catalyst anchored to acid-modified clinoptilolite in the reaction of low-temperature carbon monoxide oxidation. *Visn. Odes. Univer. Khimiya*, 16 (2011) 5 (in Russian).
3. Tarasevich Y.I., Ovcharenko F.D. Adsorption on Clay Materials, Naukova dumka, Kiev, 1975, 362 p. (in Russian).
4. Tarasevich Y.I., Ovcharenko F.D. Structure and Chemistry of Surface of Layered Silicates, Naukova dumka, Kiev, 1988, 248 p. (in Russian).
5. Tyagi B., Chudasama C.D., Jasra R.V. Characterization of surface acidity of an acid montmorillonite activated with hydrothermal, ultrasonic and microwave techniques. *Appl. Clay Sci.*, 31 (2006) 16.
6. Nogueira F.G.E., Lopes J.H., Silva A.C. et al. Catalysts based on clay and iron oxide for oxidation of toluene. *Appl. Clay Sci.*, 51 (2011) 385.
7. Clearfield A. Preparation of pillared clays and their catalytic properties in *Advanced Catalysts and Nanostructured Materials: Modern Synthetic Methods*, Academic Press, San Diego, 1996, 345.
8. Rakitskaya T.L., Kiose T.A., Volkova V.Y., Ennan A.A. The use of Ukrainian natural aluminosilicates for development of new metal-complex catalysts for air purification from gaseous toxic substances, *Energo-tehnologii i resursosberezhnie*, 6 (2009) 18 (in Russian).
9. Rhodes C.N., Franks M., Parkes G.M.B., Brown D.R. The effect of acid treatment on the activity of clay supports for ZnCl₂ alkylation catalysts, *J. Chem. Soc., Chem. Commun.*, 12 (1991) 804.
10. Rakitskaya T.L., Kiose T.A., Reznik L.I. Natural and chemically modified basalt tuffs. Phase composition and catalytic activity of surface Cu(II)-Pd(II) complexes in the reaction of carbon monoxide with oxygen, *Chemistry, Physics and Technology of Surface*, 3 (2012) 215 (in Russian).
11. Rakitskaya T.L., Kiose T.A., Truba A.S. et al. Adsorption of water vapour by natural and chemically modified clinoptilolite and mor-denite samples, *Chemistry, Physics and Technology of Surface*, 3 (2012) 455.
12. Dellisanti F., Minguzzi V., Valdre G. Thermal and structural properties of Ca-rich montmorillonite mechanically deformed by compaction and shear, *Appl. Clay Sci.*, 31 (2006) 282.
13. Onal M., Sarikaya Y. Thermal behavior of bentonite, *J. Therm. Anal. Calorim.*, 90 (2007) 167.
14. Nogueira F.G.E., Lopes J.H., Silva A.C. et al. Catalysts based on clay and iron oxide for oxidation of toluene, *Appl. Clay Sci.*, 51 (2011) 385.
15. Rakitskaya T.L., Kiose T.A., Zryutina A.M. et al. Solid-state catalysts based on bentonites and Pd(II)-Cu(II) complexes for low-temperature carbon monoxide oxidation, *Solid State Phenomena*, 200 (2013) 299.
16. Rakitskaya T.L., Kiose T.A., Oleksenko L.P. et al. Effect of a water content on the activity of Pd(II)-Cu(II) catalyst anchored to acid-modified basalt tuff in carbon monoxide oxidation, *Zhurn. Priklad. Khimii*, 85 (2012) 1422 (in Russian).

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