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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect Exerted by Acid Modification of Bazalt Tuff on Catalytic Activity of Fixed Acido Complexes of Palladium(II) and Copper(II) in the Reaction of Carbon(II) Oxide Oxidation with Air Oxygen

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Abstract—The physicochemical and structural characteristics of bazalt tuff were studied. The optimal conditions of its acid modification, at which the high-activity catalyst Pd(II)-Cu(II)-Br-/H-bazalt tuff of a low-temperature oxidation of carbon(II) oxide with air oxygen is formed, were determined.

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Pd(II) and Cu(II) acido complexes anchored to oxide carriers (SiO_2, Al_2O_3, and TZK-M tripoli) are effective catalysts of a low-temperature oxidation of carbon(II) oxide with air oxygen [1–3]. On other carriers (such as for example aluminum silicates or synthetic zeolites), high-activity Pd(II)–Cu(II) catalysts ensuring air quality standards for carbon monoxide are not necessarily formed [1].

The physicochemical properties of a carrier, mainly its proton acidity, essentially affect the mechanism of the formation of surface metal complexes. Pd(II) acido complexes, while anchored on a carrier, are more sensitive to the change of its acidic properties than Cu(II) complexes. It was shown in particular that with use of the K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O impregnating solution with the same ratio of the components, the Pd(II) hydroxo bromide complexes are formed on a natural carrier, TZK-M tripoli (S_{sp}=12 $m^2 g^{-1}$, pH of aqueous suspension 5.32), whereas the Pd(II) chlorobromide complexes having lesser activity are formed on a less acid silica gel MSMK (S_{sp}=490 $m^2 g^{-1}$, pH of aqueous suspension 2.4) [5,6].

Natural mono- and polymineral zeolites are widely used as sorbents and catalysts [7–12], whereas as catalyst support, they have been studied poorly [7–12]. It is known [13] that natural zeolite containing montmorillonite as major component is used to fix gold nanopartciles and thus to obtain a catalysts of CO oxidation with air oxygen at 298 K [13]. Bazalt tuff (natural polymineral zeolite) is a promising carrier for the Pd(II) and Cu(II) acido complexes catalyzing the above reaction [14]. At the same time, owing to the low activity of this catalyst, a need arises to optimize the physicochemical properties of the tuff to obtain Pd(II) acido complexes of a necessary composition.

This study is concerned with the effect exerted by acid modification on the phase and chemical composition, specific surface area, and acidic properties of the bazalt tuff, and on the catalytic activity of the Pd(II) and Cu(II) acido complexes anchored on in the reaction of low-temperature oxidation of carbon(II) oxide.

EXPERIMENTAL

Natural polymineral zeolite, bazalt tuff (Rovenskaya obl.), contains the following zeolite phases (wt %): clinoptilolite and mordenite 35–40, montmorillonite 30–40, and feldspar, silica, hematite, and rutile, remainder. The chemical composition (in terms of oxides) is as

Table 1. Effect of the number of acid treatments on the physicochemical and structural properties of samples of bazalt tuff

Carrier	CO oxidation in the steady-state mode, $w_{st}\times10^9$ mol g^{-1} s^{-1}	Rate constant, k_I s^{-1}	Final concentration c^f_{CO}, mg m^{-3}	Degree of CO conversion in steady-state mode, x_{st}, %
P-BT	4.2	0.4	230	23
N-BT3*	15.1	2.6	48	84
N-BT6	16.8	3.8	20	93
N-BT9	17.2	4.4	13	96
N-BT12	16.2	3.2	30	90
N-BT15	16.3	3.3	28	91

* Numbers denote the total duration of the acid treatment (h).

follows (wt %): SiO_2 67.25, Al_2O_3 12.92, Fe_2O_3 11.96, MgO 7.00, Na_2O 4.87, CaO 2.79, TiO_2 1.98, K_2O 1.48, SO_3 0.30, MnO 0.17, and P_2O_5 0.14 [15,16].

The chemical modification of the BT samples included a step-wise treatment in a 3M HNO_3 at 98°C. The time of each step was 3 h, and the number of steps varied from one to five. After each step the samples were washed with distilled water to negative reaction with respect to nitrate ions and to constant pH of an aqueous extract (5.0–6.0).

The chemical analysis of the initial and modified BT samples was performed by the generally accepted procedures [17–19].

The specific surface area of samples was determined by thermal desorption [20]. The samples were preliminarily kept in a helium flow at 200°C. The measurements were performed on a gas chromatographic installation (LKhM-8MD chromatograph, heat-conductivity detector, carrier gas 80%He + 20%Ar). The determination error S_{sp} was no more than 10%.

The X-ray diffraction patterns in the region $8° < 2\theta < 40°$ were recorded on a DRON-3M diffractometer ($Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, voltage 30 kV, current 28 mA). The crystallinity of the samples was estimated by the integral intensity of the chosen peaks.

The catalyst samples were obtained by impregnation of a carrier with a solution containing palladium(II) chloride, copper(II) nitrate, and potassium bromide. A carrier (10 g) of constant fractional composition, 1.0-0.5-mm fractions (average size 0.75 mm), was impregnated with a 4 ml of the solution with a prescribed ratio of the components. The obtained wet sample was dried at 110°C in air to constant mass, then placed into a dessicator and kept there over a 30–35% sulfuric acid till 0.03 g of H_2O was absorbed per 1 g of the carrier. The catalyst samples obtained are the K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O/BT multicomponent systems. In all cases, the content of the catalyst components in terms of the mass of dry carrier was calculated to be (mol g^{-1}): $c_{K2PdCl4} = 1.36 \times 10^{-5}$, $c_{Cu(NO_3)_2} = 2.90 \times 10^{-5}$, and $c_{KBr} = 1.02 \times 10^{-4}$.

The catalytic activity of the samples in the reaction of CO oxidation at 20°C was determined in a thermostated flow-through installation in the reactor with a fixed catalyst bed. The sizes of the reactor, fineness of samples, and the linear velocity of flow of the gas-air mixture (GAM)(U = 4.2 cm s^{-1}) corresponded to the conditions of ideal displacement and the kinetic region of proceeding of the reaction [14].

The gas-air mixture with a CO concentration of 300 mg m^{-3} was obtained by dilution of concentrated gas (98–99 vol % CO) with purified air. The initial, $c^{in}_{CO,}$ and final, $c^{fin}_{CO,}$ concentrations (M) were determined with a 621EkhO4 gas analyzer (sensitivity 2 mg m^{-3}). The relative humidity of GAM, $\varphi_{GAM,}$ was maintained constant (76%). The reaction rate (mol g^{-1} s^{-1}) was calculated by the formula:

$$w = \frac{\omega(c^{in}_{CO} - c^{fin}_{CO})}{m_c}, \quad (1)$$

where $w = 1.67 \times 110^{-2}$ is the space velocity of the GAM (l $s^{-1)}$ and m_c is the mass of the catalyst sample (g).

The steady-state parts of the kinetic curves were used for calculating the rate constant (s^{-1}):

$$k_I = \frac{1}{\omega'}\ln\frac{c^{in}_{CO}}{c^{fin}_{CO}}, \quad (2)$$

where τ' is hypothetical time of contact.

The most effective method of change of the physicochemical properties of natural zeolites is the treatment with mineral acids (HCl, HNO_3, H_2SO_4, $HcClO_4$, $HClO_4$) [7, 10, 12].

Table 1 presents results of the chemical analysis of samples of natural BT (P-BT) and acid-modified BT

(N-BT3, N-BT6, N-BT9, N-BT12, and N-BT15) for the content of the main components (SiO_2, Al_2O_3, and Fe_2O_3), whose ratio may essentially affect the catalytic properties of anchored Pd(II) and Cu(II) complexes in the reaction of carbon(II) oxide oxidation. As seen, with increasing number of the acid treatments (maximum total time of the treatments was 15 h), the concentrations of Al_2O_3 and Fe_2O_3 decrease relatively similarly, i.e., their ratio remains virtually constant, whereas the SiO_2/Al_2O_3 ratio increases.

The acid treatment changed not only the chemical composition of BT samples but also their specific surface area (Table 1). The S_{sp} increased nearly two-fold after the first 3-h treatment (Table 1, N-BT3 sample) and varied only slightly on further treatment.

The X-ray powder diffraction patterns of the samples of natural and acid-modified bazalt tuffs and that of the Pd(II)–Cu(II)–Br^-/N-BT catalyst are demonstrated in Fig. 1. The zeolite phases (heulandite-clinoptilolite, mordenite, and montmorillonite), along with α-SiO_2, Fe_2O_3, and TiO_2, were identified using the data of [21] and the International Center Powder Diffraction Data (JCPDS) File.

Samples of the Pd(II)–Cu(II)–Br^-/N-BT catalyst are well-homogenized. The analysis revealed no initial Pd(II) and Cu(II) salts and products of their conversion (PdO, Pd^0, CuO, and Cu_2O), which may be formed during impregnation and drying of the carrier. This result is consistent with the data of [10, 22, 23].

Though diffraction patterns of the basalt tuff subjected to acid modification and impregnation with the K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O solution changed only slightly in comparison with the spectrum of initial sample, the crystallinity of the modified samples was decreased. The crystallinity was determined from the change in the integral intensity of the main peaks corresponding to clinoptilolite (2θ 9.91° and 29.85°), mordenite (2θ 23.51°, 25.78°, and 27.86°), and montmorillonte (2θ 20.96°). It was established that a decrease in crystallinity of the basalt tuff samples results from the acid treatment and, as consequence, catalyst formation. The maximum decrease in crystallinity (42%) was observed for Pd(II)–Cu(II)–Br^-/H-BT15 catalyst. By data of [22], the crystallinity of the Pd(II)–Cu(II)/mordenite catalyst, used in NO reduction, also decreases by approximately 40% in comparison with the crystallinity of mordenite.

The data of Fig. 2 and Table 2 demonstrate the effect exerted by the SiO_2/Al_2O_3 molal ratio on the kinetic characteristics of the K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O/BT catalyst of a low-temperature oxidation of carbon(II) oxide with air oxygen. The effect increases as the total duration of the acid treatment of basalt tuff grows.

For example, in CO oxidation on natural BT in the presence of a catalyst the reaction rate and the conversion degree of carbon(II) oxide x are low, decreasing to zero value after 100 minutes. However, even upon the first acid treatment of BT the properties of a catalyst change dramatically, which is reflected in the process kinetics. After 50 min of treatment, the reaction rate becomes constant (w_{st}) and the degree of the CO conversion in the steady-state mode (x_{st}), equal to 84%. The maximum activity is exhibited by the Pd(II)–Cu(II)–Br^-/N-BT9 catalyst. The final CO concentration, attainable at $x = 96\%$ in this case, is lower than the maximum concentration permissible for the working zone (20 mg m^{-3}). On further acid modification of the tuff the activity of the catalyst decreases.

The scope of the data obtained shows that the acid modification of bazalt tuff changes its physicochemical properties and structure, which leads to a marked increase in the activity of the metal complex catalyst (Fig. 2,

Table 2. Catalytic activity of Pd(II) and Cu(II) acido complexes anchored to natural and acid-modified bazalt tuff in reaction of low-temperature oxidation of carbon(II) oxide

Number of treatments	Sample	Concentration, wt %			SiO_2/Al_2O_3 molal ratio	S_{sp}, $m^2 g^{-1}$
		SiO_2	Al_2O_3	Fe_2O_3		
0	P-BT	68.44	12.82	10.14	9.1	17.0
1	N-BT3*	69.16	12.54	9.82	9.3	30.0
2	N-BT6	70.56	11.93	9.02	10.1	30.0
3	N-BT9	74.02	9.68	8.28	13.0	29.0
4	N-BT12	75.62	8.74	6.48	14.7	27.0
5	N-BT15	78.74	7.09	5.61	18.9	27.0

* Numbers denote the total duration of the acid treatment (h)

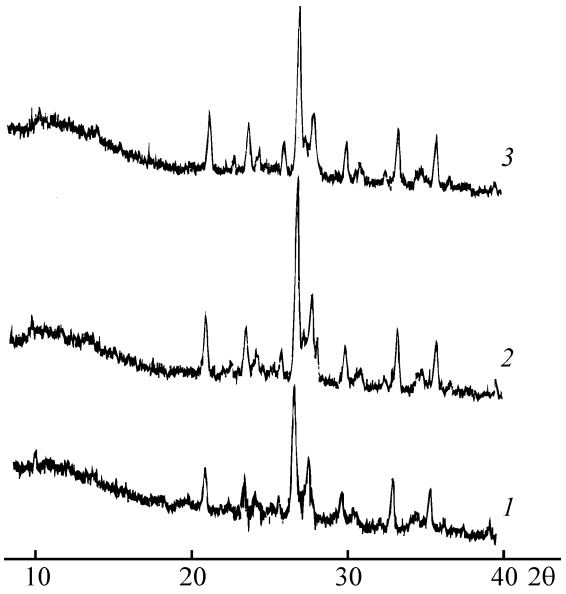

Fig. 1. X-ray diffraction patterns of (*1*) natural bazalt tuff (sample P-BT), (*2*) acid-modified bazalt tuff (sample N-BT9), and (*3*) $PdCl_2$–$CuCl_2$–Br–/H-BT9 catalyst. (2θ) Bragg angle (deg).

Table 2). A sharp increase in S_{sp} of the bazalt tuff modified during 3 hours shows that its structural characteristics are changed so that for both the catalyst components, Pd(II) and Cu(II), and the CO molecules the inner channels of zeolite phases become more accessible. As the total duration of the acid modification increases further, S_{st} changes only slightly (within the determination error). However, the crystallinity of the samples decreases owing to disordering of the zeolite skeleton. The optimum crystallinity decrease corresponding to the highest catalytic activity (Table 2) is 30%. As the crystallinity decreases further, the activity of the catalyst decreases.

The acid modification transforms basalt tuff into the H form and causes OH groups, both terminal (Si–OH, Al–OH) and bridging (such as Al–OH–Si in particular), to form. The above groups have different acidities, depending on the SiO_2/Al_2O_3 ratio, crystallinity [24], and OH position (at the zeolite surface or inside its channels) [25].

Evidently, the acidity on the surface for N-BT9 is optimal, and it is this carrier, on which a catalyst possessing highest activity is formed after impregnation with a K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O solution and following drying (Table 2). The result obtained is in line with the data of [4]. Therefore, it is not improbable that palladium(II) hydroxo bromide complexes, which, jointly with Cu(II) complexes, ensure high degree of the carbon(II) oxide oxidation with air oxygen, are formed on the N-BT9 sample.

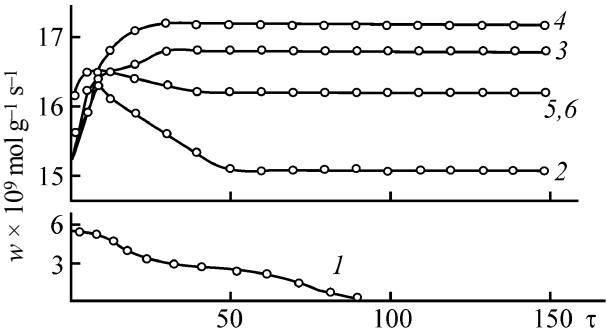

Fig. 2. Variation of the reaction rate w (mol g^{-1} s^{-1}) with time τ (min) in the reaction of CO oxidation with oxygen in the presence of the K_2PdCl_4–$Cu(NO_3)_2$–KBr–H_2O/BT catalyst. The SiO_2/Al_2O_3 molal ratio in BT: (*1*) 9.1 (P-BT), (*2*) 9.3 (N-BT3), (*3*) 10.1 (N-BT6), (*4*) 13.0 (N-BT9), (*5*) 14.7 (N-BT12), and (*6*) 18.9 (N-BT15).

CONCLUSIONS

(1) The kinetics of the carbon(II) oxide oxidation with air oxygen in the presence of the catalysts obtained by anchoring Pd(II) and Cu(II) acido complexes on samples of basalt tuff (natural and acid-modified at various times) were studied.

(2) The analysis of the data obtained showed that the highest activity is exhibited by the catalyst anchored on N-BT sample. The total duration of the acid treatment of this sample was 9 h. This sample is characterized by the molar ratio SiO_2/Al_2O_3 = 9.5 and its crystallinity is decreased by 30% in comparison with natural basalt tuff. At the inlet CO concentration in air of 300 mg m^{-3} its outlet concentration in the presence of the given catalyst was 13 mg m^{-3}, which is lower than maximum permissible concentration (MPC) in the air of the working zone.

REFERENCES

1. Rakitskaya, T.L., Ennan, A.A., and Volkova, V.Ya., *Nizkotemperaturnaya kataliticheskaya ochistka vozdukha ot monooksida ugleroda* (Low-Temperature Catalytic Treatment of Air to Remove Carbon Monoxide), Odessa: Ekologiya, 2005.
2. Arellano, M.A., Rodina, T.A., Solonina, N.A., et al., *Trudy I Mezhdunarodnoi Nauchno-Prakticheskoi Konferentsii "Zashchita okruzhayushchei sredy, zdorov'e i bezopasnost' v svarochnom proizvodstve* (Proceeding, I Intern. Scientific and Practical Conf. "Environmental Protection. Health, and Accident Prevention in Welding"), Odessa: Astroprint, 2002, pp. 397–400.
3. RF Patent 2267354.

4. Rakitskaya, T.L., Paina, V.Ya., and Ennan, A.A., *Koord. Khim.,* 1987, vol. 13, no. 10, pp. 1393–1397.

5. Rakitskaya, T.L., and Paina, V.Ya., I*zv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol*., 1988, vol. 31, no. 7, pp. 49–52.

6. Rakitskaya, T.L., and Paina, V.Ya., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1991, vol. 34, no. 12, pp. 63–66.

7. Tarasevich, Yu.I., *Prirodnye sorbenty v protsesse ochistki wod* (Natural Sorbents in Water Purification), Kiev: Naukova Dunka, 1981.

8. Vasylechko, V.O., Lebedynets, I.O., Gryshchouk, G.V., et al., *Adsorption Sci. Technol*., 1996, vol. 14, no. 5, pp. 267–277.

9. Vasylechko, V.O., Gryshchouk, G.V., Kuz'ma, Yu.B., et al., *Micropor. Mezopor. Mater*., 2003, vol. 60, nos. 1–3, pp. 183–196.

10. Korkuna, O., Leboda, R., Skubiszewska-Zieba, J., et al., *Micropor. Mezopor. Mater*., 2006, vol. 87, nos. 1–3, pp. 243–254.

11. Smola, V.I., and Kel'tsev, N.V., *Zashchita atmosfery ot dvuokisi sery* (Protection of the Atmosphere from Sulfur Dioxide), Moscow: Metallurgiya, 1976.

12. Tsitsishvili, G.V, Andronikashvili, T.G., Kirov, G.N., and Filozova, L.D., Prirodnye tseolity (Natural Zeolites) Moscow: Khimiya, 1985.

13. Garriazo, J.G., Martinez, L.M., Odriozola, J.A., et al., *Appl. Catal. B: Environmental,* 2007, vol. 72, nos.1–2, pp. 157–165.

14. Rakitskaya, T.L., Kiose, T.A., and Volkova, V.Ya., *Vestn. Odess. Nat. Univ., Khim.*, 2003, vol. 8, nos. 7–8, pp. 153–158.

15. Golyar, N.G., *Tufi: vikoristannya v galuzyakh ekonomiki* (Tuffs. Economical Applications), Rivne, 2002.

16. Shvets, A.N., and Voloshchuk, A.G., *Vestn. Odess. Nat. Univ., Khim.,* 2004, vol. 9, no. 7, pp. 138–145.

17. *Analiz mineral'nogo syr'ya* (Analysis of Minerals), Knipovich, Yu.N., and Morachevskii, Yu.V. (Eds.), Leningrad: Goskhimizdat, 1956.

18. Arnautov, N.V., *Standartnye obraztsy khimicheskogo sostava prirodnykh mineral'nykh veshchestv* (Reference Samples of Chemical Composition of Natural Mineral Materials), Novosibirsk: Nauka, 1990.

19. Katskov, D.A., and Orlov, K.A., *Atomno-absorbtsionnyi analiz geologicheskikh obraztsov. Elektrotermicheskaya atomizatsiya* (Atomic Absorption Analysis of Geological Samples. Eletrothermal Atomization), Murmansk: Apatity, 1990.

20. Yakerson, V.I., and Rozanov, V.V., *Itogi Nauki Tekh., Ser. Fiz. Khim. Kinet.*, 1979, no. 3.

21. Treacy, M.N.J., and Higgins, J.B., *Collection of Simulated XRD Powder Patterns for Zeolites*, Amsterdam: Elsevier, 2001.

22. Olivera, A.M., Crize, L.E., da Silveira, R.S., et al., *Catal. Commun*., 2007, vol. 8, no. 8, pp. 1293–1297.

23. Dams, M., Drijkoningen, L., Pauwels, B., et al., *J. Catal.,* 2002, vol. 209, no. 1, pp. 225–236.

24. Simon-Masseron, A., Marques, J.P., Lopes, J.M., et al., *Appl. Catal. A: General,* 2007, vol. 316, no. 1, pp. 75-82.

25. Datka, J., Gil, D., and Kubacka, A., *Zeolites*, 1996, vol. 17, nos. 5–6, pp. 428–433.