# Hydrothermal Synthesis of Porous Al<sub>2</sub>O<sub>3</sub>/Al Metal Ceramics: III. Effect of the Thermal Dehydration of Bayerite on the Formation of a Porous Al<sub>2</sub>O<sub>3</sub>/Al Composite

A. I. Rat'ko\*, V. E. Romanenkov\*\*, E. V. Bolotnikova\*, and Zh. V. Krupen'kina\*

\* Institute of General and Inorganic Chemistry, Belarussian Academy of Sciences, Minsk, 270072 Belarus \*\* Institute for the Advanced Training and Retraining of Personnel, Ministry of Education of the Republic of Belarus, Minsk, Belarus

Received December 5, 2001; in final form, March 14, 2003

**Abstract**—It was found that the diffusion permeability of a porous cover on aluminum particles increased as a result of the structural transformations of bayerite into active aluminum oxide on the thermal treatment of a porous  $Al(OH)_3/Al$  composite. The cyclic treatment (each cycle included a treatment with water at 100°C and a thermal treatment at 550°C) eliminated diffusion limitations and resulted in the formation of porous  $Al_2O_3/Al$  metal ceramics with a required set of adsorption–structure and mechanical properties. The following two competing processes were found to affect the formation of the mechanical properties of the synthesized material: the formation of "new" contacts in the course of the precipitation of aluminum hydroxide and the degradation of "old" contacts under the action of mechanical stresses that appear in the course of synthesis.

#### INTRODUCTION

Previously [1, 2], we reported on the studies of the kinetics of oxidation of aluminum powder with water and the structure formation of a porous Al(OH)<sub>3</sub>/Al composite, proposed a mechanism of synthesis, and calculated the diffusion coefficient of the hydroxo complexes of aluminum through a bayerite layer. We found that the synthesis of the porous composite obeys the Wagner law, when the formation of a solid product in the course of an oxidation reaction results in the inhibition of diffusion. The elimination of diffusion limitations in the Al-Al(OH)<sub>3</sub>-H<sub>2</sub>O system is of considerable interest because it provides an opportunity to control the synthesis and to prepare porous metal ceramics with required properties. It is well known [3–5] that the dehydration of all modifications of aluminum hydroxide occurs within the temperature range 300-550°C with the formation of an active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure and a considerable change in the pore structure of the material due primarily to an increase in the specific surface area and the sorption pore volume. The bayerite layer on aluminum particles would be expected to change its adsorption-structure characteristics upon thermal dehydration. Therefore, in this (third) paper, we report the results of experimental studies on the effect of bayerite structure transformations on the kinetics of oxidation of aluminum powder and on the formation of the structure and properties of a porous Al<sub>2</sub>O<sub>3</sub>/Al composite.

#### EXPERIMENTAL

Thermograms, which illustrate thermal effects in the course of structural transformations in the thermal decomposition of bayerite, were obtained on a Q-500D instrument (Paulik, Hungary) at a heating rate of 5 K/min in air; the DTA, DTG, and TG curves were recorded simultaneously. The electron-microscopic, adsorption, and texture characteristics and the mechanical strength of synthesized samples; changes in the conversion of aluminum with time; and the phase composition of thermal degradation products were determined with the use of procedures described previously [1].

The porous Al(OH)<sub>3</sub>/Al composite samples as cylinders ( $10 \times 10$  mm) were formed by oxidation with water at 100°C for 2 h at atmospheric pressure. Next, they were dried at 120°C for 30 min and calcined at 550°C for 1 h until the complete conversion of bayerite into active alumina. Thereafter, this cycle of sample treatment was repeated several times. Simultaneously, the evolution of the adsorption and texture characteristics, the mechanical strength, and the microstructure of the porous Al<sub>2</sub>O<sub>3</sub>/Al composite was studied after each cycle.

To determine the adsorption and texture characteristics, the adsorption–desorption isotherms of benzene vapor at 20°C were analyzed, which were obtained gravimetrically in a vacuum system with the McBain–Bakr quartz spring balance. The samples were preheated at 140°C in a vacuum for 4 h. Experimental points were measured to the relative pressure  $P/P_s = 0.9$ ; next, extrapolation to  $P/P_s = 1.0$  was performed.



Fig. 1. DTA curve of a bayerite precipitate.

The specific surface area, average pore radius, and sorption pore volume were calculated from the adsorption isotherms with the use of the BET theory.

The total pore volume of the material synthesized was determined by gravimetry; the samples were predried at 120°C for 1 h and then impregnated with water for 0.5 h. The macropore surface area was determined by mercury porosimetry using a PA-3M instrument.

## **RESULTS AND DISCUSSION**

# Structure Transformations of Bayerite in the Course of Its Thermal Dehydration

The DTA curve of a flakelike precipitate of bayerite, which was obtained by the oxidation of aluminum powder with water with intense stirring, exhibits four endo peaks within the temperature range 100–550°C (Fig. 1). These peaks due to the thermal decomposition of the precipitate were interpreted as described below. At 108°C, the removal of physisorbed water occurred (a broad endo peak). Two endo peaks of different intensities at 220 and 310°C resulted from the thermal decomposition of amorphous aluminum hydroxide and bayerite, respectively. Finally, a small endo peak at 530°C resulted from the decomposition of pseudoboehmite. As found by X-ray diffraction analysis, this resulted in the formation of active alumina. Upon the thermal treatment of the precipitate, the sorption volume and the specific surface area increased from 0.045 to 0.260 cm<sup>3</sup>/g and from 53 to 368 m<sup>2</sup>/g, respectively. Such a pore-structure transformation is characteristic of aluminum hydroxides [5]; this transformation is due to an increase in the true density of the material upon dehydration. The isotherm of benzene adsorption-desorption on the precipitate thermally treated at 550°C. which is shown in Fig. 2, can be assigned to type 2 according to the IUPAC Classification [6].

Almost all of the thermal effects accompanying the thermal treatment of the porous  $Al/(OH)_3/Al$  composite (Fig. 3) are weakly pronounced, and they differ significantly from those considered above. The first endo peak (113°C) is also due to the removal of physisorbed



**Fig. 2.** Isotherm of benzene adsorption–desorption at 20°C on active alumina obtained by the thermal treatment of a bayerite precipitate at 550°C.

water. The second and third endo peaks (295 and 420°C) conceivably are the consequence of the decomposition of bayerite and pseudoboehmite, respectively. The fourth endo peak ( $660^{\circ}$ C) is due to the melting of aluminum. The conversions of bayerite into pseudoboehmite and of pseudoboehmite into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are accompanied by an increase in the density of the porous precipitate and, consequently, by a decrease in its volume. As a result, spots of the metal nucleus of a particle become naked. Therefore, the first broad exo peak at 380°C and the second exo peak at 648°C are associated with heat release in the oxidation of aluminum with atmospheric oxygen. Effects of this kind, which are a consequence of structure transformations in the oxide film and the oxidation of the naked spots of an aluminum nucleus, were observed previously [1] in the oxidation of the parent ASD-1 aluminum powder in air. Thus, structural transformations of aluminum hydroxide and the oxidation of aluminum metal simultaneously occur in the course of thermal treatment of the porous Al(OH)<sub>3</sub>/Al composite in air. As mentioned above, a lower intensity of peaks related to the thermal decomposition of bayerite and a shift of the temperature ranges of the conversion of various aluminum



Fig. 3. DTA curve of the porous  $Al(OH)_3/Al$  composite synthesized at 100°C for 2.5 h.

hydroxide species are observed because of the superposition of thermal effects due to the above parallel processes and the low concentration of bayerite in the porous  $Al(OH)_3/Al$  composite.

The phase transformations of aluminum hydroxides in the course of the thermal treatment of a porous composite synthesized under hydrothermal conditions were studied [7-10]. Anan'in et al. [7] found that monophase boehmite (AlOOH) was formed at  $T \ge 180^{\circ}$ C, whereas the presence of aluminum hydroxide  $(Al(OH)_3)$  (no more than 20%) in reaction products was observed at a lower temperature. Tikhov with coauthors [8, 9], who used thermal analysis, X-ray diffraction, and IR spectroscopy, found that, in the course of hydrothermal synthesis at 150–250°C for 0.5–6.5 h, an amorphous layer of boehmite (AlOOH) was formed on the surface of aluminum particles; this boehmite was converted into crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> upon the thermal treatment of the material. The desorption of water and the thermal decomposition of boehmite were accompanied by endo effects at 120 and 520°C, respectively, whereas the structural rearrangement of the oxy hydroxide was accompanied by an exo effect at 320...330°C. The thermal-analysis curve of reaction products obtained by the oxidation of aluminum powder in a free volume [10] exhibited three endothermic peaks of water release: the removal of physisorbed (nonstructure) water at 120°C, the decomposition of boehmite at 230–290°C, and the decomposition of pseudoboehmite at 420-450°C. Moreover, an endo peak due to the melting of residual aluminum at 660°C was sometimes observed. The predominant phase formed in the course of the chemical reaction of aluminum with water under hydrothermal conditions was pseudoboehmite with an effective pore radius of 3 nm and a specific surface area of up to  $320 \text{ m}^2/\text{g}$ . The above data suggest that the phase composition of aluminum hydroxides formed in the course of hydrothermal synthesis primarily depends on the reaction temperature. The concentration of bayerite in the precipitated products increased as the synthesis temperature was decreased, whereas the concentration of boehmite increased with temperature. This corresponds to the phase diagram of the Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system [11].

In the thermal decomposition of gibbsite prepared by colloid-chemical methods [3], a small endo effect at 200°C was due to the partial degradation of the gibbsite structure. In the region of the second endo effect at 375°C, gibbsite was completely decomposed to form boehmite. A small amount of crystalline y-Al<sub>2</sub>O<sub>3</sub> appeared simultaneously with the boehmite. In the region of the third endo effect (500°C), the structure of the boehmite completely decomposed, and it was converted into an amorphous state. The thermal decomposition of aluminum hydroxide can occur in several steps; in this case, the removal of water molecules corresponds to each of the endothermic effects (two molecules for gibbsite or one molecule for boehmite). Usually, the endothermic effects of the dehydration of gibbsite, which is structurally similar to bayerite in many respects [11], correspond to temperatures of 225–275, 200-300, and 510-550°C. Thus, an amorphous hydroxide, bayerite, gibbsite, pseudoboehmite, or boehmite can be formed depending on the temperature at which the porous composite ceramics were synthesized. At temperatures of  $\leq 100^{\circ}$ C, bayerite of gibbsite is formed, the dehydration of which always initially resulted in the formation of boehmite as a transient phase in the formation of active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Table 1 summarizes the results of a study on the effect of the thermal decomposition of bayerite on the adsorption and texture characteristics of the porous composite. Thermal treatment, which caused the transformation of Al(OH)<sub>3</sub>/Al into Al<sub>2</sub>O<sub>3</sub>/Al, almost doubled the sorption pore volume and increased the specific sur-

Synthesis duration, h	Sorption pore volume ( $V_s$ ), cm <sup>3</sup> /g		Specific surface area ( $S_{sp}$ ), m <sup>2</sup> /g		Average pore radius (r), nm	
	Al(OH) <sub>3</sub> /Al	Al <sub>2</sub> O <sub>3</sub> /Al	Al(OH) <sub>3</sub> /Al	Al <sub>2</sub> O <sub>3</sub> /Al	Al(OH) <sub>3</sub> /Al	Al <sub>2</sub> O <sub>3</sub> /Al
2	0.035	0.05	26	28.3	2.0	3.0
3.5	0.035	0.058	28	45	2.3	2.8
5	0.04	0.08	34	57	2.4	2.8
7	0.04	0.08	36	58	1.9	3.05

Table 1. Effect of thermal treatment on the adsorption and texture characteristics of the porous composite



**Fig. 4.** Dependence of the degree of aluminum conversion on the temperature of thermal pretreatment of the porous Al(OH)<sub>3</sub>/Al composite.

face area by 10 to 60%. The average pore radius, which was calculated using the equation  $r = 2V_s/S_{sp}$ , was only slightly affected by this treatment.

The bayerite layer on aluminum particles is a porous membrane semipermeable to diffusing species (water molecules and the hydroxo complexes of aluminum). A change in the structure of this membrane on thermal decomposition is primarily related to an increase in the porosity. At the little affected effective pore radius, this is equivalent to an increase in the number of pores per unit surface area of the membrane, that is, to an increase in its permeability.

# Effect of the Thermal Decomposition of Bayerite on the Rate of Oxidation of the Porous Composite with Water

The autoclave synthesis of a porous composite exhibits undeniable advantages in terms of the control of a chemical reaction and the obtaining of a required aluminum conversion into hydroxides with different phase compositions because it provides an opportunity to increase the temperature. In turn, the temperature is responsible for dissolution, reprecipitation, and structural evolution processes in the precipitate, which provide a continuous access of water to the reaction surface [7–9, 12, 13]. The capabilities of the synthesis at 100°C are considerably restricted by a rate-limiting step, the diffusion supply of water to the surface of aluminum and the counterdiffusion of the hydroxo complexes of aluminum through the growing porous layer of bayerite to the deposition surface. However, the above studies demonstrated that thermal dehydration is responsible for a significant structural rearrangement of the porous cover on aluminum particles. Consequently, this process can be used not only as a final operation for producing active alumina but also as a technique for increasing the diffusion permeability of deposited products.



**Fig. 5.** Dependence of the degree of aluminum conversion on the number of cycles including thermal treatment and oxidation with water.

Figure 4 demonstrates the experimental dependence of the conversion of aluminum on pretreatment temperature. The initial porous Al(OH)<sub>3</sub>/Al composite with a conversion of 0.14 was thermally treated in air under stationary conditions for 1 h at 100-600°C. Thereafter, it was treated with water at 100°C for 2 h at atmospheric pressure. The conversion of the initial sample on the initial horizontal portion of the curve remained almost unchanged. This fact suggests that the thermal treatment of the composite at 400°C cannot overcome diffusion limitations and does not activate the chemical reaction. An increase in the temperature of thermal treatment to 500°C resulted in a stepwise increase in the conversion  $\alpha$  to ~0.23 and a twofold increase of  $\alpha$  = 0.28 after thermal treatment at 600°C. A comparison of the dependence obtained with the results of thermal analysis demonstrates the coincidence between the temperature range of pretreatment that results in the activation of the chemical reaction and the temperature ranges of bayerite conversion into active alumina. This suggests the direct dependence of the chemical interaction of aluminum powder with water on the pore structure of covers on aluminum particles. Consequently, the pore structure of active alumina formed upon the thermal decomposition of bayerite is no barrier for water diffusion to the reaction surface.

In a cyclic treatment, when each cycle included thermal treatment at 550°C for 1 h and treatment with water at 100°C for 2 h, the linear dependence of the conversion on the number of cycles n was observed (Fig. 5). This is likely due to increased access to the surface of aluminum not only because of the formation of active alumina upon the thermal dehydration of bayerite but also as a consequence of oxide cover degradation under the action of mechanical stresses, which appeared in the porous composite as the volume of the solid phase increased.

Degree of conversion (α), %	$P/P_{\rm s}$ at the be- ginning of hysteresis	Adsorption volume, cm <sup>3</sup> /g		Specific surface area ( $S_{sp}$ ), m <sup>2</sup> /g		Average pore
		at the beginning of hysteresis	total	micro- and meso- pores	macropores	radius, nm
0.01	0.20	0.005	0.025	16.0	5.0	2.0
0.09	0.20	0.009 (0.1)	0.029 (0.32)	52.2	10.4	2.0
0.14	0.20	0.025 (0.167)	0.076 (0.507)	72.8 (485)	13.3 (89)	2.05
0.23	0.20	0.026 (0.113)	0.077 (0.335)	82.0 (356)	17.5 (76)	2.0
0.30	0.22	0.035 (0.117)	0.102 (0.34)	89.4 (298)	26.4 (88)	2.3
0.35	0.20	0.040 (0.114)	0.103 (0.294)	106.0 (303)	27.0 (77)	2.0
0.42	0.24	0.042 (0.1)	0.104 (0.248)	109.2 (260)	28.0 (67)	1.9
0.50	0.24	0.052 (0.104)	0.146 (0.292)	149.5 (299)	29.5 (59)	1.95

**Table 2.** Dependence of the adsorption and texture characteristics of the porous  $Al_2O_3/Al$  composite and the oxide phase on the degree of conversion

Note: Calculated values for the oxide phase are given in parentheses.

### Evolution of the Texture Characteristics of the Porous Composite Depending on the Degree of Conversion

Table 2 summarizes the results of a study on the dependence of the adsorption and texture characteristics of the porous Al<sub>2</sub>O<sub>3</sub>/Al composite, as well as the calculated values for only the oxide phase (in parentheses), on the degree of conversion or the number of cycles. Each cycle included treatment with water at 100°C for 2 h and thermal treatment at 550°C for 1 h. As can be seen in Table 2, the adsorption volume of the Al<sub>2</sub>O<sub>3</sub>/Al composite (both the total volume and the volumes at the initial points of hysteresis loops) increased with aluminum conversion, whereas the adsorption volume of the oxide phase, in both cases, initially increased, passed through a small maximum at  $\alpha = 0.14$ , and then stabilized. The value of *P*/*P*<sub>s</sub> at the begin-



**Fig. 6.** Isotherms of benzene adsorption–desorption at 20°C on the porous Al<sub>2</sub>O<sub>3</sub>/Al composites with the conversions  $\alpha = (1) \ 0.50$  and (2) 0.14.

ning of hysteresis was almost independent of the degree of conversion. It is well known [3] that a decrease in the coordination number and an increase in the diameter of the primary particles that form the adsorbent structure shift a hysteresis loop to the right (i.e., toward a higher relative pressure of adsorbate vapor) and decrease its width. The absence of a shift of the beginning of a hysteresis loop toward higher values of  $P/P_s$  resulted from the uniform packing (the same coordination number) of the primary particles in all of the test samples regardless of the degree of conversion. The average pore radius was also independent of conversion, and it was approximately the same in all the samples; the set of these data suggests that the pore structure and the mechanism of its formation remained unchanged with increasing conversion. The specific surface area and the



**Fig. 7.** Integrated mesopore-size distribution curves for the  $Al_2O_3/Al$  composites with the conversions  $\alpha = (1)$  0.5 and (2) 0.14.

KINETICS AND CATALYSIS Vol. 45 No. 1 2004



Fig. 8. Electron micrographs of the Al<sub>2</sub>O<sub>3</sub>/Al composites with the conversions  $\alpha = (a) 0.14$  and (b) 0.50.

sorption volume of the porous ceramics increased with conversion; this was due to an increase in the weight of the resulting active alumina. The dependence of the specific surface area and sorption volume on the degree of conversion was practically linear; this fact provides support for the hypothesis of the removal of diffusion limitations because of the conversion of aluminum hydroxide into active alumina. The adsorption and texture properties of the porous composite depend on the oxide phase formed because of the thermal decomposition of the precipitated bayerite.

KINETICS AND CATALYSIS Vol. 45 No. 1 2004

Figure 6 demonstrates the isotherms of benzene adsorption on the porous Al<sub>2</sub>O<sub>3</sub>/Al composite with conversions of 0.5 and 0.14. A portion of isotherms at  $P/P_s = 0.8-1.0$  is almost parallel to the axis of  $P/P_s$ ; this fact is indicative of almost complete adsorption at this value of the relative pressure of the adsorbate. A hysteresis loop is characteristic of the adsorption–desorption process over the entire rage of ascending isotherms. At  $P/P_s \approx 0.2$ , polymolecular adsorption changed to capillary condensation. At the initial stage of desorption, an isotherm declined smoothly; next, at  $P/P_s \approx 0.5$ , it dramatically declined to the connection with an adsorption



**Fig. 9.** Dependence of the mechanical strength of the porous Al<sub>2</sub>O<sub>3</sub>/Al composite on the degree of conversion.

isotherm. This loop is typical of adsorbents with open capillaries having approximately the same effective radius (for example, aluminosilicates). The shape of the isotherms of benzene vapor adsorption on the test material (the slopes of adsorption–desorption branches, the width of a hysteresis loop, and the value of  $P/P_s$  before hysteresis) remained unchanged with changes in the concentration of active alumina. The only difference consisted in the sorption pore volumes. The isotherms can be assigned to type 2 according to the IUPAC Classification [6].

Based on the isotherms of adsorption, the pore-size distribution was calculated with the use of the Thompson equation (Fig. 7). As can be seen in Fig. 7, the plots are uniform for porous Al<sub>2</sub>O<sub>3</sub>/Al composites with different conversions; they exhibit no maximum characteristic of commercial active alumina. The pore size lies within a very narrow range of 4.5–7.5 nm. This is due to special features of the formation, diffusion, and precipitation of hydroxo complexes. The hydroxo complexes of aluminum or clusters are formed in a restricted volume: the pore volume of bayerite. They are deposited as nanoparticles onto a solid support: the growing layer of bayerite. This support is a stabilizer. which almost completely restricts the mobility of the nanoparticles and prevents agglomeration processes [14].

# Effect of the Cyclic Treatment on the Ultramicropore Structure and Mechanical Strength of the Porous Composite

Electron-microscopic studies of the samples synthesized allowed us to distinguish different steps in the formation of the composite depending on the degree of conversion. Initially, aggregation occurred without a detectable change in the surface morphology of particles with the formation of weakly pronounced contacts (Fig. 8a). Individual particles retained their structural identity; their size and shape were almost the same as in the initial aluminum powder. As the degree of conversion increased, the volume of the resulting oxide phase increased so that the consolidation of the porous material under the action of mechanical stresses took place; this consolidation was accompanied by the degradation of porous covers around aluminum particles. In this case, the initially formed contacts were destroyed and new contacts were formed. As a result, an agglomerate of particles was formed; the size and shape of these particles were essentially different from the initial ones (Fig. 8b). The fraction of aluminum metal considerably decreased, and the volume of ultramacropores decreased; the volume of micropores and mesopores increased. The structure of the porous material approached the structure formed by the methods of colloid chemistry in its characteristics. The total pore volume of the samples decreased somewhat from 0.45 to 0.34-0.38 cm<sup>3</sup>/g as the degree of conversion increased from 0.14 to 0.5.

Figure 9 illustrates the dependence of the compression strength of the porous Al<sub>2</sub>O<sub>3</sub>/Al composite on the degree of conversion of aluminum. The strength increased from 10 to 40 MPa with conversion and then remained practically unchanged. Evidently, the strength of composite metal ceramics depends on the quantity and quality of contacts between aluminum particles, as well as on the structure and properties of these contacts, which are formed in the course of precipitation from solution followed by thermal decomposition. The occurrence of two competing processes (the formation of "new" contacts in the course of hydroxide precipitation from solution and the mechanical degradation of "old" contacts) resulted in the fact that an increase in the mechanical strength of composite ceramics was completed at the instant of the onset of the intense consolidation of a porous solid.

Thus, we studied in detail the structure formation of the porous Al(OH)<sub>3</sub>/Al composite using a cyclic treatment method. We found that this treatment provides an opportunity to control the conversion of aluminum because intermediate thermal treatment increases the diffusion permeability of a porous cover on aluminum particles. We found that the limiting sorption volume and the specific surface area of the composites increased in the subsequent cycles of treatment because of the growth of an oxide cover without significant structural changes. We also noted that the following two competing processes affected the formation of the strength properties of the material synthesized: the formation of new contacts in the course of Al(OH)<sub>3</sub> precipitation and the degradation of previously formed contacts under the action of mechanical stresses. Thus, the cyclic treatment allowed us to control the degree of conversion and to form a porous material with the required properties.

#### REFERENCES

- 1. Rat'ko, A.I., Romanenkov, V.E., Bolotnikova, E.V., and Krupen'kina, Zh.V., *Kinet. Katal.*, 2004, vol. 45, no. 1, p. 154.
- Rat'ko, A.I., Romanenkov, V.E., Bolotnikova, E.V., and Krupen'kina, Zh.V., *Kinet. Katal.*, 2004, vol. 45, no. 1, p. 162.
- Ermolenko, N.F. and Efros, M.D., *Regulirovanie poristoi struktury okisnykh adsorbentov i katalizatorov* (Control of the Porous Structure of Oxide Adsorbents and Catalysts), Minsk: Nauka i Tekhnika, 1971.
- 4. Anderson, J., *Structure of Metallic Catalysts*, London: Academic, 1975.
- Dzis'ko, V.A., Karnaukhov, A.P., and Tarasova, D.V., *Fiziko-khimicheskie osnovy sinteza okisnykh katalizatorov* (Physicochemical Fundamentals for the Synthesis of Oxide Catalysts), Novosibirsk: Nauka, 1978.
- 6. Gregg, S.J. and Sing, K.S.W., Adsorption, Surface Area, and Porosity, London: Academic, 1967.

- Anan'in, V.N., Belyaev, V.V., Romanenkov, V.E., et al., Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, 1987, no. 5, p. 17.
- 8. Tikhov, S.F., Sadykov, V.A., Potapova, Yu.V., et al., Stud. Surf. Sci. Catal., 1998, vol. 118, p. 797.
- 9. Tikhov, S.F., Salanov, A.N., Palesskaya, Yu.V., et al., React. Kinet. Catal. Lett., 1998, vol. 64, no. 2, p. 301.
- Yakerson, V.I., Dykh, Zh.L., Subbotin, A.N., et al., Kinet. Katal., 1995, vol. 36, no. 6, 918.
- Physical and Chemical Aspects of Adsorbents and Catalysts, de Boer J.H. and Linsen, B.G., Eds., London: Academic, 1970.
- Tikhov, S.F., Fenelonov, V.B., Sadykov, V.A., Potapov, Yu.V., and Salanov, A.N., *Kinet. Katal.*, 2000, vol. 41, no. 6, p. 907 [*Kinet. Catal.* (Engl. Transl.), vol. 41, no. 6, p. 826].
- Tikhov, S.F., Zaikovskii, V., Fenelonov, V.B., Potapova, Yu.V., Kolomiichuk, V.N., and Sadykov, V.A., *Kinet. Katal.*, 2000, vol. 41, no. 6, p. 916 [*Kinet. Catal.* (Engl. Transl.), vol. 41, no. 6, p. 835].
- 14. Suzdalev, T.P. and Suzdalev, P.I., Usp. Khim., 2001, vol. 70, no. 3, p. 203.