ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 1, pp. 121–126. © MAIK "Nauka/Interperiodica" (Russia), 2008.
Original Russian Text © I.M. Kurchatov, N.I. Laguntsov, M.V. Tsodikov, A.S. Fedotov, I. I. Moiseev, 2008, published in Kinetika i Kataliz, 2008, Vol. 49, No. 1, pp. 129–134.

The Nature of Permeability Anisotropy and Catalytic Activity

I. M. Kurchatov[a,b], N. I. Laguntsov[a,b], M. V. Tsodikov[c], A. S. Fedotov[c], and I. I. Moiseev[d]

[a] *OAO Akvaservis, Moscow, Russia*

[b] *Moscow Institute of Engineering Physics, Moscow, 115409 Russia*

[c] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*

[d] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 117907 Russia*

E-mail: tsodikov@ips.ac.ru

Received February 15, 2007

Abstract—The phenomena of permeability anisotropy and an increase in the rates of catalytic reactions in porous membranes modified with highly dispersed catalytic systems were analyzed. A model of stochastic gas motions was proposed; this model is based on the hypothesis of the specific interaction of molecules with the inner surface of pores resulting in a nonisotropic distribution of molecules over traveling directions. The effects of asymmetric gas transfer in porous and gradient-porous membranes were considered to explain differences in the rates of heterogeneous catalytic reactions in a nanoporous membrane reactor under changes in the direction of supplying a reaction mixture. From the model proposed, it follows that the transversal diffusion of gas molecules is most probable in the porous medium of a ceramic membrane with a pore-size distribution gradient from large to small pores along the flow direction. This diffusion results in an increase in the frequency of molecular collisions with the wall of a microchannel and, correspondingly, in an increase in the contact time. The model proposed explains the intensification of a number of heterogeneous catalytic reactions performed in the porous media of catalytic porous membranes.

DOI: 10.1134/S0023158408010151

Membrane methods for separating mixtures, fine gas cleaning, and purifying liquids are generally recognized tools for decreasing power inputs in the modern chemical industry, which is among the most energy consuming branches of industry [1–3]. Interest in membrane-catalytic reactors—devices that combine the processes of chemical transformations in raw materials and separation of products—has increased in the past few years [4–10].

Recently, membranes and porous block materials with channels 10–100 nm in diameter have been used as reactor elements for a number of catalytic processes. The gas flow in these channels is characterized by a considerable increase in the fraction of free molecular flow. In this case, molecules mainly collide with pore walls rather than with each other and the effect of molecular collisions with pore walls on the gas flow noticeably increases.

The recently found phenomena of anisotropic gas transfer in a gradient porous medium [6, 10–12] can affect the process of catalysis. The characteristics of this medium (pore radius and porosity) change in a given direction in accordance with a specific law. Changes in the gas permeability of a membrane and the rates of catalytic reactions under changes in the gas flow direction belong to these phenomena.

In this work, we explain the nature of anisotropic gas transfer in the channels of porous membranes. Previously, we hypothesized that the appearance of anisotropic (nonsymmetric) gas-transfer and catalysis phenomena was due to the specific interaction of gas molecules with a surface (scattering from the rough edges of the inner pore surface) under conditions of a free molecular flow; this interaction led to an anisotropic distribution of molecules over traveling directions [11, 12].

Under conditions of a free molecular flow, molecular motion can be either regular, when molecular coordinates and velocities depend on boundary conditions at the channel inlet, or stochastic (random), when the molecule "forgets" boundary conditions and its motion depends on only the properties of the system (in our case, on the interaction of the molecule with the wall).

The mirror reflection of a molecule incident to a smooth pore wall is the simplest model of regular gas flow in a pore. The mirror-diffuse model of the interaction of molecules with a surface is more widely used; it implies that a fraction of molecules, which depends on the accommodation coefficient, is adsorbed on the surface and thermally equilibrated with it. Thereafter, the molecules are desorbed with the Maxwell distribution of velocities; in this case, the distribution of molecules over traveling directions is isotropic and the molecular motion is stochastic [13]. The other molecules are specularly reflected from the wall, and their motion is regular.

Models based on the assumption that the molecular motion is stochastic but the distribution of molecules over traveling directions is anisotropic are promising

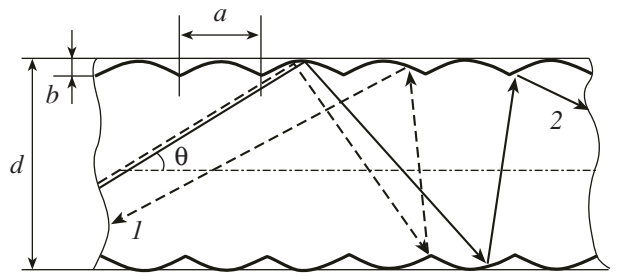

Fig. 1. Schematic diagram of the model of mixing billiards (see the text for comments).

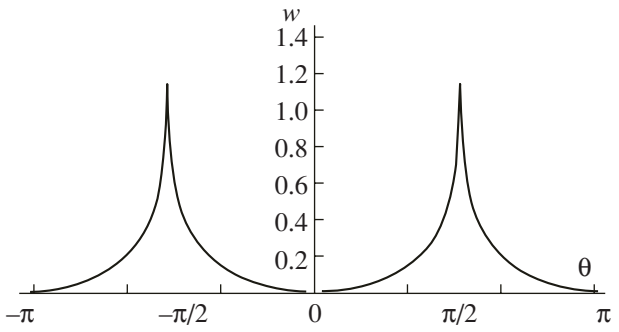

Fig. 2. Probability distribution over traveling directions for the model of mixing billiards.

for explaining asymmetric gas-transfer effects [11]. We will designate this interaction as specific.

The anisotropic stochastic molecular motion in pores can occur in the case when the molecules are specularly reflected from the wall but the pore surface is specifically shaped, for example, like convex or concave arcs. In this case, the model referred to as mixing billiards is applicable to analyze the molecular motion; this model was developed to describe the motion of a particle in the case of specular reflection from a wall, which restricts the region of particle motion [14]. In the simplest case, the surface of a pore channel can be considered, for example, as repeating parabolic holes of the same geometry (Fig. 1). If the hole depth is b, the width is a, the channel diameter is d, and $d \gg a \gg b$, two initially close paths (*1* and *2* in Fig. 1) of molecular motion in this channel diverge after several collisions with the walls so that the angle between the trajectories of these molecules may be anything on the condition that the stochasticity criterion is $K = 16db/a^2 > 1$ [14]. In other words, a small change in the trajectory results in a considerable change in the direction after a finite number of collisions. By this is meant that, in this system, the molecule rapidly forgets the initial direction of its motion and the molecular motion depends on the properties of the system. Assuming, for simplicity, that the molecules move in a plane that passes through the axis of the channel, we can write a distribution function of the molecules over traveling directions as the simple relationship [14]

$$w(\theta) = \frac{|\ln|\cos\theta||}{2\pi\ln 2}; \quad -\pi < \theta < \pi, \tag{1}$$

where θ is the angle between the direction of molecular motion and the axis of the channel (see Fig. 1).

It should be emphasized that relationship (1) is valid at any channel and hole sizes; only the ratio between sizes is of importance. Note that the channel and channel surface parameters do not appear in distribution function (1).

Figure 2 shows the shape of distribution function (1). As can be seen in Fig. 2, molecules mainly move perpendicularly to the channel surface; this inevitably increases the number of collisions with channel walls, as compared with a cylindrical channel with smooth walls in which the diffuse model of interaction is valid. As a consequence, the projection of the average velocity on the axis of the channel $\langle V_x \rangle$ is much smaller than the projection of the average velocity on the perpendicular to the surface $\langle V_y \rangle$:

$$\langle V_y \rangle = \int_0^\pi V_T w(\theta)\cos\theta d\theta; \tag{2}$$

$$\langle V_x \rangle = \int_0^\pi V_T w(\theta)\sin\theta d\theta, \tag{3}$$

where $w(\theta)$ is the distribution function of molecules over traveling directions, which is determined by Eq. (1); $V_T = \sqrt{\frac{8RT}{\pi M}}$ is the average thermal velocity of molecules with the molecular weight M at the temperature T; and R is the universal gas constant. In deriving Eqs. (2) and (3), we assumed that all of the molecules move with the same velocity V_T; that is, we ignored the distribution of molecular velocities.

As estimated from Eqs. (2) and (3), the average projections of the velocity on the axis of the channel and the normal to the channel axis are $\langle V_x \rangle \approx 0.14V_T$ and $\langle V_y \rangle \approx 0.48V_T$, respectively, whereas the calculated average projections of the velocity are $\langle V_x \rangle = \langle V_y \rangle = 0.32V_T$ in the case of complete accommodation [13].

A decrease in the average velocity of molecules projected onto the axis of the channel is equivalent to an increase in the lifetime of a molecule in the pore. At the same time, an increase in the molecular velocity component normal to the axis of the channel is equivalent to an increase in the number of collisions with pore walls.

If the flow parameters in a porous medium are such that the assumption of the free molecular flow regime does not hold and a gas flows in the transition regime, the Weber hypothesis of the additivity of flows can be used [15]. Then, the flow through a membrane is combined of two independent flows: a free molecular flow

(J_k) and a viscous flow (J_{ps}), which, in turn, consists of a viscous Poiseuille flow (J_p) and a slip flow (J_s). With consideration for the contributions of flows at arbitrary Knudsen numbers $Kn = \lambda/\rho$, we can write an expression for molar flow density (J) in the form

$$J = J_p + J_s + J_k = -\left(\frac{\pi\rho V_T}{32RT}\right)\frac{\Delta P}{\delta} \times\left\{\left(f\frac{\rho}{\lambda}+h\right)\frac{\chi\rho/\lambda}{1+\chi\rho/\lambda}+g\left(\frac{1}{1+\chi\rho/\lambda}\right)\right\}, \quad (4)$$

where $\lambda = \pi\eta V_T/4P$ is the molecular free path; η is the dynamic gas viscosity; P is the pressure; ρ is the average hydraulic radius (the ratio of the doubled pore volume to the pore surface area for straight cylindrical channels $\rho = d/2$); T is the temperature; ΔP is the pressure drop across the membrane; δ is the membrane thickness; $\chi = \dfrac{V_T}{2\langle V_{x1}\rangle}$ is a coefficient that takes into account a change in the fractions of collisions in the bulk and with the walls because of an anisotropic distribution of molecules over traveling directions; f, h, and g are experimentally determined correction factors, which depend on the parameters characterizing the shapes of pore channels (porosity, tortuosity, etc.) and the distribution of molecules over traveling directions. At this stage, the introduction of correction factors allowed us to restrict ourselves to the simplest assumptions and to ignore the particular pore structure.

In the general case, the value of χ depends on the degree of nonisotropy of the traveling direction distribution, that is, on the distribution peak width. For the model of mixing billiards, a calculation with the use of Eqs. (1)–(3) afforded the value $\chi = 1.05$. For the diffuse model, $\chi = 2.00$ [13]. As can be seen in Eq. (4), a decrease in the coefficient χ is equivalent to an increase in the fraction of the free molecular flow component.

Equation (4) is valid over wide ranges of pressures and porous medium parameters; however, the pore size is bounded above by the requirement that the contribution of surface diffusion and other flows that appear in narrow channels should be small [16]. Equation (4) allows us to explain the decrease in the flow anisotropy as the pressure is increased. Indeed, as the pressure is increased, the free path λ decreases; consequently, the fraction of the Poiseuille slip flow increases, whereas the fraction of the free molecular flow decreases. The decrease of the fraction of a free molecular flow implies that a smaller number of molecules move in the anisotropic stochastic regime, which depends on the surface structure, and the distribution of molecules over traveling directions tends to an isotropic distribution as the pressure is increased.

Let us demonstrate that the effects of increasing the lifetimes of molecules in a membrane and increasing the number of collisions with pore walls can increase many times in membranes with a gradient porosity.

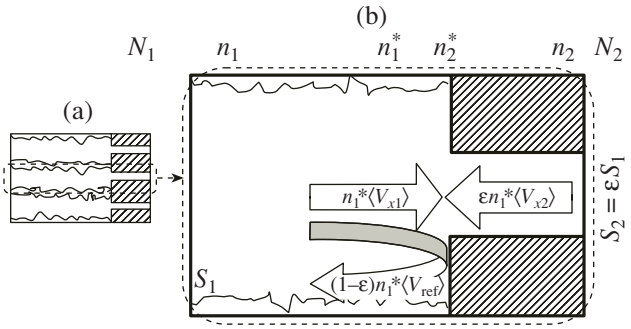

Fig. 3. Schematic diagram of flows in a bilayer membrane: (a) the overall view of a bilayer membrane; (b) the fragment shown by a dashed line in Fig. 3a (see the text for comments).

Let us consider a bilayer membrane the first layer of which is interpreted as a porous medium with anisotropic stochastic gas motions (for definiteness, like mixing billiards). With the use of a resistance model, it is easy to find that the membrane permeability depends weakly on the flow direction (the difference is 3–5%) [17]. This can be explained taking into account the change of the average pressure under viscous flow conditions [18]. However, a qualitatively different approach should be used to describe the permeability of multilayer membranes when the flows supplied at the opposite sides of a membrane differ many times [5, 6, 11].

Figure 3 schematically shows a gas flow in a bilayer porous membrane. Let us assume that the anisotropic stochastic regime of a gas flow occurs in the first layer with relatively large pores but with the retention of the free molecular flow regime. The pore cross sections in the first and second layers are designated as S_1 and $S_2 = \xi S_1$, respectively. Molecular concentrations in an environment at the inlet of the first layer, that is, before the membrane, and after the membrane are N_1 and N_2, respectively. Within the first layer, the concentration of molecules changes from n_1 at the boundary with the environment to n_1^* at the boundary with the second layer, whereas it changes within the second layer from n_2^* at the boundary with the first layer to n_2 at the boundary with the environment. Note that, generally, a jump in the molecular concentration would be expected because of different gas flow conditions in the environment and in the membrane layers.

Upon supplying a flow to the first layer, the molecules initially passed the porous layer and arrived at the boundary region between the porous (first) and finely porous (second) layers. Only a limited fraction of molecules passed through the second layer because of its smaller porosity. The remainder of molecules reflected from the interface between the two layers (the interface is perpendicular to the flow) acquired a traveling direc-

tion distribution with the predominant motion along the channel axis because of specific interaction with the interface. As a result, the average velocity of molecules reflected from the interface along the channel axis $\langle V_{\text{ref}}\rangle$ was much higher than the velocity $\langle V_{x1}\rangle$ before the interaction with this interface. Moreover, a portion of molecules reflected in the opposite direction to the total flow after the interaction with the interface.

The molecules reflected from the interface returned to the region of the first porous layer and acquired a "polarization" perpendicular to the channel axis after interacting with channel walls (that is, their motion was mainly oriented perpendicularly to the channel axis). Consequently, the average lifetime of a molecule in the porous layer increased. Thus, the occurrence of the second layer with a smaller porosity also increased the lifetime of a molecule in the first porous layer of the membrane (recall that the initial effect was due to a nonisotropic distribution of molecules over traveling directions) and, correspondingly, increased the number of collisions with pore walls.

Balance equations at the beginning of the first layer, at the interlayer boundary, and at the outlet of the second layer can be written in the form

$$\begin{aligned} J_{01} &= 1/4N_1V_T - n_1\langle V_{x1}\rangle, \\ J_{12} &= n_1^*\langle V_{x1}\rangle - \xi n_2^*\langle V_{x2}\rangle - (1-\xi)n_1^*\langle V_{\text{ref}}\rangle, \\ J_{20} &= \xi(n_2\langle V_{x2}\rangle - 1/4N_2V_T). \end{aligned} \quad (5)$$

In combination with diffusion Eqs. (4) for both layers, balance Eqs. (5) allowed us to evaluate the effect of porous layer parameters on the flow through the system. We found that the anisotropy of a molecular distribution over traveling directions after the interaction of molecules with the pore surface is a necessary condition for the anisotropy of flows. On the condition that $\langle V_{x1}\rangle < \langle V_{\text{ref}}\rangle$, a flow with an anisotropic molecular motion with respect to directions from the side of the first layer can be several times lower than a flow supplied from the side of the second (finely porous) layer. As the pressure drop is decreased, the flow through the membrane on the side of the first layer can decrease to almost zero at a finite pressure drop. In this case, the role of surface flows increases; this explains the change in the shape of the temperature dependence of membrane permittivity [5, 10]. Indeed, Teplyakov et al. [10] found that, on supplying a gas from the side of the second (finely porous) layer, the permeability behaves as a decreasing function of temperature in accordance with the free molecular flow regime ($J_k \propto 1/\sqrt{MT}$), whereas the permeability increases with temperature on supplying a gas from the side of the first layer. In this case, this allows us to consider the flow as a surface flow (the temperature dependence of the molar surface flow density has the form of $J_{\text{surf}} \propto \dfrac{(A + BT\exp(\Delta/RT))}{\sqrt{MT}}$, where A, B, and Δ are constants [19]). We also note that, as expected, the effect of flow anisotropy disappears in the case of an isotropic stochastic gas flow in the first layer.

We compare the numbers of molecular collisions with walls in the cases of isotropic and anisotropic stochastic regimes of the motion of gas molecules.

The average residence time of a gas molecule in a pore channel depends on the transport velocity $\langle V_f\rangle = J/\langle n\rangle$, where $\langle n\rangle$ is the average particle number density in the flow. If the transport channel length is δ, the average residence time of a particle in the channel is $\Delta\tau = \delta/\langle V_f\rangle$. On the other hand, the physical rate of molecular motion is equal to the average thermal velocity V_T; because the time between successive collisions in a channel with hydraulic radius ρ is close to $2\rho/V_T$, the number ν of collisions of a molecule with the inner surface of pores is proportional to the quantity

$$\nu \propto \frac{V_T}{\langle V_f\rangle}\frac{\delta}{2\rho}. \quad (6)$$

Substituting the resulting estimate for $\langle V_f\rangle$ into (6), we rewrite (6) in the form

$$\nu \propto \frac{V_T}{2}\frac{\langle n\rangle}{J}\frac{\delta}{\rho}. \quad (7)$$

From expression (7), it follows that the number of molecular collisions with pore channel walls is inversely proportional to the square of the hydraulic radius because the gas flow density in the pore is proportional to the hydraulic pore radius, as can be seen in Eq. (4). This fact suggests that a change to nanoporous membrane catalytic reactors is promising. The effect of the anisotropy of molecules with respect to traveling directions is governed by the dependence of $\langle n\rangle$ and J on the distribution of molecules over traveling directions.

Figure 4 shows the dependence of the flow density J (Fig. 4a) and average concentrations $\langle n_1\rangle$ in a porous layer (Fig. 4b) on the reduced pressure (the ratio of the pressure P_{in} at the membrane inlet to the outlet pressure P_{out}) for the cases of anisotropic stochastic (curves *1*) and isotropic stochastic (curves *2*) gas flows in a bilayer porous membrane at the permeability ratio between the first and second layers $\varsigma = 5.0$ and the ratio between the porosity factors of the second and first layers $\xi = 0.75$. It was assumed that the gas moved from the first to the second layer. The set of Eqs. (2)–(5) was solved assuming that the gas flowed through a porous layer in the free molecular regime. It can be seen in Fig. 4a that, as the pressure drop across the membrane was decreased, the flow decreased to almost zero at a finite pressure drop if the movement of gas molecules was anisotropic with respect to directions. Moreover, the concentration in the porous layer with anisotropic gas motions was noticeably higher than that in the case of an isotropic flow (Fig. 4b). In combination with an increase in the lifetime of molecules in the channel, this resulted in an increase in the number of collisions between gas mole-

cules and the inner surface walls of pores. Thus, for example, at $P_{in}/P_{out} = 5$, the number of collisions increased by a factor of more than 2 because of the increase in the concentration and by a factor of 7 because of the decrease in the flow density; the total number of collisions with pore walls increased by a factor of almost 16.

Thus, the appearance of an anisotropic stochastic molecular motion regime in membranes with gradient porosity can result in asymmetric gas-transport phenomena and, consequently, in a multiple increase in the effects of an increase in the lifetimes of molecules in a membrane and a corresponding increase in the number of collisions with pore walls.

Qualitatively, the results obtained illustrate the special features of mass transfer in membrane pores related to the structure of the inner surface, which can affect the rates of catalytic reactions. The intensification of heterogeneous catalytic reactions in nanoporous gradient media, which was observed previously [6, 10, 20], can be due to a change in the interaction of a substrate (gas molecules) with the active surface of membrane channels. An increase in the density of active centers as a result of the modification of the inner surface of a membrane with nanosized catalytic systems simultaneously with an increase in the number density of substrate molecules results in a nonadditive increase in the number of molecular collisions with the surface. Both of these effects, particularly, in combination with asymmetric gas-transport phenomena, can be responsible for an increase in the rates of catalytic reactions.

A gradient-porous system was constructed with the use of sol–gel methods. In this system, a uniform porous coating of the phosphorus-modified titanium oxide $P_{0.03}Ti_{1.97}O_{2\pm x}$ with the average pore size $\langle d\rangle \sim$ 2 nm was formed on the surface of a cermet membrane with sequential layers with the pore sizes $\langle d\rangle \sim 0.12$ and ~2–3 μm, respectively, and the inner surface of membrane channels was modified with the $ZnO–Cr_2O_3–Al_2O_3$ system, which is used as a catalyst for methanol dehydrogenation [6, 9].

We found that the permeability of the membrane to a number of gases in a flow oriented from the side of large pores to the nanoporous coating was lower that in the reverse flow direction by a factor of 5–8. We were the first to detect an anisotropy of catalytic activity in methanol dehydrogenation reactions in addition to the observed anisotropy of gas permeability: at the same pressure drop, the reaction rate of dehydrogenation on supplying a reaction mixture from the side of membrane-support macropores was higher by a factor of 5–8 than that on supplying from the side of a nanoporous layer [6]. The effects observed were adequately explained by the model of a gas flow in a bilayer porous membrane.

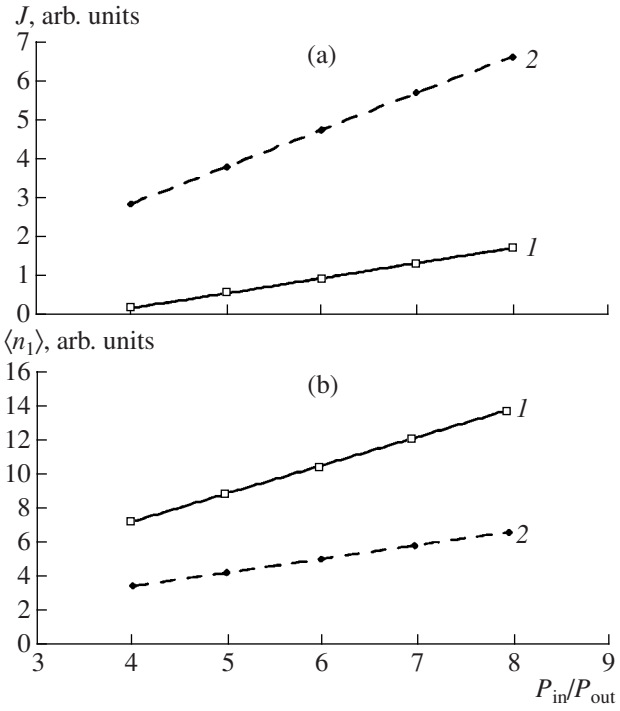

Fig. 4. Dependence of (a) the flow density and (b) the average concentration in the first (porous) layer on the reduced pressure P_{in}/P_{out}: (*1*) anisotropic stochastic and (*2*) isotropic stochastic gas motions.

ACKNOWLEDGMENTS

We are grateful to V.D. Borman, V.N. Tronin, and V.V. Teplyakov for the discussions of the results and for helpful remarks.

REFERENCES

1. Bernardo, P., Algieri, C., Barbieri, G., and Diroli, E., *7th Int. Conf. on Catalysis in Membrane Reactors*, Cetraro, Italy, 2005.
2. Kilgus, M., Phikipp, K., Gepert, V., Merten, C., Eigenberger, G., and Schiestel, T., *7th Int. Conf. on Catalysis in Membrane Reactors*, Cetraro, Italy, 2005.
3. Fayyaz, B., Harale, A., Park, Byoung-Gi., Sahimi, M., and Tsotsis, Th.T., *7th Int. Conf. on Catalysis in Membrane Reactors*, Cetraro, Italy, 2005.
4. Kapteijn, F., Heiszwolf, J.J., Nijhuis, T.A., and Moulijn, J.A., *Bultzer Sci. Publ.*, 1999, vol. 3, no. 1, p. 24.
5. Pisarev, G.I., Magsumov, M.I., Spiridonov, P.V., Kapteijn, F., Gora, L., Tsodikov, M.V., and Teplyakov, V.V., *Book of Abstracts of the Membrane Science and Technology Conference of Visegrad Countries—PERMEA 2005*, Planica Zdroj, Poland, 2005, p. 115.
6. Teplyakov, V.V., Tsodikov, M.V., Magsumov, M.I., and Kaptein, F., *Kinet. Katal.*, 2007, vol. 48, no. 1, p. 139 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 1, p. 132].
7. Tsodikov, M.V. Laguntsov, N.I., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2004, no. 12, p. 2613.

8. Khasin, A.A., *Zh. Vses. Khim. O–va. im. D. I. Mendeleeva*, 2003, vol. 47, p. 36.
9. Tsodikov, M.V., Teplyakov, V.V., Magsumov, M.I., Shkol'nikov, E.I., Volkov, V.V., Kaptein, F., Gora, L., Trusov, L.I., and Uvarov, V.I., *Kinet. Katal.*, 2006, vol. 47, no. 1, p. 29 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 1, p. 25].
10. Teplyakov, V.V., Pisarev, G.I., Magsumov, M.I., Tsodikov, M.V., Zhu, W., and Kapteijn, F., *Catal. Today*, 2006, vol. 118, p. 7.
11. Kurchatov, I.M., Laguntsov, N.I., Pisarev, G.I., Tronin, V.N., and Uvarov, V.I., *Proc. XXI Int. Symp. on Physico-Chemical Methods of Separation—Ars Separatoria 2006*, Torun, Poland, 2006, p. 55.
12. Kurchatov, I.M., Laguntsov, N.I., et al., *Al'ternativnaya Energetika i Ekologiya*, 2007, no. 5 (49), p. 134.
13. Lifshits, E.M., and Pitaevskii, L.P., et al., *Fizicheskaya kinetika* (Physical Kinetics), vol. 10 of *Teoreticheskaya fizika* (Theoretical Physics), Moscow: Nauka, 1979.
14. Zaslavskii, G.M., *Stokhastichnost' dinamicheskikh sistem* (Stochasticity of Dynamic Systems), Moscow: Nauka, 1984.
15. Barrer, R.M. and Nicholson, D., *Brit. J. Appl. Phys.*, 1966, vol. 17, p. 1091.
16. Xiao, J. and Wei, J., *Chem. Eng. Sci.*, 1992, vol. 47, no. 5, p. 1143.
17. Henis, J.M.S. and Tripodi, M.K., *J. Membr. Sci.*, 1981, vol. 8, p. 233.
18. Thomas, S., Shaefer, R., Caro, J., and Seidel-Morgenstern, A., *Catal. Today*, 2001, vol. 68, p. 205.
19. Dytnerskii, Yu.I., Brykov, V.P., and Kagramanov, G.G., *Membrannoe razdelenie gazov* (Membrane Separation of Gases), Moscow: Khimiya, 1991.
20. Magsumov, M.I., Fedotov, A.S., Tsodikov, M.V., Teplyakov, V.V., Shkrebko, O.A., Uvarov, V.I., Trusov, L.I., and Moiseev, I.I., *Ross. Nanotekhnol.*, 2006, vol. 1, nos. 1–2, p. 142.