

Adsorption of Nitrogen, Oxygen, and Argon Vapors on Supermicroporous Oxides

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Abstract—The adsorption of N_2 , O_2 , and Ar vapors on a number of supermicroporous tin dioxide and zirconia xerogels at 77.4 K was studied. The micropore volumes calculated with the use of sorbate densities at the corresponding temperature were found to be in satisfactory agreement for all of the sorbates. At the same time, the volumes of larger pores measured using nitrogen were greater than the values found with other sorbates. The previously found behavior of oxygen and nitrogen molecules in the geometrically restricted space of supermicropores was substantiated. In particular, this behavior manifests itself in a change in the adsorption properties of a unit surface area of supermicropores as compared with the surface of mesopores. However, the effects of this kind were not found for the argon–nitrogen sorbate pair.

INTRODUCTION

The formation of a microporous structure is typical of the synthesis of porous Group IV element oxides, including binary oxides, by precipitation. These oxides are in wide current use as selective adsorbents, ion exchangers, catalyst supports, and catalytically active substances [1]. It was also noted [2] that the catalytic properties of organometallic palladium complexes supported on activated carbon in the reaction of cyclohexane hydrogenation depend on the micropore and supermicropore structure parameters of the support. The adsorption study of such microporous structures is also required for solving a number of other problems, for example, in studies of the intercalation of ions or the introduction of a titania phase as pillars into the interlayer space of naturally occurring pillared clay minerals [3–5].

At the same time, the use of traditional adsorption methods for studying the texture of these samples involves a number of problems. This is primarily due to the special behavior of sorbate molecules in the geometrically restricted space of micropores, which exhibits an increased adsorption potential. The behavior of a sorptive in the pore space of supermicropores is the least understood aspect.

Recall that a division between “true” micropores and supermicropores, which was first introduced by Dubinin [6], is mainly based on geometric pore sizes. Micropores with $r < 0.6$ – 0.7 nm are considered as “true” micropores, whereas the size of supermicropores lies within a range from 0.6– 0.7 to 1.5–1.6 nm; the upper limit is restricted by a minimum size of mesopores.

It is well known that true micropores are filled by the mechanism of volume filling, whereas it is likely that adsorption in the supermicropore volume primarily occurs by the mechanism of layer-by-layer filling

[6–8]. In this context, it would be expected that the fundamental dependence of the sorption mechanism on the pore size of a sorbent is also responsible for different behaviors of various sorbate molecules in the space of supermicropores.

The aim of this work was to study the physical adsorption of nitrogen, oxygen, and argon vapors in the supermicropores of tin dioxide and zirconia, which were prepared by precipitation, at 77.4 K.

EXPERIMENTAL

The samples of SnO_2 and ZrO_2 were prepared by precipitation in accordance with the previously published procedure [9, 10]. To extend the range of test structures, a portion of the samples was additionally modified, for example, by varying the time τ (h) of gel aging in an intermicellar medium [11].

The adsorption isotherms of N_2 , O_2 , and Ar vapors at 77.4 K were measured on a Digisorb-2600 Micro-metrics automated volumetric instrument (USA). The oxide samples were trained in a vacuum at 160°C for 6 h to retain their developed but thermally labile micropore structures. To exclude the possible effect of an irreproducibility in the texture parameters of samples prepared at different times and to compare correctly the experimental results, the adsorption measurements with all of the sorbates were performed using the same weighed portions of samples.

The vapor adsorption isotherms were treated by the comparative method [12], which is an analog of the well-known t -method [13], with the use of published data [13–15] for the test sorbates as reference isotherms. Thus, the surface areas S_a (m^2/g) and the micropore volumes V_μ (cm^3/g) accessible to sorbate molecules were calculated for an isotherm region of

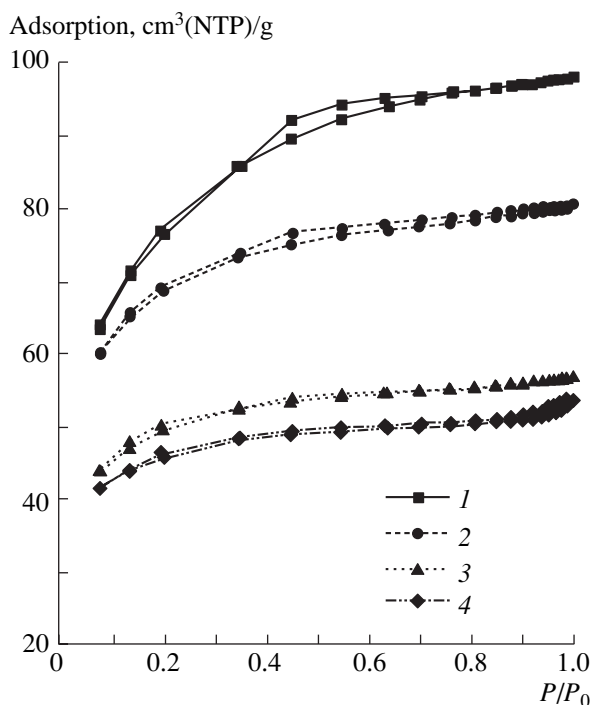


Fig. 1. Adsorption isotherms of nitrogen vapor at 77.4 K on ZrO_2 samples prepared at pH (1) 5.5, (2) 5.0, (3) 4.5, and (4) 4.0 (aging for 10 h).

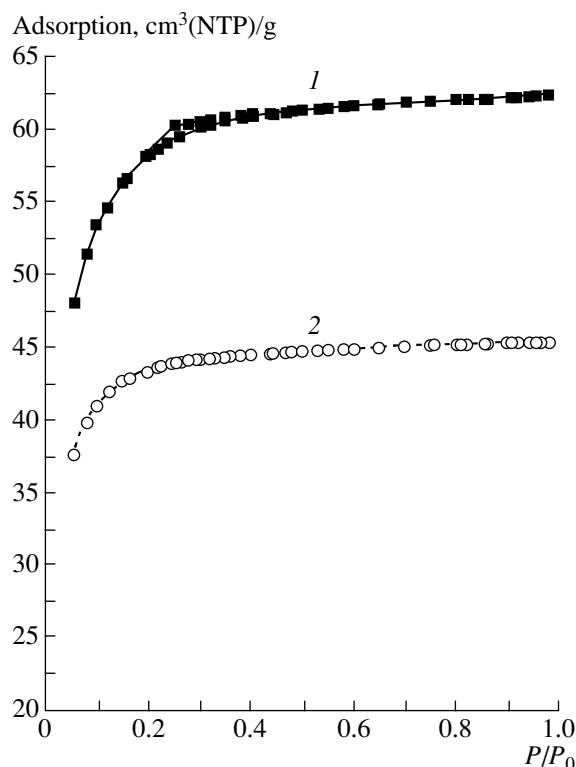


Fig. 2. Adsorption isotherms of oxygen at 77.4 K on SnO_2 samples prepared at pH (1) 6 and (2) 8.

$P/P_0 = 0.1\text{--}0.3$. The supermicropore volume V_{sm} (cm^3/g) can be calculated using the comparative method in the region of $P/P_0 = 0.8\text{--}0.9$ for the samples whose adsorption isotherms exhibit no capillary-condensation hysteresis (hence, a noticeable mesopore volume is absent from these samples). The surface area at which layer-by-layer adsorption occurs (this value is negligible in the absence of a noticeable mesopore volume) and the total volume $V_{\mu + \text{sm}}$ of micro- and supermicropores filled with a sorbate can be calculated by this procedure. The volume of supermicropores was then calculated by the obvious relation $V_{\text{sm}} = (V_{\mu + \text{sm}} - V_{\mu})$ [16].

The true density of samples ρ (g/cm^3) was measured on an Autopycnometer-1320 Micrometrics instrument (USA) using helium. The X-ray diffraction analysis was performed on a URD-63 diffractometer in filtered $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

The sorbates employed in this work are most commonly used in the adsorption studies of pore structures [12]. This is because they are versatile with respect to test samples (the chemical composition and texture parameters can be varied over a wide range) and readily available, and their individual physical properties are well understood.

The X-ray diffraction data (the absence of clear-cut characteristic lines from X-ray diffraction patterns) and

the measurements of the true densities of the test xerogels suggest that all of the test samples were mainly amorphous. Indeed, the values of ρ were equal to 3.9–4.0 and 4.9–5.0 g/cm^3 for ZrO_2 and SnO_2 xerogels, respectively. The above true densities are much lower than the corresponding values for crystalline modifications: 5.89 g/cm^3 for monoclinic zirconium dioxide [17] and 6.95 g/cm^3 for tin dioxide as cassiterite [18]. Consequently, both the structure of xerogel framework elements and the pore space formed by them would be expected to be irregular.

Figures 1 and 2 demonstrate the isotherms of N_2 and O_2 adsorption at 77.4 K on ZrO_2 and SnO_2 xerogels that were prepared by precipitation at various pH values and aged for different times. It can be seen in Figs. 1 and 2 that some isotherms (primarily, on ZrO_2) showed weakly pronounced capillary-condensation hysteresis, whereas tin dioxide prepared under certain conditions exhibited no capillary-condensation hysteresis (consequently, the mesopore volume seems to be negligible).

Tables 1 and 2 summarize the following main texture parameters of xerogels: the limiting volume V_s of the sorption space, the micropore volume V_{μ} , and the surface area S_{α} , which were calculated from the sorption of the test sorbates. The set of these data indicates that the values of V_s measured with nitrogen are noticeably higher than those obtained from the adsorption of oxygen and argon; in turn, the latter values are close to

Table 1. Parameters of the porous structure of ZrO₂ samples calculated from the adsorption isotherms of N₂, O₂, and Ar

Sample no.	Precipitation pH	$V_s(\text{N}_2)$, cm ³ /g	$V_s(\text{O}_2)$, cm ³ /g	$V_s(\text{Ar})$, cm ³ /g	$V_\mu(\text{N}_2)$, cm ³ /g	$V_\mu(\text{O}_2)$, cm ³ /g	$V_\mu(\text{Ar})$, cm ³ /g	$S_\alpha(\text{N}_2)$, m ² /g	$S_\alpha(\text{O}_2)$, m ² /g	$S_\alpha(\text{Ar})$, m ² /g
1	5.5	0.152	0.135	0.134	0.018	0.010	0.022	240	335	292
2	5.0	0.125	0.109	0.108	0.038	0.032	0.037	165	221	210
3	4.5	0.080	0.076	0.075	0.030	0.031	0.031	102	127	131
4	4 (10 h)*	0.083	0.076	0.071	0.034	0.034	0.032	87	107	112
5	4 (22 h)*	0.092	0.079	0.071	0.038	0.034	0.034	79	104	101

* The time of aging is given in parentheses.

Table 2. Parameters of the porous structure of SnO₂ samples calculated from the adsorption isotherms of N₂, O₂, and Ar

Sample no.	Precipitation pH	$V_s(\text{N}_2)$, cm ³ /g	$V_s(\text{O}_2)$, cm ³ /g	$V_s(\text{Ar})$, cm ³ /g	$V_\mu(\text{N}_2)$, cm ³ /g	$V_\mu(\text{O}_2)$, cm ³ /g	$V_\mu(\text{Ar})$, cm ³ /g	$S_\alpha(\text{N}_2)$, m ² /g	$S_\alpha(\text{O}_2)$, m ² /g	$S_\alpha(\text{Ar})$, m ² /g
6	6	0.078	0.073	0.072	0.036	0.036	0.036	85	108	108
7	8	0.057	0.053	0.052	0.033	0.034	0.033	49	55	59

each other. At the same time, as a rule, the micropore volumes for all sorbates were in mutual agreement. There is no agreement between the surface areas S_α determined with different sorbates by the comparative method. Table 3 gives the supermicropore volumes $V_{s\mu}$ for the samples with no detectable contribution from capillary condensation and the corresponding ratios between surface areas.

Previously [16, 19], a preliminary analysis of data on the adsorption of N₂ and O₂ vapors on tin oxide and zirconia at 77.4 K was performed. It was found that the experimental supermicropore surface areas measured by oxygen and nitrogen adsorption ($S_\alpha(\text{O}_2)$ and $S_\alpha(\text{N}_2)$, respectively) as functions of the volume of supermicropores in the sample ($V_{s\mu}$), as measured by oxygen adsorption, are described by the following simple linear equation with two terms:

$$S_\alpha(\text{O}_2)/S_\alpha(\text{N}_2) = 1 + k(V_{s\mu} - V_{s\mu}^*), \quad (1)$$

where k is the slope, which is equal to 15.9 m²(O₂) g m⁻² (N₂) cm⁻³ in the case of ZrO₂, and $V_{s\mu}^*$ is the calculated threshold value of the supermicropore volume, which is determined from the obvious constraints

$$S_\alpha(\text{O}_2)/S_\alpha(\text{N}_2) = 1 \quad \text{at } V_{s\mu} \leq V_{s\mu}^* \quad \text{and}$$

$$S_\alpha(\text{O}_2)/S_\alpha(\text{N}_2) > 1 \quad \text{at } V_{s\mu} > V_{s\mu}^*.$$

For ZrO₂, this parameter is ≈ 0.022 cm³/g. It was noted that ZrO₂ samples prepared under essentially different synthesis conditions exhibited a uniform experimental function. For tin dioxide, the value of k was 13.6 m²(O₂) g m⁻² (N₂) cm⁻³ and $V_{s\mu}^* \approx 0.011$ cm³/g. It can be seen that the values of k differ insignificantly,

whereas the difference between the threshold parameters $V_{s\mu}^*$ is more pronounced.

Figure 3 shows a correlation of the supermicropore volumes with the ratio between supermicropore surface areas for different sorbates based on the entire set of experimental data obtained both in this work and previously [16, 19]. It can be seen that, in general, the behavior found earlier was retained.

A good agreement between the volume V_μ of micropores accessible to various sorbate molecules (Tables 1, 2) is indicative of either the unchanged densities of sorbates under these conditions, as compared with their bulk phase densities at the given temperature, or the same change in the densities. The fulfillment of the so-called Gurvich rule for other microporous materials, zeolites, the pore-space volume of which can be determined using X-ray techniques, was considered in detail [20]. It was found that, as a rule, the density of a sorbed phase is equal to the value for the bulk phase under the same temperature conditions if the pore space is fully accessible to sorbate molecules.

At the same time, the limiting volume V_s of the sorption space measured by oxygen and argon adsorption with consideration for the density of the sorbate bulk phase at the given temperature is somewhat lower than that measured by nitrogen adsorption. A similar phenomenon was observed previously [21, 22] in argon adsorption on mesoporous heterogeneous catalysts at 77.4 K, and it was associated with the possible phase transitions of argon in a supercooled state. Data on the adsorption of various gases on mesoporous samples were also compared in recent times. For example, the sorption of nitrogen, argon, krypton, and carbon dioxide on regular mesoporous silicate materials MCM-48 and MCM-41 at different temperatures [23, 24] and the adsorption of nitrogen, oxygen, and argon on several

regular mesoporous silicates different in morphology [25] were studied. In general, the problem of the density of a sorbate in mesopores at a temperature lower than the boiling point was considered with caution, and the appearance of anomalous values was not excluded.

Phase transitions in supercooled nanosized heterogeneous systems are multifactor processes, which affect structural, thermodynamic, and electronic properties. Presently, it is difficult to predict the behavior of such systems on the quantitative level [26].

The temperature at which the adsorption measurements were performed (77.4 K) is also lower than the boiling temperature of oxygen (90 K). Consequently, the behavior of a bulk sorbate phase in pores larger than true micropores can also be anomalous for this sorbate. In the test oxide series, these are primarily supermicropores. Consequently, it is reasonable to believe that the phase properties of Ar and O₂ in supermicropores at 77.4 K are closer to sorbate properties in mesopores rather than true micropores. Thus, it may be considered that, under these conditions, only the density of a sorbed nitrogen phase is constant in pores of different sizes, and it is consistent with the value for the bulk phase of liquid nitrogen at the temperature of the experiment.

The heat of sorption is the main factor responsible for the behavior of sorbate molecules in the space of pores. It depends on both the molecular structure of the sorbate and the properties of the surface [27, 28]. The molecules of N₂ are characterized by specific sorption on energetically nonuniform surfaces due to a considerable quadrupole moment -4.67×10^{-40} C m², as compared with the quadrupole moment of the O₂ molecule -1.34×10^{-40} C m². Moreover, the nonspecific dispersion interaction, which considerably depends on the polarizability of sorbate molecules, is predominant in nitrogen as compared with O₂ and Ar molecules (according to reference data [18], the sorbate polarizability coefficients are 1.74, 1.57, and 1.63 Å³, respectively). Because of this, as a rule, the heat of physisorption for nitrogen is higher than that for oxygen or argon on the same samples [13, 29]. For example, in a particular case of typical mesoporous materials, this manifests itself in the fact that the energy constant *C* of the BET equation (this constant characterizes the pure heat of adsorption) for nitrogen (*C* ≈ 100) is higher than the corresponding values for oxygen and argon (*C* ≈ 50–60) [12].

It is likely that the greater heat of nitrogen adsorption, as compared with the other test sorbates (as expected, also on the surface of supermicroporous oxides), is favorable for the retention of a constant value of the sorbed phase density regardless of pore size. The stronger interaction of nitrogen simultaneously affects its adsorption properties.

Table 3 summarizes the supermicropore volumes *V*_{sp}(N₂) measured by nitrogen adsorption; these data make it possible to check the above correlation $S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2) = f(V_{\text{sp}})$. Taking into account the above

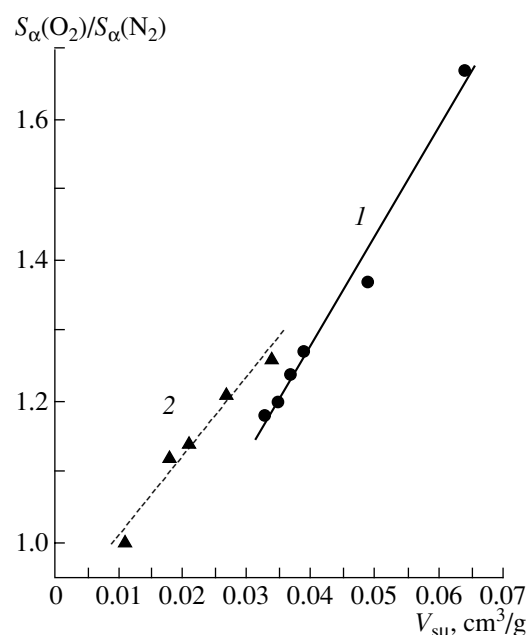


Fig. 3. $S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2)$ ratio between surface areas as a function supermicropore volume (V_{sp}) measured using oxygen for (1) ZrO₂ or (2) SnO₂.

consideration on the change in sorbate density in supermicropores, this relationship seems to be more justified.

Figure 4 demonstrates the relevant data for zirconia. It can be seen that, in contrast to the results obtained using oxygen adsorption, which are qualitatively consistent with Fig. 3, the values of $S_{\alpha}(\text{Ar})/S_{\alpha}(\text{N}_2)$ remained almost constant rather than changed with increasing volume of supermicropores. In general, tin dioxide exhibited a similar tendency.

Previously [16], it was assumed that the value of *k* in Eq. (1) reflects relative changes in the absolute values of adsorption in supermicropores and mesopores for the test sorbates. Consequently, in the case of the argon–nitrogen pair of sorbates, these changes are absent. The fact that the ratio $S_{\alpha}(\text{Ar})/S_{\alpha}(\text{N}_2)$ is different

Table 3. Comparison between the surface areas S_{α} measured using different sorbates

Sample no.	$V_{\text{sp}}(\text{O}_2)$, cm ³ /g	$V_{\text{sp}}(\text{N}_2)$, cm ³ /g	$S_{\alpha}(\text{O}_2)/S_{\alpha}(\text{N}_2)$	$S_{\alpha}(\text{Ar})/S_{\alpha}(\text{N}_2)$
1	—	—	1.40	1.22
2	—	0.083	1.34	1.28
3	0.045	0.056	1.25	1.29
4	0.035	0.041	1.23	1.29
5	0.032	0.035	1.32	1.28
6	0.034	0.040	1.27	1.26
7	0.018	0.022	1.13	1.20

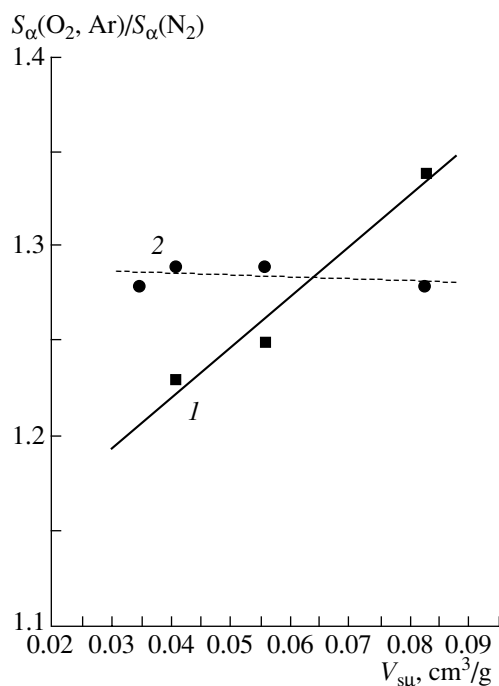


Fig. 4. $S_{\alpha}(\text{O}_2, \text{Ar})/S_{\alpha}(\text{N}_2)$ ratio between surface areas as a function supermicropore volume (V_{sm}) measured using nitrogen on ZrO_2 for (1) O_2 or (2) Ar as a sorbate.

from unity is indicative of some differences between the specific adsorption properties of zirconia and tin dioxide with respect to the given sorbates. Evidently, these differences are not related to the specific behaviors of these sorbates in supermicropores.

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REFERENCES

- Gavrilov, V.Yu., *Doctoral (Chem.) Dissertation*, Novosibirsk: Inst. Catal., 1999.
- Diaz-Aunon, J.A., Roman-Martinez, M.C., Salinas-Martinez de Lecea, C., L'Argentiere, P.C., Cagnola, E.A., Liprandi, D.A., and Quiroga, M.E., *J. Mol. Catal., A: Chem.*, 2000, vol. 153, nos. 1–2, p. 243.
- Nijs, H., Cool, P., and Vansant, E.F., *Interface Sci.*, 1997, vol. 5, nos. 2–3, p. 83.
- Sychev, M., Shubina, T., Rozwadowski, M., Sommen, A.P.B., De Beer, V.H.J., and van Santen, R.A., *Micropor. Mesopor. Mater.*, 2000, vol. 37, nos. 1–2, p. 187.
- Kostoglod, N.Yu., Sychev, M.V., Prikhod'ko, R.V., Astrelin, I.M., Stepanenko, A.V., and Razvadovski, M., *Kinet. Katal.*, 1998, vol. 39, no. 4, p. 593.
- Dubinin, M.M., *Characterization of Porous Solids*, Gregg, S.J., Sing, K.S.W., and Stoeckli, H.F., Eds., London: Soc. Chem. Ind., 1979, p. 1.

- Dubinin, M.M. and Astakhov, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, no. 1, pp. 5, 11, 17.
- Kadlets, O. and Dubinin, M.M., in *Adsorbenty, ikh polucheniye, svoystva i primeneniye* (Adsorbents, Their Preparation, Properties, and Applications), Dubinina, M.M. and Plachenova, T.G., Eds., Leningrad: Nauka, 1985, p. 47.
- Gavrilov, V.Yu. and Zenkovets, G.A., *React. Kinet. Catal. Lett.*, 1998, vol. 64, no. 1, p. 79.
- Gavrilov, V.Yu. and Zenkovets, G.A., *Kinet. Katal.*, 1996, vol. 37, no. 4, p. 617.
- Gavrilov, V.Yu. and Zenkovets, G.A., *Kinet. Katal.*, 2000, vol. 41, no. 4, p. 617.
- Karnaukhov, A.P., *Adsorbtsiya. Tekstura dispersnykh i poristykh materialov* (Adsorption: Texture of Porous Materials), Novosibirsk: Nauka, 1999.
- Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Areas, and Porosity*, New York: Academic, 1982.
- Karnaukhov, A.P., Fenelonov, V.B., and Gavrilov, V.Yu., *Pure Appl. Chem.*, 1989, vol. 61, no. 11, p. 1913.
- Gavrilov, V.Yu., *Kinet. Katal.*, 1994, vol. 35, no. 4, p. 435.
- Gavrilov, V.Yu., *Kinet. Katal.*, 2000, vol. 41, no. 5, p. 786.
- Ruff, O. and Ebert, F., *Z. Anorg. Allg. Chem.*, 1929, vol. 180, no. 1, p. 19.
- Spravochnik khimika: Osnovnye svoystva neorganicheskikh i organicheskikh soedinenii* (Handbook on Chemistry: Main Properties of Inorganic and Organic Compounds), Nikol'skii, B.A., Ed., Leningrad: Khimiya, 1971, vols. 1, 2.
- Gavrilov, V.Yu., *Kinet. Katal.*, 2000, vol. 41, no. 2, p. 304.
- Breck, D., *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, New York: Wiley, 1974.
- Fasman, A.B. and Usenov, B.Zh., *React. Kinet. Catal. Lett.*, 1978, vol. 9, no. 1, p. 85.
- Usenov, B.Zh., *Issledovanie adsorbtsionnykh protsessov i adsorbentov* (Studies of Adsorption Properties and Adsorbents), Dubinin, M.M., Ed., Tashkent: Fan, 1979, p. 134.
- Thommes, M., Kohn, R., and Froba, M., *J. Phys. Chem.*, 2000, vol. 104, no. 33, p. 7932.
- Sonwane, C.G., Bhatia, S.K., and Calos, N., *Ind. Eng. Chem. Res.*, 1998, vol. 37, no. 6, p. 2271.
- Inoue, S., Tanaka, H., Hanzawa, Y., Imagaki, S., Fukushima, Y., Buchel, G., Unger, K.K., Matsumoto, A., and Kaneko, K., *Characterization of Porous Solids. V*, Unger, K.R., Kreysa, G., and Baselt, J.P., Eds., Amsterdam: Elsevier, p. 167.
- Uvarov, N.F. and Boldyrev, V.V., *Usp. Khim.*, 2001, vol. 70, no. 4, p. 307.
- Kiselev, A.V., *Discuss. Faraday Soc.*, 1965, vol. 40, no. 2, p. 205.
- Kiselev, A.V., *Mezhmolekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* (Intermolecular Interactions in Adsorption and Chromatography), Moscow: Vysshaya Shkola, 1986, p. 360.
- Adamson, A.W., *Physical Chemistry of Surfaces*, New York: Wiley, 1976.