Kinetics and Catalysis, Vol. 46, No. 3, 2005, pp. 403–406. Translated from Kinetika i Kataliz, Vol. 46, No. 3, 2005, pp. 430–433.
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Adsorption of Nitrogen, Oxygen, and Argon Vapors on Fine-Pore Oxide Materials

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Received October 21, 2003

Abstract—A comparative study of the adsorption of N_2, O_2, and Ar vapors on supermicroporous and fine-mesopore silica at 77 K is carried out. The oxygen sorption properties of these silica materials, like those of tin oxide and zirconia (earlier studied materials), are affected by supermicropores. Argon sorption is insensitive to the presence of supermicropores. Fine mesopores also have an effect on the oxygen sorption properties of silica.

The pore structure of heterogeneous catalysts, supports, adsorbents, and other finely dispersed and porous materials is commonly studied by sorption methods using conventional sorbates such as N_2, O_2, and Ar at liquid-nitrogen temperature (77 K). In most cases, mutually consistent procedures have been developed for processing adsorption isotherms for meso- and macroporous materials [1, 2].

At the same time, the existence of micropores and supermicropores in the pore space of the materials examined gives rise to specific behaviors of various sorbates in the pore space with an increased adsorption potential [3]. These features of sorption necessitate additional reconciliation of data, for example, specific surface areas calculated for various adsorbates. Recently, research in this field has become much more intensive. On the one hand, this rising interest is due to the impressive progress in the development of new synthetic procedures for fine-pore materials and is focused on the search for new applications. On the other hand, this interest is due to the possibility of investigating readily available, chemically diversified materials with regular supermicroporous and fine "zeolite-like" mesoporous textures, whose parameters can also be reliably measured by methods other than gas adsorption [4, 5].

The goal of this work is to study the behavior of N_2, O_2, and Ar molecules in the supermicropores and fine mesopores of oxide materials.

EXPERIMENTAL

The following porous oxide materials were examined: tin oxide and zirconia, which had already been reported in an earlier paper [3]; the fine-mesopore material MCM-41, with a hexagonal structure, which had been studied in detail [6]; and silica materials with a fine-pore structure named SM-1 and SM-2.

N_2, O_2, and Ar adsorption isotherms at 77.4 K were measured on a DigiSorb-2600 Micromeritics (United States) automated volumetric setup. Samples were pumped at 300°C for 5 h immediately before adsorption runs. To rule out any irreproducibility of structural parameters and to compare the results correctly, sorption measurements for all sorbates were carried out on the same sample.

Adsorption isotherms were processed by a comparative method [1], which is an analogue of the widely known t and α_s methods [2], with the use of known data for Ar [2], N_2 [7], and O_2 [8] adsorption on oxide materials. Comparative plots were constructed for $P/P_0 = 0.05–0.20$, a region lying before the onset point of capillary condensation, which causes deviations from linearity. Analysis of these plots allows one to calculate the specific surface area S_α (m^2/g) and the micropore volume accessible to each sorbate V_μ (cm^3/g).

The limiting volume of the sorption space V_s (cm^3/g) was calculated from the ultimate adsorption data and from molar sorbate volumes at 77 K (N_2, 34.7 cm^3/mol; O_2, 26.2 cm^3/mol; Ar, 27.3 cm^3/mol). The equivalent pore-size distribution of the mesopore volume was evaluated from the desorption branch of the nitrogen adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method [2].

RESULTS AND DISCUSSION

As has been shown in [3], the behaviors of nitrogen, oxygen, and argon molecules in supermicropores differ substantially. This difference manifests itself as the fact that the supermicropore surface in tin oxide and zirconia shows different relative sorption properties toward oxygen and nitrogen molecules, whereas this effect is not observed for the argon–nitrogen pair. This results in a linear dependence of the parameter $S_\alpha(O_2)/S_\alpha(N_2)$ on the supermicropore volume $V_{s\mu}$ (this parameter exceeds unity noticeably) and in the absence of such a dependence for $S_\alpha(Ar)/S_\alpha(N_2)$. It was demonstrated [3] that $S_\alpha(N_2)$ is a reference value owing to the higher energy of interaction between the nitrogen molecule and the surface. The question arises of whether these features

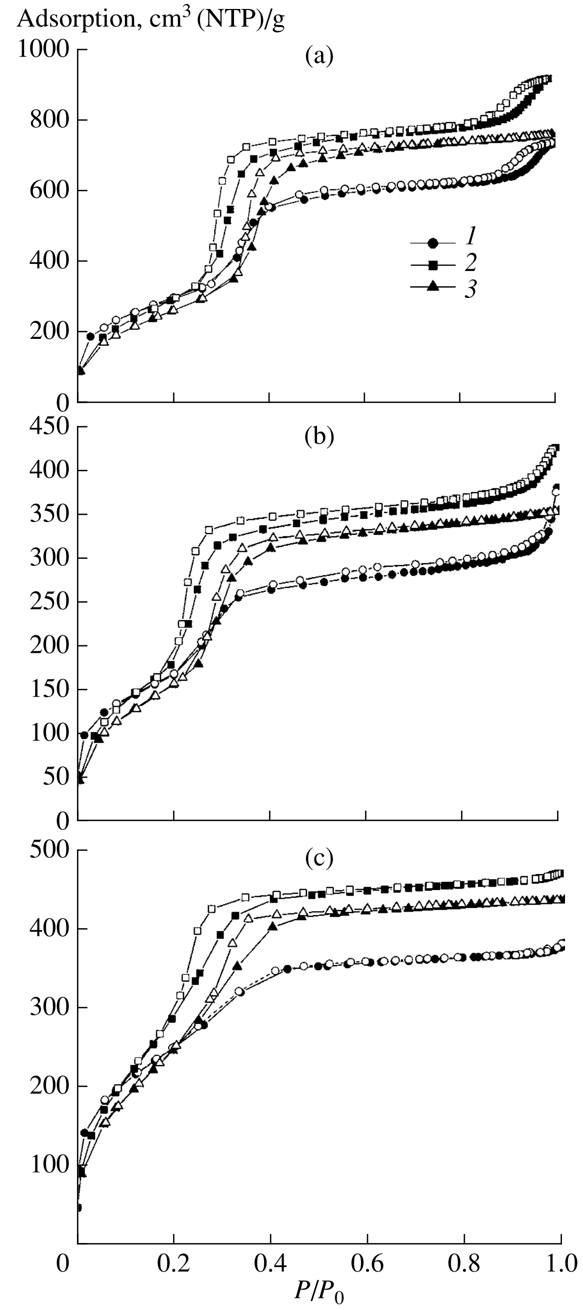

Fig. 1. (*1*) Nitrogen, (*2*) oxygen, and (*3*) argon adsorption isotherms at 77 K for (a) MCM-41, (b) SM-1, and (c) SM-2.

are also characteristic of the finest mesopores bordering on supermicropores. In this connection, it seems obvious that, even in typical mesoporous systems, the adsorption properties of the surface toward the sorbates considered are not specific and, therefore, the calculated values of specific surface area must be mutually consistent.

Figure 1 presents adsorption isotherms for the fine-pore adsorbents MCM-41, SM-1, and SM-2, and the table lists the texture parameters of these adsorbents.

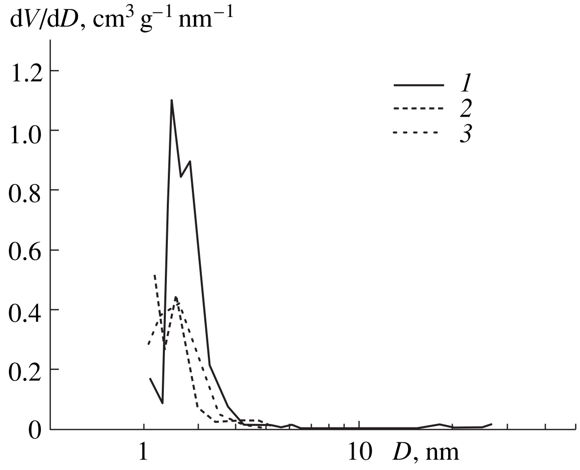

Fig. 2. $S_\alpha(O_2)/S_\alpha(N_2)$ versus supermicropore volume: (*1*) ZrO_2, (*2*) SnO_2 [3], and (*3*) silica materials studied.

The shape of the sorption isotherms, especially the shape of the capillary condensation loop, indicates that the mesopores are mainly fine. This inference is confirmed by differential pore-size distribution data (Fig. 2). However, true micropores of volume V_μ are absent in these samples. This follows from the analysis of the comparative plots of sorption isotherms for the sorbates examined (no typical positive ordinate intercepts) as well as from the parameters of the BET equation (energy constants C_{BET}; table), which do not exceed values typical of these sorbates on macro- and mesoporous materials.

The substantial difference in the limiting sorption space V_s between the sorbates, specifically, the fact that the ΔV_s values derived from the nitrogen sorption isotherms are higher, is likely due to the changes in the density of adsorbed argon and oxygen in the overcooled state and in larger mesopores. As can be seen from Fig. 1a, such pores are present in MCM-41 probably as gaps between ordered mesophase blocks. The possibility of variations in sorbate density below the boiling point was discussed previously [3].

At the same time, the limiting volume of the sorption space (V_s) differs markedly from the cumulative mesopore volume (V_c) derived by the BJH method from nitrogen desorption isotherms for the whole range of mesopore sizes in the SM samples. The V_c/V_s ratio is approximately equal to ≈1 for MCM-41, whereas this ratio is 0.94 for SM-1 and 0.86 for SM-2. One can assume that the deficient pore volume (the difference between the limiting volume of the sorption space and the cumulative mesopore volume) is due to supermicropores, that is, pores with typical sizes from 0.6–0.7 to 1.5–1.6 nm [9, 10], which cannot be analyzed by the capillary condensation method. Hence, the supermicropore volume is estimated at ~0.01 cm^3/g for MCM-41, ~0.04 cm^3/g for SM-1, and 0.08 cm^3/g for SM-2.

Textural characteristics of MCM-41, SM-1, and SM-2 calculated from N_2, O_2, and Ar sorption isotherms at 77 K

Sorbate	S_α, m^2/g	V_s, cm^3/g	V_c, cm^3/g	S_{BET}, m^2/g	C_{BET}	$S_\alpha(i)/S_\alpha(N_2)$	ΔV_s, cm^3/g
MSM-41							
N_2	1195	1.142	1.132	1094	75	1	–
O_2	1374	1.072	–	1211	32	1.15	0.07
Ar	1186	0.931	–	1101	39	1	0.21
SM-1							
N_2	637	0.589	0.553	613	87	1	–
O_2	837	0.500	–	983	12	1.31	0.09
Ar	654	0.432	–	658	40	1.02	0.16
SM-2							
N_2	1034	0.596	0.519	932	70	1	–
O_2	1547	0.553	–	1331	19	1.50	0.04
Ar	1066	0.537	–	1048	31	1.03	0.06

It follows from the table that $S_\alpha(O_2)/S_\alpha(N_2) > 1$ for all of the materials examined, particularly for the SM ones. This is not the case for $S_\alpha(Ar)/S_\alpha(N_2)$. This fact confirms earlier data indicating that oxygen sorption, unlike argon sorption, is sensitive to the presence of supermicropores [3].

According to [3], the phenomenological correlation between $S_\alpha(O_2)/S_\alpha(N_2)$ and supermicropore volume can be expressed as

$$S_\alpha(O_2)/S_\alpha(N_2) = 1 + k(V_{s\mu} - V^*_{s\mu}), \tag{1}$$

where k is the relative change in the absolute values of oxygen adsorption in supermicropores and mesopores. It follows from Fig. 3 that k is significantly lower for the fine-pore silica materials than for tin and zirconium dioxides [3]. Furthermore, there is no “threshold” $V^*_{s\mu}$ value starting at which $S_\alpha(O_2)$ grows relative to $S_\alpha(N_2)$. One can assume that the change in the above dependence is due to the fact that the texture compositions of the oxides under consideration are fundamentally different.

The oxide systems considered are not texturally uniform and contain pores of various types, whose adsorption properties are fundamentally different. At the same time, the series of samples studied supplement one another. The tin and zirconium oxides studied in [3] were microporous and supermicroporous and contained no considerable volume of mesopores. By contrast, the adsorbents MCM-41, SM-1, and SM-2 contain no true micropores but have a developed fine-mesopore texture and some volume of supermicropores, which is estimated above.

The absence of a threshold value of the supermicropore volume $V^*_{s\mu}$ for SM suggests that this parameter is related to a boundary region between micropores and supermicropores. In this case, $V^*_{s\mu}$, which takes different values for tin and zirconium oxides, can serve as a characteristic of this region. The reliability and usefulness of this characteristic will increase with accumulation of new experimental data for other porous materials with a similar transition region.

It follows formally from ratio (1) and Fig. 3 that $S_\alpha(O_2)/S_\alpha(N_2)$ for the fine-pore silica materials is somewhat larger than unity even if supermicropores are absent from the sample. Therefore, the changes in the relative oxygen sorption properties of the surface cover the region of the finest mesopores. In this case, ratio (1) can be presented in a more general form:

$$S_\alpha(O_2)/S_\alpha(N_2) = b(D) + k(V_{s\mu} - V^*_{s\mu}), \tag{2}$$

where $b(D)$ is the parameter taking into account the contribution from the finest mesopores. Ratio (2) is valid only for part of the pore space, and it is likely due to this fact that $b(D)$ is constant for MCM-41 and SM, which are characterized by different pore size distributions (Fig. 2). It follows from the data for the silica materials (Fig. 3) that b has a constant value of ~1.1. Note again that the dependence of $b(D)$ on pore size and

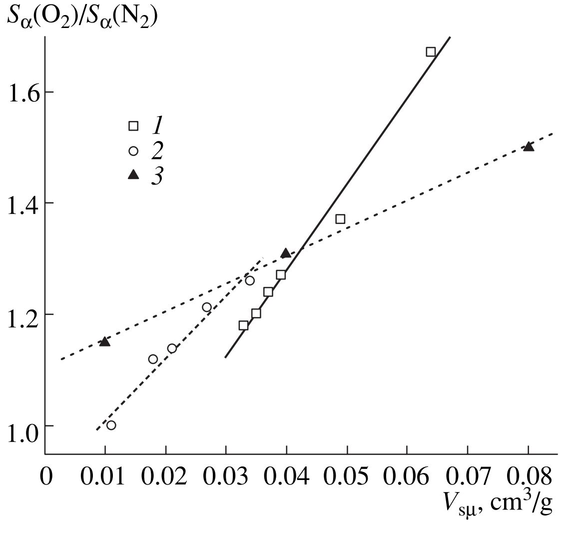

Fig. 3. Pore size distribution of the pore volume calculated from nitrogen desorption isotherms: (*1*) MCM-41, (*2*) SM-1, and (*3*) SM-2.

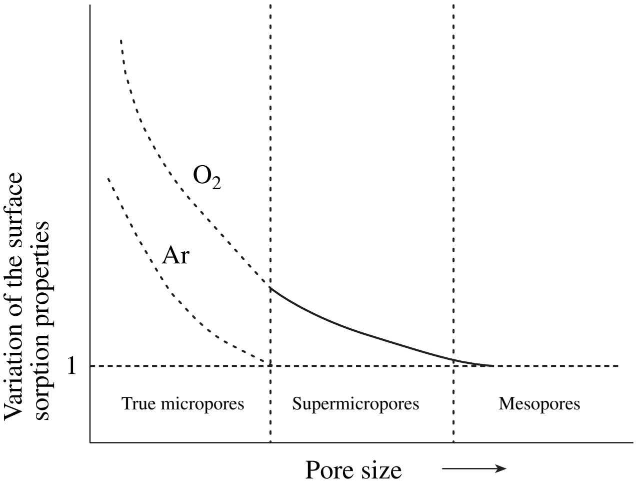

Fig. 4. Scheme illustrating how adsorption capacity depends on the pore size and type.

the fact that *b* approaches unity for larger mesopores follow from general considerations.

It is appropriate to assume that *k*, which changes from 15.4 m^2 for ZrO_2 [3] to 5 m^2 for the silica materials, depends on the chemical nature of the surface. For a more comprehensive study of the behavior of this parameter, it is necessary to examine a wider variety of systems. This will be the subject of forthcoming publications.

Figure 4 presents a scheme showing how the O_2 and Ar sorption capacities of the surface change with the size of the main types of fine pores. This scheme sums up the data presented here and in [3]. The difference in sorption properties between the pores considered and the meso- and macropores, which manifests itself in the specific behavior of oxygen molecules, covers the region of supermicropores and the finest mesopores. At the same time, no specific behavior was observed for argon adsorption. It is well known that argon adsorption in true micropores proceeds via a bulk filling mechanism [9] and its value is not proportional to the geometric surface area (the solid–gas interface). Therefore, the comparison and analysis of the sorption properties by the method described in the work are incorrect. This is indicated by a dotted line in the scheme.

Thus, if $S_\alpha(O_2)/S_\alpha(N_2)$ exceeds unity, regions of supermicropores and finest mesopores are present in the pore space.

ACKNOWLEDGMENTS

The author is grateful to A.P. Karnaukhov for his interest in this work and to M.S. Mel'gunov for the SM samples.

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