Specific Features of the Comparative Adsorption Analysis of the Texture of Ultrafine Microporous/Mesoporous Materials

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Abstract—N_2 adsorption on the uniformly mesoporous material MCM-41, zeolite ZSM-5, and their mechanical mixtures at 77 K is reported. The use of the differential comparative method in the analysis of adsorption isotherms for this class of materials is complicated by the weak sorbate–MCM-41 surface adsorption interaction and, for adsorbent mixtures, by the compensation effect caused by the introduction of adsorption sites with an increased adsorption potential. Specific features of sorption on the two-component system are analyzed in the framework of the conventional BET model.

At present, the porous structure of catalysts and adsorbents is usually studied by adsorption methods, which provide reliable information for a wide range of structure parameters. The experimental procedures used in these methods, which are mostly based on the analysis of low-temperature nitrogen adsorption isotherms, are well proven [1] and, for some texture parameters, are standardized. However, the wide variety of recently synthesized ultrafine materials with a regular mesoporous structure [2–5] requires refinement of some standard sorption analysis procedures, in particular, specific surface area measurements.

The purpose of the study reported here was to refine the comparative adsorption isotherm analysis procedure used in the measurement of the micropore volume and the specific surface area of ultrafine microporous/mesoporous materials.

EXPERIMENTAL

The objects of this study were MCM-41, a uniformly mesoporous ultrafine silicate material with a hexagonal pore structure; the channeled zeolite ZSM-5 (Si/Al ≈ 40); and their mechanical mixtures. The composition of a mixture was expressed in terms of the ratio of the zeolite weight to the total mixture weight, X (g/g). We examined two ZSM-5 samples, which were designated ZSM-5*a* and ZSM-5*b*. These samples had slightly different degrees of crystallinity, and ZSM-5*a* contained a minor amount of an amorphous phase.

Nitrogen adsorption isotherms were measured at 77 K using a Digisorb 2600 Micromeritics automated volumetric device. The samples to be examined were conditioned in vacuo at 400°C (ZSM-5) or 350°C (MCM-41) for 5 h.

Nitrogen vapor adsorption isotherms were processed by a comparative method [1] similar to the well-known *t*-method [6], with the reference isotherm derived from averaged data for a wide variety of disperse oxide materials [7]. For the isotherm pressure range of $P/P_0 = 0.08$–0.25, which precedes the onset of the capillary condensation of the sorbate in the mesopore space, we calculated the specific surface area (S_α, m²/g) and the micropore volume accessible to nitrogen molecules (V_μ, cm³/g). Processing of multilayer adsorption isotherms (classical BET method) [6] was also used.

The limiting sorption volume V_s was derived from the amount sorbed at a relative sorbate vapor pressure of 0.995 and the density of liquid hydrogen at the measurement temperature.

RESULTS AND DISCUSSION

Figure 1 plots the adsorption branches of the nitrogen sorption isotherms for the initial samples, and the calculated texture parameters are listed in Table 1. It is clear from Table 1 that the energy constant C_{BET} is substantially smaller for MCM-41 than for ordinary mesoporous materials in which there is no specific, directed interaction, for which it is approximately equal to 100. A similar weakening of sorption interaction as a decrease in C_{BET} was observed earlier for O_2 and Ar sorption on the ultrafine mesoporous materials MCM-41, CM-1, and CM-2 [8]. Abnormally small C_{BET} values for a wide variety of MCM-like materials were also observed by other authors [9]. The difference between the ZSM-5 samples used in this work is that ZSM-5*a* has a somewhat larger limiting sorption volume V_s and, at the same time, a smaller micropore volume.
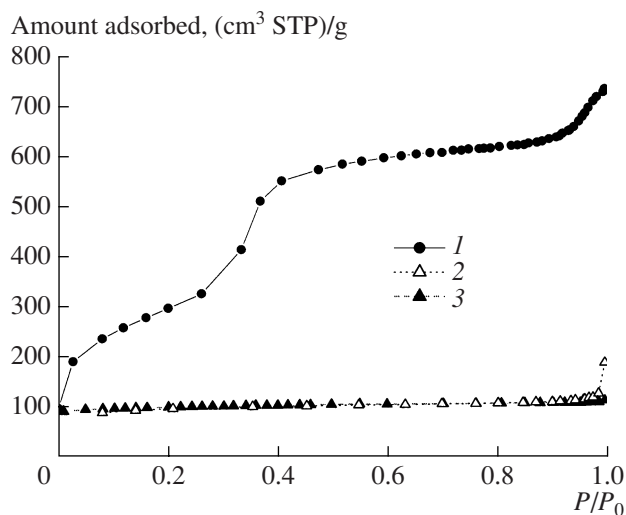
Amount adsorbed, (cm³ STP)/g

Fig. 1. Nitrogen adsorption isotherms (T = 77 K) for (*1*) MCM-41, (*2*) ZSM-5*a*, and (*3*) ZSM-5*b*.

Amount adsorbed, (cm³ STP)/g

Fig. 2. Nitrogen adsorption isotherms for MCM-41 + ZSM-5 mixtures (x = (*1*) 0.2, (*2*) 0.405, and (*3*) 0.59) and adsorption data calculated for the additive adsorption on the mixture components (points).

In physical adsorption, the sorbate–sorbate interaction is the sum of elementary, pairwise, intermolecular dispersion interactions: $U \approx \sum\limits^{n} \varepsilon(x)$ [6, 10]. In adsorption on extremely fine mesoporous materials (for which the structure parameter characterizing their high degree of fineness can be either the size of primary particles, as in the case of globular structures, or the thickness of the pore wall, as in the case of MCM-41), a smaller number of surface atoms (n) are the nearest neighbors of a sorbate molecule and are involved in pairwise dispersion interaction. As a consequence, the total adsorption interaction energy U is lower. In an earlier study [11], we examined this situation for the physical adsorption of hydrogen molecules on mesoporous materials at 77 K. It is likely that the weakening of the dispersion interactions between the sorbate and the MCM-41 surface due the smaller number of summed terms takes place in nitrogen sorption as well.

The total sorbate–solid interaction energy can be varied by introducing structural elements characterized by a higher sorption energy. Such samples are obtained, for example, by mixing MCM-41 and zeolite ZSM-5 in appropriate proportions. The texture parameters of the mixed samples examined in this study are given in Table 2.
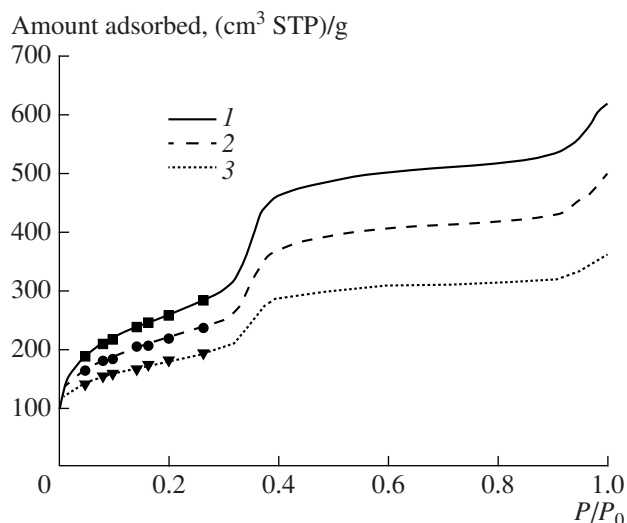
In the pressure range corresponding to the initial portion of the isotherm, nitrogen sorption on MCM-41 and in the micropore space of the zeolite occurs via different mechanisms, namely, monolayer adsorption the former case and the bulk filling of micropores in the later case [12]. These processes are likely independent. For a mixed sample, the overall, experimentally measurable sorption isotherm $A_\Sigma(P)$ is the superposition of the isotherms $A_a(P)$ and $A_b(P)$ for the mixture components taking into account their weight fractions:

$$A_\Sigma(P) = A_a(P)X + A_b(P)(1 - X), \qquad (1)$$

where X is the weight fraction of the zeolite in the mechanical mixture of the sorbents.

In Fig. 2, we compare the observed sorption isotherms with adsorption data calculated using the above additive scheme. Clearly, the calculated and observed data are in good agreement. Thus, we know the actual micropore volume introduced in all the mixed samples.

At the same time, it is clear from Table 2 that the micropore volume determine by the comparative method (V_μ) is well below the true micropore volume in the samples ($V_\mu^{ZSM} X$); furthermore, for the $X = 0.2$ sample, micropores are not detected at all.

Figure 3 presents a complete comparison between the micropore volume determined in the mixtures by

Table 1. Texture parameters of the MCM-41 and ZSM-5 samples

Sample	S_{BET}, m²/g	C_{BET}	S_α, m²/g	V_μ, cm³/g	V_s, cm³/g
MCM-41	1094	75	1195	0	1.141
ZSM-5*a*	322	−107	110	0.10	0.293
ZSM-5*b*	317	−50	60	0.13	0.176

Table 2. Texture parameters of mechanical mixtures of MCM-41 and ZSM-5

Sample	S_{BET}, m²/g	C_{BET}	S_α, m²/g	V_μ, cm³/g	$V_\mu^{ZSM} X$, cm³/g	S_α^{add}, m²/g
$X = 0.43$ (*a*)	770	117	732	0.018	0.043	728
$X = 0.544$ (*a*)	680	143	624	0.027	0.054	604
$X = 0.2$ (*b*)	937	100	934	0	0.026	968
$X = 0.405$ (*b*)	785	165	723	0.031	0.053	735
$X = 0.59$ (*b*)	631	387	512	0.058	0.078	525

the comparative method and the micropore volume calculated taking into account the weight fractions of the components for both zeolites. Evidently, the micropore volume determined is smaller than the actual micropore volume in the samples (dashed line) by a constant value $(-\Delta V)$ for all absolute values of the micropore volume above 0.26 cm³/g.

For the BET model of multilayer adsorption, the additive scheme summing the amounts sorbed on each mixture component allows relationship (1) to be written as

$$A_\Sigma(h) = \frac{a_m^a h C_{BET}^a X}{(1-h)[1 + (C_{BET}^a - 1)h]}$$
$$+ \frac{a_m^b h C_{BET}^b (1-X)}{(1-h)[1 + (C_{BET}^b - 1)h]}, \quad (2)$$

where the subscripts *a* and *b* stand for ZSM-5 and MCM-41, respectively; a_m is the BET monolayer capacity for each component; and *h* is the relative vapor pressure of the sorbate (P/P_0). Note that the BET equa-

tion is only formally applied to adsorption on zeolite ZSM-5 in this context and does not reflect the actual mechanism of nitrogen sorption in the micropore space of the zeolite.

Figure 4 illustrates the fit between the sorption isotherms calculated using relationship (2) and sorption data calculated using the additive scheme and presented in Fig. 2. Clearly, the isotherms calculated using the BET model are, on the whole, consistent with the assumptions made. Therefore, Eq. (2) allows us to calculate reliably the change in the energy constant C_{BET}^Σ, which governs the shape of the adsorption isotherm for the mixed sample:

$$C_{BET}^\Sigma = \frac{A_\Sigma(1-h)}{h(a_m + A_\Sigma(h-1))}, \quad (3)$$

where A_Σ and a_m are determined by the value of *X*.

Figure 5 plots C_{BET}^Σ numerically calculated using Eqs. (2) and (3) and observed C_{BET}^Σ as a function of *X*. Note that it seems impossible to obtain a general ana-
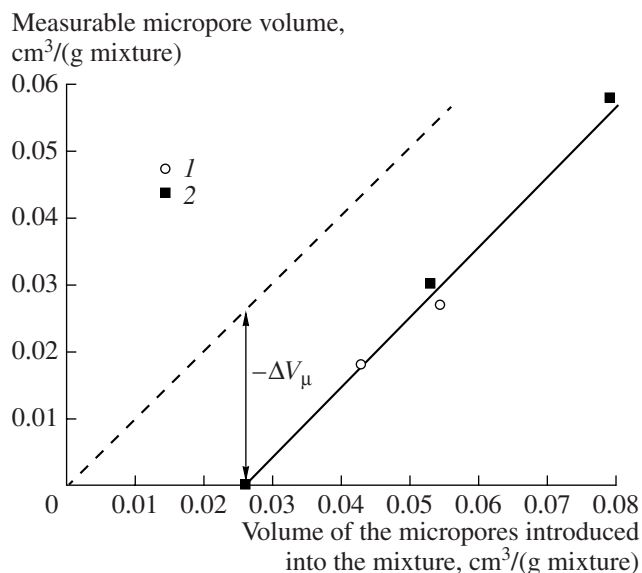

Fig. 3. Comparison between experimental micropore volume data and the volumes of the micropores occurring in the mixed samples as a result of the introduction of zeolite (*1*) ZSM-5*a* and (*2*) ZSM-5*b*.
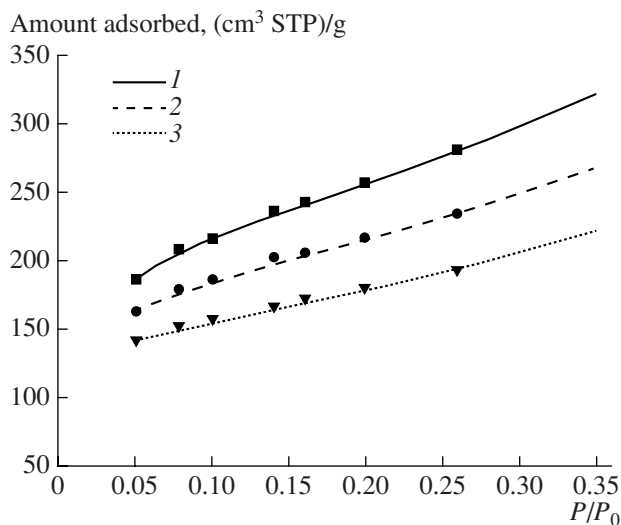

Fig. 4. Nitrogen adsorption isotherms calculated using the BET method (Eq. (2)) for $X = $ (*1*) 0.2, (*2*) 0.405, and (*3*) 0.59 and adsorption data calculated for the additive adsorption of the mixture components.

lytical expression for $C_{BET}^{\Sigma}(X)$ in the framework of the assumptions made here because of the complicated dependence of the parameters of expression (3) on X. It follows from Fig. 5 that the set of calculated data has a discontinuity at $X \approx 0.77$. This discontinuity of the $C_{BET}^{\Sigma}(X)$ dependence (the passage of C_{BET} to the region of negative, physically meaningless values) is a characteristic feature manifested by the BET equation when it is formally used in the processing of adsorption isotherms for materials having a considerable micropore volume along with small mesopore and macropore surface areas [1].

Figure 5 demonstrates satisfactory agreement between the observed and calculated data. Furthermore, the calculated data indicate that, for the mixtures of the two sorbents considered, the characteristic value of the energy constant for nitrogen sorption, $C_{BET}^{\Sigma} = 100$ (shown with a horizontal line in the plot), is reached at $X \approx 0.2$, which is in agreement with experimental data.

The totality of the above results suggests that the introduction of nitrogen sorption sites with an increased sorption potential gradually transforms the shape of the overall isotherm, changing the C_{BET}^{Σ} value. For the sorbent pair MCM-41 + ZSM-5, the threshold value V_{μ}^{*}, at which the initial weakening of the interaction between the sorbate and the surface of the ultrafine material is fully counterbalanced, is approximately 0.026 cm³/g. The further increase of the micropore volume in the mixture is adequately revealed by processing the isotherms both by the BET method (C_{BET} exceeding the characteristic value of 100) and by the comparative method (detection of micropores, but with a volume exceeding the true micropore volume by the above-mentioned value $-\Delta V$).

At the same time, the specific surface areas of the mixed samples determined by the comparative method (S_{α}) and those calculated from the additive contributions of the mixture components ($S_{add} = S_{\alpha}^{MCM}(1 - X) + S_{\alpha}^{ZSM} X$) are, on the whole, in satisfactory agreement (Table 2).

Let us represent the sorption isotherm in general form as the sum of two functions existing in different domains of the argument P:

$$A(P) = A_1(P) + A_2(P), \qquad (4)$$

where the $A_1(P)$ function exists at low pressures and describes sorption in the micropore space and specific sorption up to the monolayer coverage and $A_2(P)$ describes multilayer sorption. Note that this simplification is the basis of the differential comparative analysis of vapor sorption isotherms since the former function becomes constant already at low pressure and the latter takes on the conventional form of $A_2(P) = S_{\alpha}\alpha(P)$. The
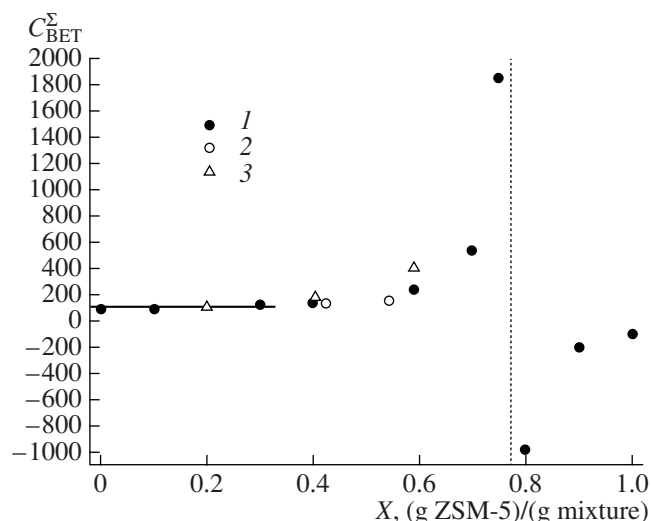

Fig. 5. C_{BET}^{Σ} as a function of X: (*1*) data numerically calculated using Eqs. (2) and (3), (*2*) experimental data for ZSM-5*a*-containing mixtures, and (*3*) experimental data for ZSM-5*b*-containing mixtures.

introduction of adsorption sites with an increased sorption potential increases the value of the $A_1(P)$ function and, as in the case considered, strengthens the total, initially weak sorption interaction between the sorbate and the surface of the ultrafine mesoporous material. At the same time, this peculiar kind of compensation reduces the micropore volume measurable by the comparative method by the value $-\Delta V$ (Fig. 3), which depends on the degree of the initial weakening of the adsorption interaction.

However, the specific surface area of the mesopores (S_{α}) is not associated with any compensation effect, because it is calculated using the isotherm region in which the function $A_1(P)$ (Eq. (4)) is already constant.

Thus, the specific features of the analysis of adsorption isotherms for ultrafine materials are that there can be compensation between sites with an increased sorption potential and surface areas with a weak sorption interaction (as compared to the interaction indicated by the reference isotherm in the comparative analysis). This leads to underestimated values of the micropore volume but does not affect the calculated specific surface area of the mesopores.

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