ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 6, pp. 799–802. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © V.Yu. Gavrilov, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 6, pp. 856–859.

Adsorption of Molecular Hydrogen on Ultrafine Microporous/Mesoporous Materials

V. Yu. Gavrilov

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: Gavrilov@catalysis.ru

Received April 17, 2006; in final form, November 14, 2006

Abstract—The comparative processing of H_2 adsorption isotherms obtained at 77 K is demonstrated to be applicable to the investigation of the microtexture of the ultrafine oxide materials MCM-41 and ZSM-5 and their mechanical mixtures. The H_2 sorption method allows the micropore volume to be determined correctly for mixed ultrafine microporous/mesoporous materials.

DOI: 10.1134/S0023158407060067

Sorption methods remain the main means of investigating the porous structure of adsorbents and catalysts. Holding the dominating position in this field of science, they nevertheless need regular improvements because of the widening variety of synthetic disperse and porous materials. The impressive advances in the synthesis of nanosized materials with various morphologies (particularly nanotubes [1–4]), with various chemical and phase compositions, and with a wide variety of molecular-sized and similar nanosized pores demand adequate progress in pore characterization techniques, including adsorption methods.

A general situation in the development of experimental investigation methods is employment of model objects and procedures whose properties and specific features are well known a priori. A conventional procedure used in adsorption methods of texture characterization is low-temperature nitrogen sorption, whose advantages and drawbacks have been studied in detail (see, e.g., [5–7]). Textural data obtained by nitrogen sorption for model samples can serve as a kind of reference in studies using other adsorbates for the same purpose. A promising sorbate for the characterization of microporous materials is molecular hydrogen at 77 K owing to the small kinetic size of the dihydrogen molecule ($\sigma_k = 0.289$ nm) and its negligible activated diffusion in micropores at 77 K.

Earlier, we demonstrated the possibility of applying the physical adsorption of molecular hydrogen at 77 K to the characterization of ultramicroporous and microporous structures and revealed the specific features of the energetically weak H_2 sorption on the mesopore surface [8, 9].

Here, we report the application of molecular hydrogen adsorption at 77 K to the microtextural study of ultrafine oxide materials and their mechanical mixtures, as well as a comparative procedure for processing adsorption isotherms.

EXPERIMENTAL

The objects of this study were MCM-41, a uniformly mesoporous ultrafine silicate material with a hexagonal pore structure [10]; zeolite ZSM-5 (Si/Al ≈ 40), which has a uniform channeled microtexture; and their mechanical mixtures. The composition of a mixture was expressed in terms of the ratio of the zeolite ZSM-5 weight to the total mixture weight, X (g/g), and was varied between 0.200 and 0.590. Two ZSM-5 samples were examined, 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. Table 1 lists the specific surface areas of mesopores (S_α), micropore volumes (V_μ), and limiting sorption volumes (V_s) derived from low-temperature nitrogen sorption data for the initial samples.

Hydrogen 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.

RESULTS AND DISCUSSION

Figures 1 and 2 plot hydrogen adsorption isotherms ($T = 77$ K) for the materials examined. The shape of the isotherms and the absolute value of the amount

Table 1. Texture parameters of MCM-41 and ZSM-5 samples derived from N_2 adsorption isotherms

Sample	S_α, m^2/g	V_μ, cm^3/g	V_s, cm^3/g
MCM-41	1195	0	1.141
ZSM-5*a*	110	0.14	0.293
ZSM-5*b*	60	0.16	0.176

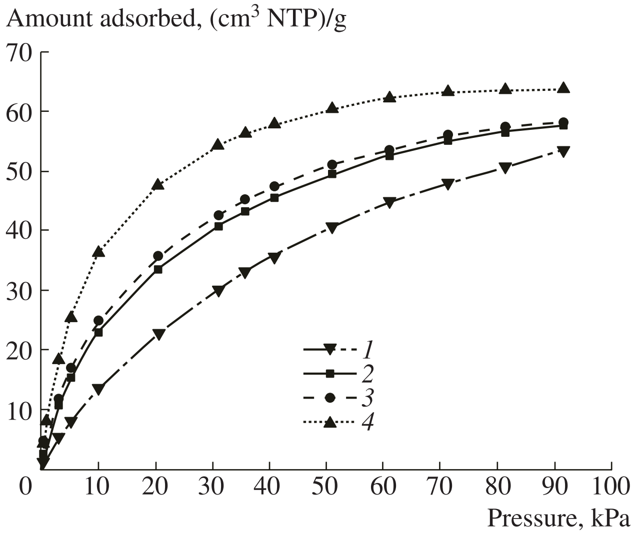

Fig. 1. Hydrogen sorption isotherms for (*1*) MCM-41, (*4*) ZSM-5*a*, and (*2*, *3*) their mixtures; X = (*2*) 0.430 and (*3*) 0.544.

adsorbed ($A_\Sigma(P)$) depend considerably on the component ratio X because the zeolite has a higher H_2 sorption capacity than the ultrafine mesoporous material MCM-41.

Hydrogen adsorbed on the mesopore surface at T = 77 K, which is above the critical temperature, is mobile and delocalized and tends to the formal monolayer coverage as the pressure is increased. However, in the pressure range examined, the amount of adsorbed hydrogen corresponds only to a small fraction of the monolayer coverage [9]. Considering the adsorption conditions in our experiments, the absence of qualitative changes in the shape of the isotherms (such as the changes caused by two-dimensional phase transitions) is evidence that the H_2 adsorbed on the mesopore surface is a two-dimensional gas. Hydrogen sorption can be quantitatively characterized by the specific quantity $\alpha(P)$ with dimensions of (cm^{3}NTP)/m^2.

Hydrogen adsorption data for zeolite ZSM-5 are more consistent with the concept of the pressure-induced growth of the effective density of the adsorbed phase throughout the micropore volume, so they can be characterized by the specific quantity $\beta(P)$ with dimensions of (cm^3 NTP)/(cm^3 micropore).

Figure 3 plots the pressure dependence of the ratio $K(P) = \beta(P)/\alpha(P)$ (cm^{-1}). Evidently, $K(P)$, which is a kind of formal sorption enhancement coefficient for micropores, is a function decreasing with increasing sorbate pressure. A comparison between the two specific adsorption characteristics clearly illustrates the role of the fact that, above the critical temperature of the sorbate, the dispersion potential of the adsorption interaction of molecules is higher in the micropore space than on the mesopore surface (the absolute value of this potential difference is not considered here). Furthermore, the form of the $K(P)$ function provides a qualitative explanation for the above-noted dependence of the isotherm shape on the composition of the mixed sample (Figs. 1, 2).

As in the case of low-temperature nitrogen adsorption on similar materials [11], there is good reason to believe that H_2 sorption on each component of the mixed samples also takes place independently. In this case, the overall experimental sorption isotherm $A_\Sigma(P)$ is the superposition of the isotherms $A_a(P)$ for ZSM-5

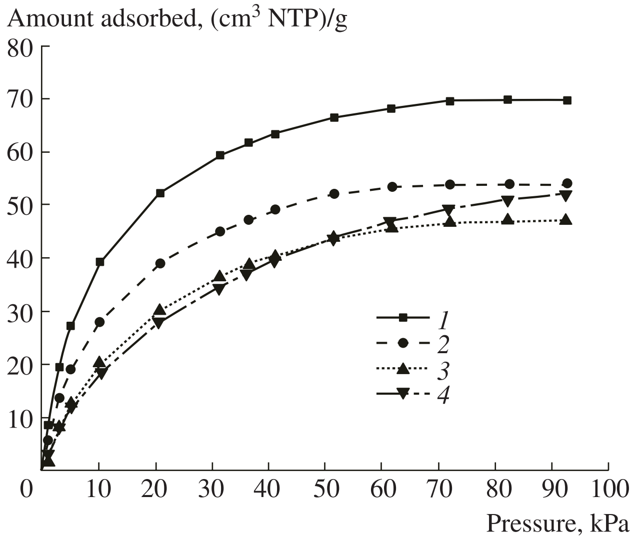

Fig. 2. Hydrogen sorption isotherms for (*1*) ZSM-5*b* and (*2*–*4*) its mixtures with MCM-41; X = (*2*) 0.590, (*3*) 0.405, and (*4*) 0.200.

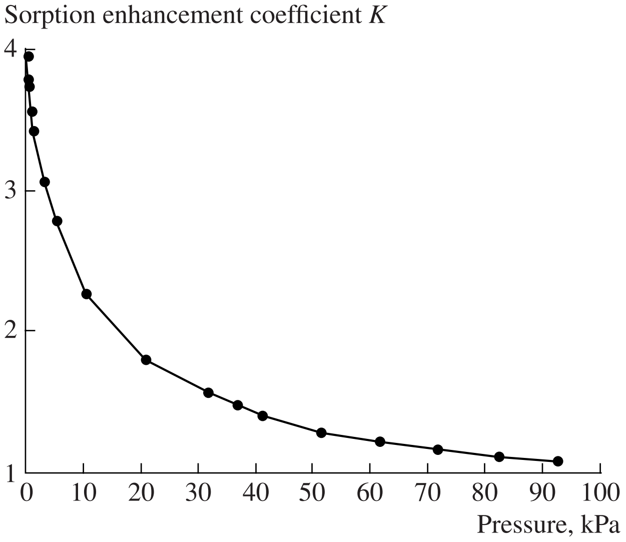

Fig. 3. Variation of $K = \beta/\alpha$ in the sorbate pressure range examined.

and $A_b(P)$ for MCM-41 taking into account the weight fractions of the mixture components:

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

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

The independence between sorption in the micropore space and sorption on the mesopore surface allows the general expression for the sorption isotherm to be represented in such a way as to take into account the texture parameters of the mixture components:

$$A_\Sigma(P) = A^0 + V_\mu(P)X + S_\alpha\alpha(P)(1 - X), \quad (2)$$

where A^0 is the total amount sorbed due to specific sorption (for example, on Lewis and other surface sites [12]) and sorption in ultramicropores (as in previous work, it is assumed here that A^0 reaches its maximum at minimal H_2 pressures and does not change as the pressure is further raised).

Note that, when taking into account sorption on the mesopore surface as $S_\alpha\alpha(P)(1 - X)$ in Eq. (2), S_α is generally assumed to be the specific surface area of MCM-41. Accordingly, the total specific surface area taking into account the contributions from both components of the mixed sample (Table 2) can be represented as $S = S_\alpha(1 - X) + S_{zeol}X \approx S_\alpha(1 - X)$; that is, for the given mixture components at $X \leq 0.6$, the contribution from the zeolite mesopore surface area S_{zeol} can be neglected (its value is usually small and is often unknown a priori). For the other mixtures of microporous and mesoporous sorbents, one can use the experimentally measured mesopore surface area.

Expression (2) makes it possible to analyze H_2 adsorption isotherms for mixed sorbents by the "volumetric" comparative method using the equation

$$A_\Sigma(P) - S_\alpha\alpha(P)(1 - X) = A^0 + V_\mu\beta(P)X$$

or

$$A_\Sigma(P) - S_\alpha\alpha(P) = A^0 + \mathrm{V}_\mu\beta(P)X. \quad (3)$$

As $\alpha(P)$ values for comparative analysis of sorption isotherms, we used averaged data obtained for the finest mesoporous materials [9]. $\beta(P)$ values were obtained by averaging a large number of sorption isotherms for ZSM-5 zeolites [8].

Figure 4 presents experimental H_2 sorption isotherms for mixed samples in the coordinates of Eq. (3). It can be seen that all comparison plots pass through the origin of coordinates, indicating that there is no significant specific sorption of hydrogen ($A^0 = 0$).

The micropore volume data derived from the initial portions of the comparison plots ($V_\mu^{H_2}$) are listed in Table 2, which also presents true values of the micropore volume based on the weight fractions of the zeolite in the samples ($V_\mu X$). As compared to the conventional procedure based on nitrogen adsorption, the V_μ determination procedure based on H_2 sorption data obtained at 77 K, suggested here for mixed ultrafine microporous/mesoporous systems, provides better agreement with independent (calculated) data, as is clear from our previous publication [11].

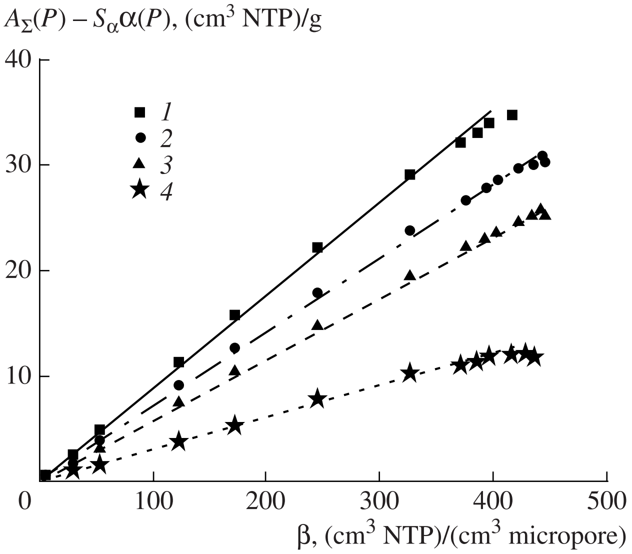

Fig. 4. Hydrogen sorption isotherms for mixed samples with X = (*1*) 0.590, (*2*) 0.544, (*3*) 0.430, and (*4*) 0.200 in the coordinates of Eq. (3).

In the case of nitrogen adsorption [11], the introduction of sites with an increased sorption potential strengthens the total, initially weak sorption interaction between the sorbate and the surface of the ultrafine mesoporous material. This peculiar kind of compensation reduces the micropore volume measurable by the conventional comparative method using reference data [6] by a value depending on the degree of the initial weakening of the adsorption interaction. The sorption of molecular hydrogen does not have this specific feature, because the comparative processing of isotherms is performed using $\alpha(P)$ values for the finest mesoporous materials, which have the weakest absolute sorption properties [9].

Thus, hydrogen adsorption on mechanical mixtures is an additive quantity. It is, therefore, possible to use the comparative analysis of adsorption isotherms in the

Table 2. Mesopore surface area (S) and calculated micropore volume ($V_\mu X$) data for mechanical mixtures of MCM-41 with ZSM-5*a* or ZSM-5*b*

X	S, m^2/g	$V_\mu X$, cm^3/g	$V_\mu^{H_2}$, cm^3/g
0.430 (*a*)	732	0.060	0.059
0.544 (*a*)	624	0.076	0.072
0.200 (*b*)	934	0.032	0.031
0.405 (*b*)	723	0.065	0.062
0.590 (*b*)	512	0.094	0.089

investigation of the microtexture of mixed ultrafine microporous/mesoporous materials.

REFERENCES

1. Dresselhaus, M.S., Dresselhaus, G., and Eklund, P., *Science of Fullerenes and Carbon Nanotubes*, San-Diego: Academic, 1996.
2. Zakharova, G.S., Volkov, V.L., Ivanovskaya, V.V., and Ivanovskii, A.L., *Usp. Khim.*, 2005, vol. 74, no. 7, p. 651.
3. Chen, Q., Du, G.H., Zhang, S., and Peng, L.M., *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.*, 2002, vol. 58, p. 587.
4. Wang, D., Yu, D., Peng, Y., Meng, Z., Zhang, S., and Qian, Y., *Nanotecnology*, 2003, vol. 14, p. 748.
5. Karnaukhov, A.P., *Adsorbtsiya. Tekstura dispersnykh i poristykh materialov* (Adsorption: The Texture of Disperse and Porous Materials), Novosibirsk: Nauka, 1999.
6. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, London: Academic, 1982.
7. Thommes, M., in *Nanoporous Materials: Science and Engineering*, Lu, G.Q. and Zhao, X.S., Eds., London: Imperial College Press, 2004, p. 317.
8. Gavrilov, V.Yu., *Kinet. Katal.*, 1995, vol. 36, no. 4, p. 631.
9. Gavrilov, V.Yu., *Kinet. Katal.*, 2005, vol. 46, no. 4, p. 642 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 4, p. 603].
10. Beck, J.S., Vartulli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., and Schlenker, J.L., *J. Am. Chem. Soc.*, 1992, vol. 114, no. 27, p. 10834.
11. Gavrilov, V.Yu. and Sokolov, E.E., *Kinet. Katal.*, 2007, vol. 48, no. 6, p. 851 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 6, p. 794].
12. Kazansky, V.B., *J. Catal.*, 2003, vol. 216, nos. 1–2, p. 192.