ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 4, pp. 609–614. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.Yu. Gavrilov, R.S. Zakharov, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 4, pp. 633–638.

Carbon Dioxide Adsorption on Carbon Nanomaterials

V. Yu. Gavrilov and R. S. Zakharov

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

Received September 26, 2009

Abstract—The adsorption of CO_2 on a number of activated carbons, thermal carbon black, and oxide materials at 195 K was studied using static and dynamic techniques. The landing surface areas $\omega(CO_2) \approx 0.19$ nm^2 on thermal carbon black and the absolute values of sorption for $P/P_0 < 0.4$ were determined. The density of adsorbed CO_2 in the micropore volume was estimated at $\rho(CO_2) = 0.91$ g/cm^3. It was demonstrated that the previously found effect of a weakening of the sorption interaction of nitrogen molecules with thin-walled materials (which manifested itself in an analysis of sorption isotherms by a comparative method) was pronounced to a lesser degree for the sorption of CO_2. At the same time, the presence of supermicropores in activated carbon samples resulted in overestimated values of surface areas. A dynamic method was proposed to measure the spectra of CO_2 desorption at 195–260 K using a SORBI-MS system for evaluating the binding energy of sorbate molecules with the surface.

DOI: 10.1134/S0023158410040221

INTRODUCTION

Adsorption methods are currently most commonly used to study the pore structure of dispersed and porous nanomaterials, including adsorbents and catalysts, for scientific and industrial purposes. The sorption of nitrogen and argon at 77 K is most widely used to study mesoporous materials; this process has been studied in sufficient detail [1, 2]. At the same time, the study of the pore structure of ultramicroporous (as a rule, carbon) materials is associated with a number of problem. The most serious problem is the frequently occurring activated diffusion of N_2 or Ar molecules into the volume of ultrafine pores at 77 K. It leads to the incomplete filling of these pores with the sorbate [3, 4], and the resulting information on the microtexture parameters of the nanomaterial becomes unreliable.

In principle, this problem can be solved in the following two ways: with the use of sorbates with smaller critical molecular sizes, for example, molecular hydrogen (σ_k = 0.289 nm as compared with σ_k = 0.364 nm for N_2) [5, 6] or by performing a sorption experiment at a higher temperature to increase the kinetic energy of sorbate molecules and to facilitate diffusion into the volume of ultrafine pores. Carbon dioxide (σ_k = 0.33 nm [7]) can be used as a sorbate for this purpose, and the corresponding sorption measurements should be performed at 195 or 273 K [8–12]. However, it should be taken into account that a directed interaction with surface sites is characteristic of the adsorption of CO_2 because of a large quadrupole moment of the sorbate molecule (0.64 Å^3, as compared with, for example, the quadrupole moment of 0.31 Å^3 for nitrogen [7]). This results in the high sensitivity of CO_2 adsorption to the occurrence of polar groups or ions on the surfaces of solids [1]. This special feature of intramolecular interactions allows us to consider the adsorption of CO_2 as a technique for testing the energy profile of the surface and its changes in the course of modification, for example, in the synthesis of supported catalysts or the grafting of catalytically active functional groups to the surface.

The aim of this work was to study the sorption of CO_2 on carbon nanomaterials at 195 K in the course of sorption experiments performed in traditional batch and flow dynamic modes to evaluate the geometric and adsorption properties of the surfaces.

EXPERIMENTAL

The adsorption isotherms of N_2 at 77 K and CO_2 at 195 K were measured on a DigiSorb-2600 instrument (Micromeritics, United States). In addition, the sorption of CO_2 from a mixture with a carrier gas (He) was measured on a SORBI-MS flow system (Joint-Stock Company META, Russia) after the establishment of sorption equilibrium at 195 K and a relative sorbate concentration of 0.1–0.2 using thermal desorption at a gradual increase in the temperature at a rate of 2 K/min over a range from 195 to 263 K and a constant concentration of the inlet gas mixture. A thermal conductivity detector was used as a gas composition analyzer. To exclude the possible irreproduciblity of the texture parameters of samples, the adsorption measurements with various sorbates were performed using the same weighed portions of the samples. The samples of test nanomaterials were pretrained under vacuum conditions (10^{-3} Torr) in the course of batch

Table 1. Texture parameters of the test nanomaterials calculated from the isotherms of nitrogen sorption

Sample	V_μ, cm^3/g	S_α, m^2/g	V_s, cm^3/g	V_{cum}, cm^3/g
Chemviron activated carbon	0.394	251	0.562	0.121
Norit Supra activated carbon	0.280	378	0.668	0.355
L-3780 activated carbon	0.043	1372	0.783	0.469
SKT activated carbon	0.367	181	0.525	0.131
SKN activated carbon	0.337	587	1.063	0.594
Super Sorbon activated carbon	0.266	501	0.542	0.155
TG-10 carbon black	0	10	–	–
Acetylene carbon black	0	82	–	–
MCM-41	0	1230	1.373	1.395
HZSM-5	0.103	138	0.218	0.110

measurements or in an inert gas flow with a flow rate of 60 cm^3/min in measurements under dynamic conditions at 300°C for 5 h.

Various commercial activated carbons, carbon black, and oxide materials were chosen as test materials. Table 1 summarizes the texture characteristics of these materials determined by using nitrogen vapor sorption at 77 K.

Experimental nitrogen adsorption isotherms were processed by a conventional comparison method [2] to calculate the micropore volume (V_μ, cm^3/g) and the mesopore surface area (S_α, m^2/g). The limiting volumes of the sorption space (V_s, cm^3/g) are listed in Table 1. The mesopore size distribution and cumulative mesopore volume (V_{cum}, cm^3/g) were calculated by the Barrett–Joyner–Halenda (BJH) method [1].

RESULTS AND DISCUSSION

Figures 1–3 show the isotherms of N_2 sorption on the test carbon samples. It can be seen that the structures of the samples were diverse in terms of a ratio between micropores and mesopores (Table 1); this allowed us to determine the possible effect of structure parameters on the sorption of CO_2 at 195 K.

For the majority of the test activated carbons, the total micropore and mesopore volume was approximately the same as the total pore volume ($V_\mu + V_{cum} \approx V_s$); the only exception was L-3780 activated carbon (for this sample, $V_\mu + V_{cum} < V_s$). Gavrilov and Sokolov [12] studied the use of a traditional comparative method for the analysis of the isotherms of nitrogen sorption on ultradispersed samples containing pores. They found that at least two elements could be recognized in these structures: with decreased and increased intermolecular sorption interactions. Mesopore struc-

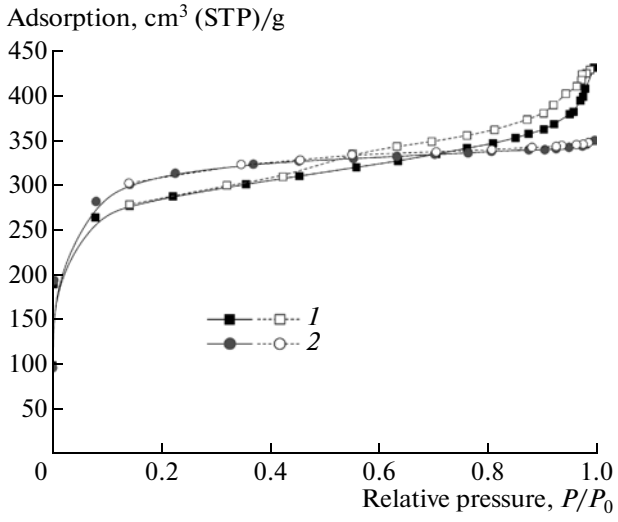

Fig. 1. Isotherms of N_2 adsorption on activated carbons: (*1*) Norit Supra and (*2*) Super Sorbon.

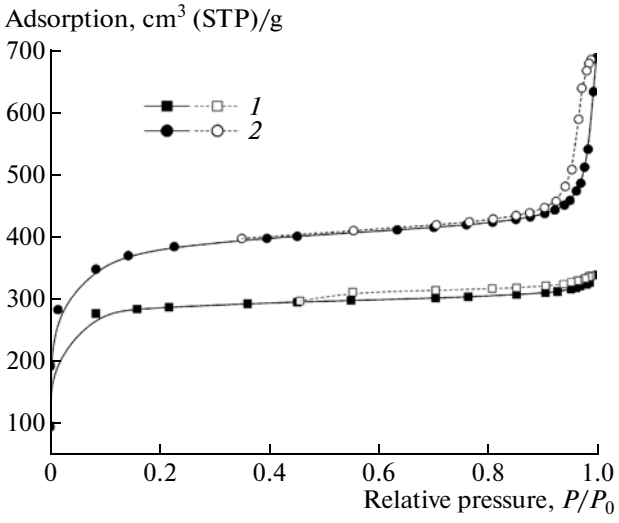

Fig. 2. Isotherms of N_2 adsorption on activated carbons: (*1*) SKT and (*2*) SKN.

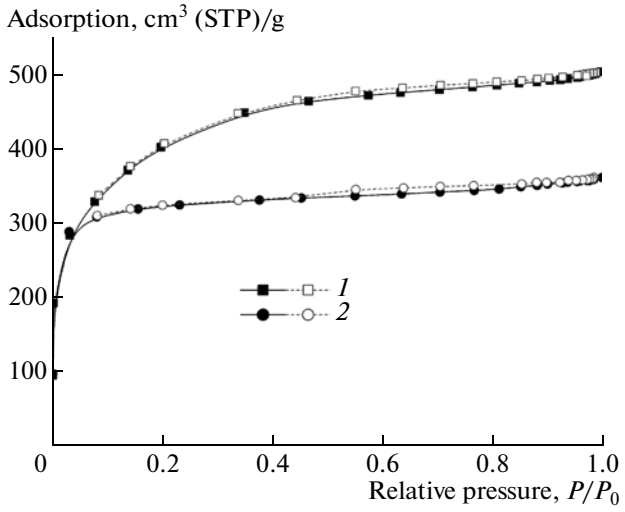

Fig. 3. Isotherms of N_2 adsorption on activated carbons: (*1*) L-3780 and (*2*) Chemviron.

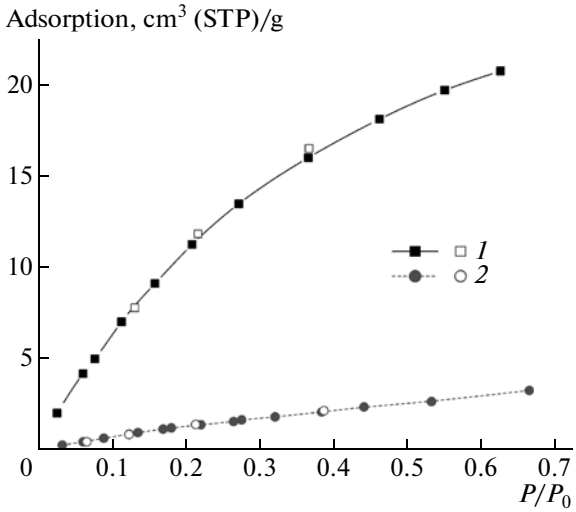

Fig. 4. Isotherms of CO_2 adsorption on thermal carbon black: (*1*) acetylene carbon black and (*2*) TG-10 carbon black (195 K).

ture regions with a weakened intermolecular interaction with sorbate molecules U because of a decrease in the summation number n of paired dispersion interactions of sorbate–sorbent molecules $U \approx \sum^{n} \varepsilon(x)$ can be ascribed to the former elements. These mesopore structure regions for activated carbons can be correlated, for example, with thin (one or two atomic layers) interpore walls. Texture regions with an increased sorption potential are typical micropores. As found by Gavrilov and Sokolov [12], a comparative analysis of the isotherms of nitrogen sorption at 77 K for these materials resulted in a reduced value of the micropore volume V_μ; at the same time, the specific surface area of mesopores S_α was determined correctly. Hence, by analogy, we can hypothesize that the L-3780 activated carbon had the thinnest carbon walls among the test series of activated carbon samples, whereas the micropore volume V_μ determined for this sample from nitrogen sorption was reduced.

To use a comparative method for the treatment of CO_2 sorption isotherms, it is necessary to determine the isotherm of the absolute values of sorption for the given sorbate on carbon materials at 195 K. It is reasonable to use thermal carbon black (Table 1 summarizes the values of S_{sp}), which is closest to the surface of the test samples in terms of chemical composition, as reference samples. These carbon samples do not contain micropores, which are determined from the sorption of nitrogen. These results are reliable because the carbon black samples do not belong to ultradisperse materials.

Figures 4–6 show the isotherms of CO_2 sorption on activated carbons and meso- and macroporous thermal carbon black samples at 195 K. It can be seen that all of the isotherms were reversible over the entire test range of relative sorbate vapor pressures ($0.01 < P/P_0 < 0.65$); this suggests the absence of secondary sorption processes from mesopores. It seems unreasonable to measure CO_2 sorption isotherms at higher values of P/P_0 because of the possible formation (in accordance with the phase diagram of CO_2) of a solid phase of carbon dioxide on the surface of mesopores at 195 K.

The landing surface area (ω) of CO_2 on a carbon surface can be calculated from the experimental isotherms of CO_2 sorption on carbon black samples (Fig. 4). Using the specific surface areas of carbon black samples measured from the adsorption of nitrogen (Table 1) and the obvious relationship $S = a_m N_0 \omega$ (where a_m is the CO_2 monolayer capacity in the BET model), we obtain $\omega(CO_2) \approx 0.19$ nm^2, which is consistent with well-known published data, for example, [1, 13].

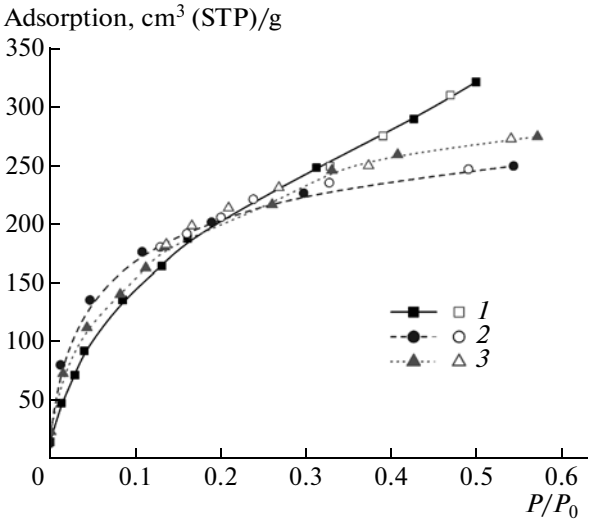

Fig. 5. Isotherms of CO_2 adsorption on activated carbons: (*1*) L-3780, (*2*) Norit Supra, and (*3*) Super Sorbon (195 K).

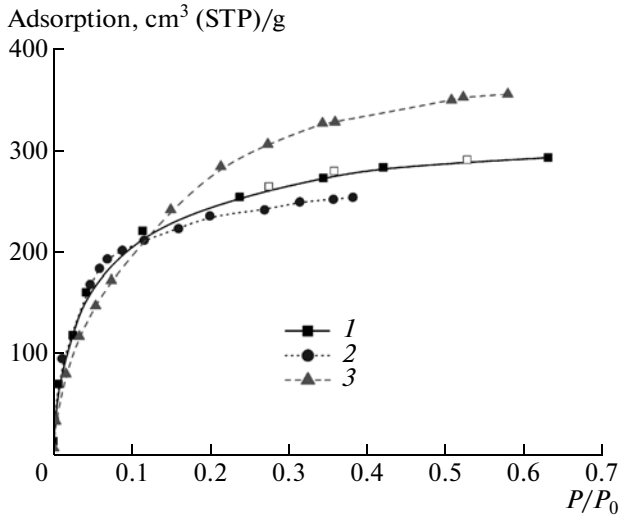

Fig. 6. Isotherms of CO_2 adsorption on activated carbons: (*1*) Chemviron, (*2*) SKT, and (*3*) SKN (195 K).

The required isotherm of the absolute values of CO_2 sorption at 195 K was derived from the isotherms shown in Fig. 4 by relating the sorption values to the unit surface area of mesopores in the corresponding carbon black sample. The results (Fig. 7) demonstrate a good agreement between the absolute values of sorption at $P/P_0 < 0.4$. An averaged sorption isotherm is adequately approximated by the power polynomial

$$\alpha = -0.0028 + 0.83709h - 1.04341h^2 + 0.80014h^3, \quad (1)$$

where α is the amount sorbed (cm^3 (STP) m^{-2}), and h is the relative pressure of CO_2 (P/P_0).

Isotherm (1) of the absolute values of CO_2 adsorption was used for the comparative treatment of the isotherms of adsorption on activated carbon samples. Figure 8 shows a typical comparative plot of this kind with the use of the isotherm of sorption on Chemviron activated carbon as an example. It can be seen that the sorption isotherm is affine to the reference isotherm, and the capacity of activated carbon micropores for CO_2 at 195 K can be determined from the intercept in the axis of ordinates. To determine the accessible volume of these micropores, the sorbate density (ρ, g/cm^3) in micropores at the experiment temperature should be used.

The density of sorbed carbon dioxide in micropores at 195 K can be estimated by comparing the capacity of the micropore volume of zeolite HZSM-5 (Table 1) for the sorption of nitrogen and CO_2 under condition (which is reasonable for the given sample) that this volume is equally accessible to these sorbates and the density of sorbed nitrogen is the same as the conventional density of a liquid phase. Based on this comparison between the sorption of nitrogen and CO_2 on ZSM-5, the density of sorbed CO_2 at 195 K in micropores is $\rho(CO_2) = 0.91$ g/cm^3.

The above density of CO_2 was used to calculate the micropore volumes $V_\mu(CO_2)$ of activated carbons measured by the comparative method (Table 2). It can be seen that the values of $V_\mu(CO_2)$ and $V_\mu(N_2)$ were approximately the same for the majority of the samples, except for the L-3780 activated carbon. For this sample, the micropore volume measured from the sorption of CO_2 was much greater than the volume measured using nitrogen. Hence, we can assume that a decrease in the sorption interaction of nitrogen molecules with thin-walled carbon samples, which manifested itself in a comparative analysis of adsorption isotherms, was less important for the sorption of CO_2, probably, because of a stronger contribution of quadrupole interaction. However, in this case, the mea-

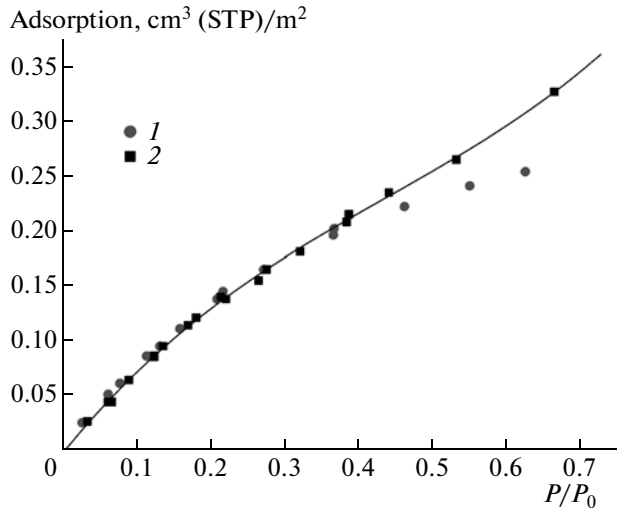

Fig. 7. Averaged isotherm of the absolute values of CO_2 adsorption on carbon black: (*1*) acetylene carbon black and (*2*) TG-10 carbon black (195 K).

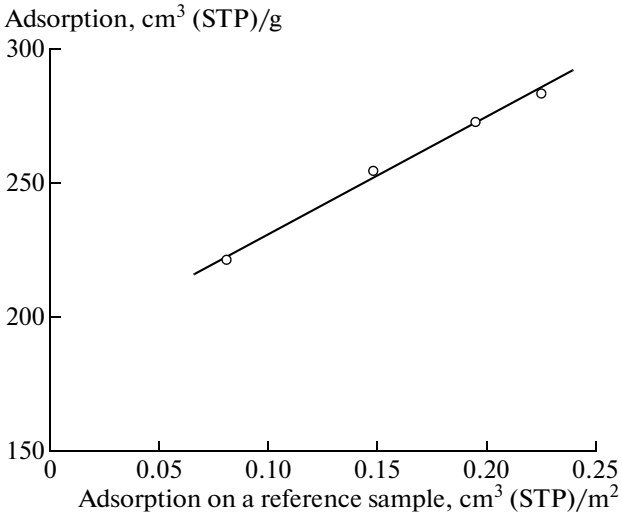

Fig. 8. Isotherm of CO_2 adsorption on Chemviron activated carbon in the comparative method coordinates (195 K).

Table 2. Texture parameters of the carbon nanomaterials calculated from the isotherms of CO_2 sorption measured under batch conditions at 195 K

Sample	$V_\mu(CO_2)$, cm^3/g	$S_\alpha(CO_2)$, m^2/g	$V_\mu(CO_2)/V_\mu(N_2)$	$S_\alpha(CO_2)/S_\alpha(N_2)$
Chemviron activated carbon	0.391	435	1.0	1.7
Norit Supra activated carbon	0.282	509	1.0	1.3
L-3780 activated carbon	0.175	940	4.1	0.7
SKT activated carbon	0.397	238	1.1	1.3
SKN activated carbon	0.294	868	0.9	1.4
Super Sorbon activated carbon	0.267	660	1.0	1.3

sured micropore volume was inconsistent with the difference between the total pore volume and the cumulative mesopore volume measured with the use of nitrogen (Table 1). Thus, the effect of the total weakening of sorption interaction for thin-walled porous materials also manifested itself in a comparative analysis of the isotherms of CO_2 adsorption at 195 K.

As a rule, the surface areas $S_\alpha(CO_2)$ given in Table 2 were noticeably higher than the surface areas measured from the sorption of nitrogen. Gavrilov [14] studied a similar phenomenon using the sorption of nitrogen, argon, and oxygen vapors on a number of supermicroporous oxides at 77 K as an example. A stable correlation of the ratio $\zeta = S_\alpha(O_2)/S_\alpha(N_2)$ with increasing volume of supermicropores in the samples up to $\zeta = 1.7$ was found for the test oxides of tin and zirconium. It is reasonable to hypothesize that the samples of activated carbons studied in this work contained a volume of supermicropores the behavior of CO_2 molecules in which was different from the behavior on the surface of mesopores. In this case, it is impossible to evaluate the volume of supermicropores with the use of the previously published procedure [14] because activated carbon samples contained a considerable volume of mesopores. However, it is well known [13] that, as a rule, activated carbons contain micropores with a wide range of sizes; this also facilitates the formation of supermicropores. As a result, the value of ζ can be considered as a criterion of sort for the occurrence of supermicropores in carbon samples.

Thus, we can state that the use of a comparative method for the analysis of the isotherms of CO_2 adsorption on activated carbons makes it possible to adequately evaluate the volume of true micropores. However, the evaluation of the surface area of mesopores is complicated by a change in the sorption properties of the surface of supermicropores present in the samples.

As noted, the adsorption of CO_2 is characterized by high sensitivity to the occurrence of various functional groups or other sorption sites on the surface. This special feature of intermolecular interactions can be used to evaluate the energetic surface heterogeneity by measuring desorption spectra upon a linear increase of the temperature.

Figure 9 shows thermal desorption spectra for a sample of MCM-41. The instantaneous rate of flow of desorbed molecules from the unit surface area of mesopores $q/(S_\alpha m_{sample})$ (ml s^{-1} m^{-2}) at current temperature (K) is plotted as ordinates. It can be seen that desorption from the surface mainly occurred in a narrow temperature range with pronounced maximums.

The resulting profile of a desorption spectrum makes it possible to evaluate the binding energy of and adsorbate molecule to surface sites E using Eq. (2) [15–17], which is used, in particular, for the analysis of spectra in the case of physical adsorption interaction:

$$\frac{E}{RT_m^2} = \frac{\nu}{\beta}\exp\left(-\frac{E}{RT_m}\right), \qquad (2)$$

where T_m is the maximum temperature of the corresponding thermal desorption peak, ν is the preexponential factor ($\sim 10^{13}$ s^{-1} [16]), and β is the rate of a linear increase of the temperature.

In Fig. 9, it can be seen that a considerable adsorbate amount was bound to the surface through weak adsorption species ($T = 201 \pm 4$ K). The heat of adsorption corresponding to these temperatures is $E = 14.0 \pm 0.3$ kcal/mol, as calculated from Eq. (2).

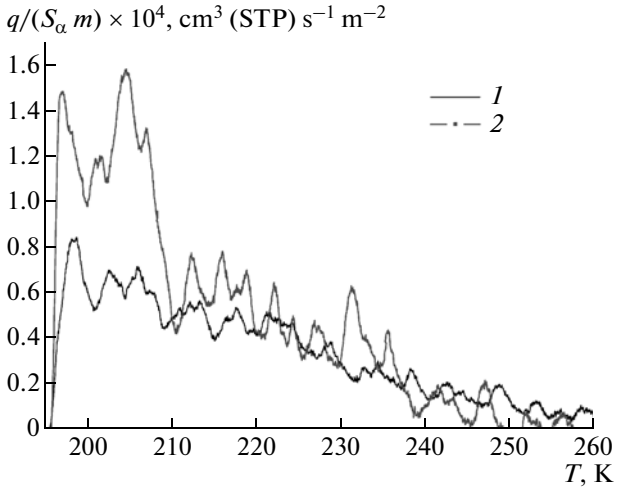

Fig. 9. Desorption spectra of CO_2 from the surface of the MCM-41 oxide material after adsorption at $P/P_0 = (1)$ 0.1 and (2) 0.2.

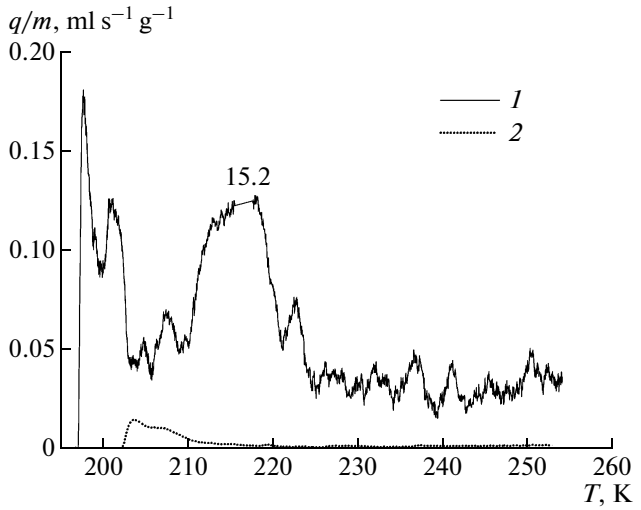

Fig. 10. Desorption spectra of CO_2 from the surfaces of (*1*) L-3780 activated carbon and (*2*) acetylene carbon black after adsorption at $P/P_0 = 0.1$.

As the preliminary adsorption was increased (with increasing adsorbate pressure from 0.1 to 0.2 in terms of P/P_0), the weakly bound species, which can be related to the completion of the formation of a monolayer coverage of the adsorptive on the surface, mainly increased. The presence of other lower intensity peaks suggests the occurrence of surface sites with other interaction energies but with a lower surface concentration. It is believed that the occurrence of various surface sites with different intramolecular interaction energies is a special feature of physical adsorption. For comparison, we refer to the heat of CO_2 sublimation $E_{sub} \approx 6$ kcal/mol ($T = 217$ K) according to reference data [18].

Figure 10 compares the spectra of CO_2 desorption for L-3780 activated carbon and thermal carbon black samples. The activated carbon sample exhibited a characteristic peak at $T \approx 218$ K, which can be attributed to desorption from the micropore volume with the heat of adsorption $E_\mu = 15.2$ kcal/mol, as calculated from Eq. (2).

Note that, in this case, the instantaneous flow of desorbed molecules was normalized not to unit surface area, but to the unit weight of the sample; this is more correct for comparing desorption from the activated carbon sample having micropores with desorption from the surface of only a mesoporous material.

Thus, we can conclude that the use of the thermal desorption of CO_2 provides an opportunity to evaluate the energy profile of the surface and its changes, for example, on the appearance of sites with an increased sorption potential.

REFERENCES

1. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area, and Porosity*, London: Academic, 1967.
2. Karnaukhov, A.P., in *Adsorbtsiya: Tekstura dispersnykh i poristykh materialov* (Adsorption: Texture of Disperse and Porous Materials), Novosibirsk: Nauka, 1999.
3. Jagiello, J. and Thommes, M., *Carbon*, 2004, vol. 42, no. 7, p. 1227.
4. Lozano-Castello, D., Cazorla-Amoros, D., and Linares-Solano, A., *Carbon*, 2004, vol. 42, no. 7, p. 1233.
5. Gavrilov, V.Yu., *Kinet. Katal.*, 1995, vol. 36, no. 4, p. 63.
6. Gavrilov, V.Yu., *Kinet. Katal.*, 2007, vol. 48, no. 6, p. 856 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 6, p. 799].
7. Breck, D.W., *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, New York: Wiley, 1974.
8. Cinke, M., Li, J., Bauschlicher, C.W., Ricca, A., and Meyyappan, M., *Chem. Phys. Lett.*, 2003, vol. 376, no. 5, p. 761.
9. Cazorla-Amoros, D., Alcaniz-Monge, J., de la Cassa-Lillo, M.A., and Linares-Solano, A., *Langmuir*, 1998, vol. 14, no. 16, p. 4589.
10. Guo, B., Chang, L., and Xie, K., *J. Nat. Gas Chem.*, 2006, vol. 15, no. 3, p. 223.
11. Zhou, L., Bai, S., Su, W., Yang, J., and Zhou, Y., *Langmuir*, 2003, vol. 19, no. 7, p. 2683.
12. 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].
13. Rouquerol, F., Rouquerol, J., and Sing, K.S.W., *Adsorption by Powders and Solids: Principles, Methodology and Applications*, London: Academic, 1999, p. 467.
14. Gavrilov, V.Yu., *Kinet. Katal.*, 2002, vol. 43, no. 4, p. 628 [*Kinet. Catal.* (Engl. Transl.), vol. 43, no. 4, p. 580].
15. Somorjai, G.A., *Introduction to Surface Chemistry and Catalysis*, New York: Wiley, 1994.
16. Lord, F.M. and Kittelberger, J.S., *Surf. Sci.*, 1974, vol. 43, p. 173.
17. Knor, Z., *Surf. Sci.*, 1985, vol. 154, p. 233.
18. *Khimicheskaya entsiklopediya* (Encyclopedia of Chemistry), Moscow: Bol'shaya Rossiiskaya Entsiklopediya, 1998, vol. 5.