CROATICA CHEMICA ACTA CCACAA **62** (1) 33—42 (1989)

YU ISSN 0011-1643
UDC 541.183
CCA-1836
Original Scientific Paper

Adsorption of Carbon Dioxide on Energetically Heterogeneous Adsorbents

D. Burevski

Faculty of Technology and Metallurgy, Kiril and Metodij University, Skopje, Yugoslavia

Received November 27, 1987

Adsorption isotherms of carbon dioxide at 295 K and 195 K and heat of adsorption at 295 K on two adsorbents, alumina and gasil silica with different degrees of surface heterogeneity, have been determined. A method for evaluation of the surface heterogeneity of the adsorbents is proposed. By the present method the degree of surface heterogeneity is estimated from the differential distribution of molar work of adsorption determined by the Dubinin-Astakhov equation. Results of the analysis of the nature of adsorbent surfaces were confirmed by the differential site energy distribution and by the data of the integral and differential molar heats of adsorption.

The adsorption isotherms were analized by the Sips and three parameters BET (k-BET) equations. The specific surface area of the adsorbents, calculated from the monolayer capacity determined from the plots of equations, is considered in relation to the adsorbent/adsorbate interaction.

INTRODUCTION

A large number of papers are devoted to adsorption on heterogeneous surfaces, some of them are listed.[1-8] The fundamental studies in adsorption on energetically heterogeneous adsorbents are based on an integral equation which relates the experimental and local adsorption isotherms and the site energy distribution function. The main task in the investigation of surface heterogeneity is the determination of differential distribution of adsorption energy. There are different approaches to solving the integral equation in regard to the site energy distribution function. One approach is to assume functions for both the experimental and local adsorption isotherms and another to choose functions for the local adsorption isotherm and for the site energy distribution so that in both cases integration is possible. Adamson *et al.*[9], however, pointed out that various local isotherm functions and the corresponding distribution functions fit the experimental adsorption data equally well. In some cases, therefore, it is not possible to choose the proper functions for the local adsorption isotherm and for the site energy distribution. An alternative procedure, proposed by Dormant and Adamson,[10] can be used to solve the integral equation by successive graphical approximations of the integral site energy distribution.

In the present study, a method is proposed to evaluate the surface heterogeneity from the differential distribution of molar work of adsorption determined by the Dubinin-Astakhov equation. The method does not involve any assumptions and gives real information on surface heterogeneity. The aim of this study is: 1) evaluation of the degree of surface heterogeneity of adsorbents employing the present method and 2) consideration of the influence of the nature of adsorbent/adsorbate interaction on the monolayer capacity values and, hence, on the adsorbent specific surface areas. For this purpose the adsorption isotherms of carbon dioxide obtained at 295 K and 195 K on alumina and gasil silica samples, with different degrees of surface heterogeneity, are analyzed. The surface heterogeneity degree determined by the method proposed in this paper is supported by the differential site energy distribution determined by the method of successive graphical approximations of the integral site energy distribution and by the variation of the integral and differential heats of adsorption of carbon dioxide with the surface coverage. In order to determine the monolayer capacity and, hence, to calculate the adsorbent surface areas, the carbon dioxide adsorption data are treated by the Sips equation and by the three parameter BET (k-BET) equation.

THEORETICAL PART

It is known that the Dubinin-Astakhov equation[11,12] is widely used to interpreat adsorption of gases on microporous adsorbents. The equation represents the distribution of the degree of volume filling of micropores, a/a_o, with the differential molar work of adsorption, A, given by the expression

$$\frac{a}{a_o} = \exp\left[-\left(\frac{A}{E}\right)^n\right] \tag{1}$$

where a is the adsorption at equilibrium pressure P, a_o is the limiting adsorption value corresponding to the filling of the whole adsorption space of micropores by the molecules adsorbed, E and n are equation parameters. The differential molar work of adsorption equals $RT\ \ln (P_o/P)$, where P_o is the saturation vapour pressure of adsorbate at temperature T. In the case of adsorption on non-porous solids (alumina and gasil silica used in the present study are non-microporous adsorbents), in the region of monomolecular adsorption, the Dubinin-Astakhov equation could be regarded as representing the integral distribution of the fraction of adsorbent surface covered by the adsorbate molecules, a/a_o, with A, where a_o whould be an adsorption value depending on the adsorbent surface area. Then, the differential distribution function can be obtained from the first derivative of the Dubinin-Astakhov equation

$$\frac{\mathrm{d}\,(a/a_o)}{\mathrm{d}A} = -\frac{n\,A^{n-1}}{E^n}\exp\left[-\left(\frac{A}{E}\right)^n\right] \tag{2}$$

The characteristic parameters of the differential distribution of a/a_o with A, A_{mean} and A_{mode} can be calculated from the expresions

$$A_{\text{mean}} = E\,\Gamma\left(\frac{1}{n} + 1\right) \tag{3}$$

and

$$A_{\mathrm{mode}} = E\left(\frac{n-1}{n}\right)^{1/n} \tag{4}$$

where Γ is gamma function.

The application procedure of the Dubinin-Astakhov equation and the derivation of expressions (3) and (4) were described previously.[13,14]

The Sips equation[1] and the modified BET (k-BET) equation[15] were applied to interpret the adsorption isotherms of carbon dioxide at 295 K and 195 K (monomolecular and polymolecular adsorption region), respectively. The equations are given in the following forms

$$\Theta = \left(\frac{P}{P+B}\right)^{c} \tag{5}$$

$$\Theta = \frac{CkX}{(1-kX)\,[1+(C-1)\,kX]} \tag{6}$$

where Θ ($\Theta = a/a_{\mathrm{m}}$) is the surface coverage, a is the adsorption at equilibrium pressure P or at relative pressure X, a_{m} is the monolayer capacity, C, B and k are constants; where the k constant is a measure of the attractive force field of the adsorbent.

EXPERIMENTAL

The alumina sample was manufactured by »Gamag« Muttenz, Switzerland, whereas gasil silica was kindly supplied by the courtesy of Dr A. Z. Groszek of the British Petroleum Company Ltd., BP Resaarch Centre, Sunburg-on-Thames. England. The adsorbate, carbon dioxide, supplied by the British Oxygen Co Ltd. was of high purity grade. The adsorption isotherms were determined using volumetric adsorption apparatus. The heat of adsorption were carried out with the flow microcalorimeter described earlier.[16,17]

RESULTS AND DISCUSSION

For practical purposes, the Dubinin-Astakhov, Sips and k-BET equations have been used in the linear forms

$$\log a = \log a_{\mathrm{o}} - \frac{0.434}{E^{n}} A^{n} \tag{7}$$

$$\log a = \log a_{\mathrm{m}} + C \log \frac{P}{P+B} \tag{8}$$

and

$$\frac{kX}{a\,(1-kX)} = \frac{1}{a_m C} + \frac{C-1}{a_m C}\,kX \tag{9}$$

The equations constants were calculated from the intercept and slope of straight lines using the method of least squares. The procedure is to select the value of the n, B and k parameters which gives the best accordance of the equations with the experimental data.

The equilibrium adsorption data of carbon dioxide at 295 K are listed in Table I, and the Dubinin-Astakhov plots are presented in Figure 1. The linearity of the plots shows good agreement of the experimental adsorption data with the equation.

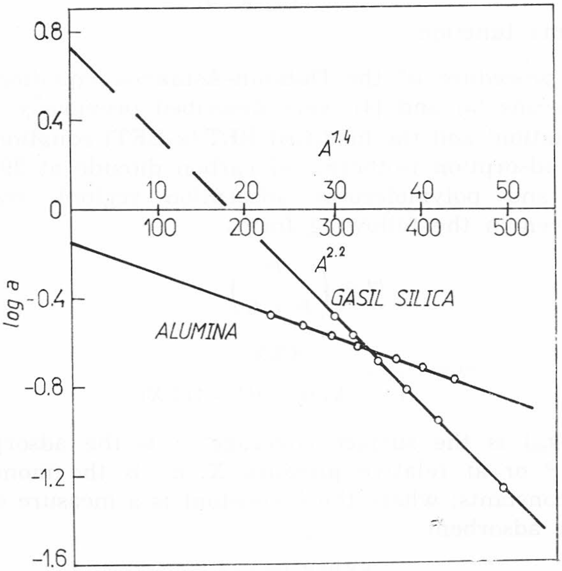

Figure 1. Dubinin-Astakhov plots for adsorption of carbon dioxide at 295 K (a in mol kg^{-1}, A in kJ mol^{-1})

TABLE I

Equilibrium adsorption data of carbon dioxide at 295 K

Alumina		Gasil silica	
P / kPa	a / mol kg^{-1}	P / kPa	a / mol kg^{-1}
9.31	0.1649	9.17	0.0544
11.89	0.1881	19.43	0.1093
15.17	0.2129	27.52	0.1526
20.53	0.2407	38.38	0.2053
25.57	0.2637	44.20	0.2329
34.12	0.2946	50.80	0.2610
48.13	0.3378		

The corresponding curves for differential distribution of a/a_0 with A are illustrated in Figure 2. Bearing in mind that the differential molar work of adsorption equals the variation in differential free energy of adsorption (with a minus sign) then the distribution curves presented in Figure 2 give evidence for surface heterogeneity. It can be seen that the distribution of a/a_0 with A is spread in a wider range in the case of alumina. It indicates that the alumina surface has a higher degree of heterogeneity than the gasil silica surface. The Dubinin-Astakhov equation constants and the values of distribution parameters, A_{mean} and A_{mode}, calculated from the expressions (3) and (4) are given in Table II.

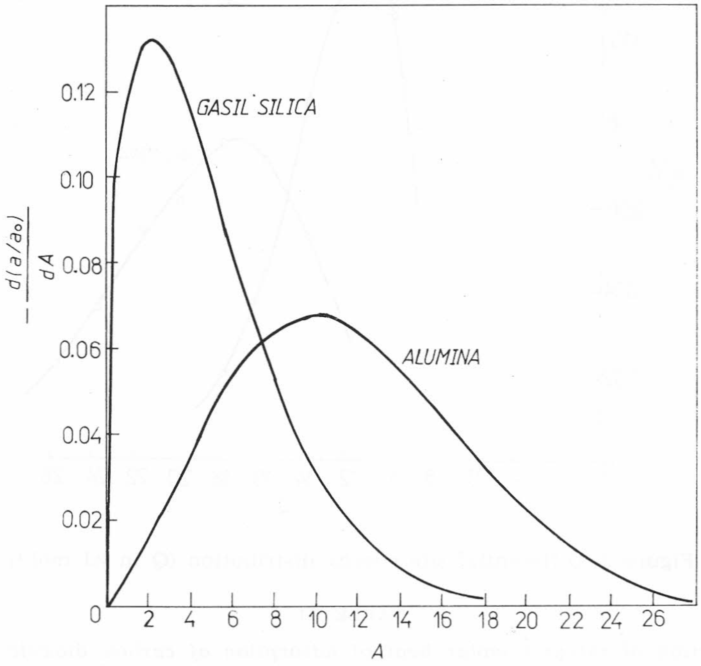

Figure 2. Differential distribution curves of a/a_0 with A obtained from the Dubinin--Astakhov equation (A in kJ mol^{-1})

TABLE II

Dubinin-Astakhov equation constants and values of A_{mean} *and* A_{mode}

Adsorbent	n	E / kJ mol^{-1}	A_{mean} / kJ mol^{-1}	A_{mdoe} / kJ mol^{-1}
Alumina	2.2	13.24	11.73	10.05
Gasil silica	1.4	5.47	4.98	2.24

The E, A_{mean} and A_{mode} parameters for adsorption on non-porous adsorbents could give information for the adsorbent/adsorbate interaction.

The finding for the degree of surface heterogeneity is supported by the site energy distribution curves, Figure 3, where F is the fraction of sites with adsorbent/adsorbate energy $\geq Q$. The site energy distribution curves were obtained by the method for successive graphical approximations of the integral site energy distribution, proposed by Dormant and Adamson.[10] The similarity between the distribution curves presented in Figure 2 and Figure 3 is evident.

Results of the analysis of the nature of adsorbent surfaces are also confirmed by the variation of the integral molar heat of adsorption, Q, Table III,

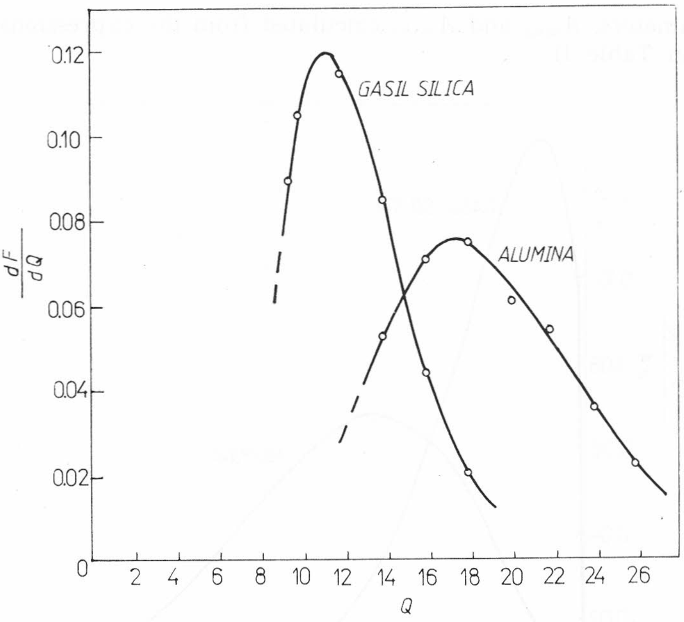

Figure 3. Differential site energy distribution (Q in kJ mol^{-1})

TABLE III

Variation of integral molar heat of adsorption of carbon dioxide with surface coverage

Alumina		Gasil silica	
Θ	$\frac{Q}{\text{kJ mol}^{-1}}$	Θ	$\frac{Q}{\text{kJ mol}^{-1}}$
0.28	33.03	0.05	13.31
0.32	31.81	0.07	13.02
0.36	30.56	0.09	12.89
0.39	29.72	0.12	12.60
		0.15	12.31

and the differential molar heat of adsorption, q_d, Figure 4, of carbon dioxide at 295 K with the surface coverage. The heats of adsorption were determined by means of the flow microcalorimetry.[16,17] Although the variation of the integral and differential heat of adsorption with the surface coverage is an approximate evidence for adsorbent surface heterogeneity, the difference in the degree of heterogeneity is considerable. In the case of adsorption on alumina, the degree of heterogenity of the adsorbent/adsorbate interaction is so high that the lateral interaction of adsorbate molecules at relatively high surface coverage is obscured.

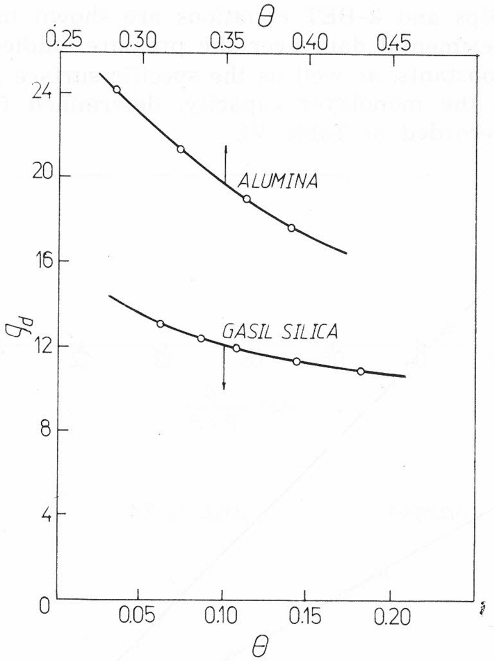

Figure 4. Differential heat of adsorption of carbon dioxide at 295 K plotted against surface coverage (q_d in kJ mol^{-1})

TABLE IV

Variation of integral and differential entropy of adsorption of carbon dioxide with surface coverage

Alumina			Gasil silica		
Θ	$-\Delta S$ J mol^{-1} K^{-1}	$-\Delta \bar{S}$ J mol^{-1} K^{-1}	Θ	$-\Delta S$ J mol^{-1} K^{-1}	$-\Delta \bar{S}$ J mol^{-1} K^{-1}
0.28	107.3	91.1	0.05	43.0	52.6
0.32	102.3	80.9	0.07	43.1	50.2
0.36	97.2	73.2	0.09	42.7	48.6
0.39	93.6	66.9	0.12	42.1	47.1
			0.15	41.5	45.4

The integral entropy of adsorption, ΔS, and the differential entropy of adsorption, $\Delta \bar{S}$, of carbon dioxide were calculated from the heats of adsorption and the equilibrium adsorption data. The entropy values, given in Table IV, indicate that carbon dioxide molecules adsorbed on the alumina surface are in a higher localized state than on the gasil silica surface.

The equilibrium adsorption values of carbon dioxide at 295 K, Table I, and at 195 K, Table V, were interpreted by the Sips and k-BET equations, respectively. The Sips plots for adsorption of carbon dioxide at 295 K and the k-BET plots for adsorption at 195 K are presented in Figures 5 and 6, respectively. The Sips and k-BET equations are shown to give good agreement with the experimental data over the pressure studied.

The *B* and *k* constants, as well as the specific surface area of adsorbents, *S*, calculated from the monolayer capacity, determined from the Sips and k-BET plots, are recorded in Table VI.

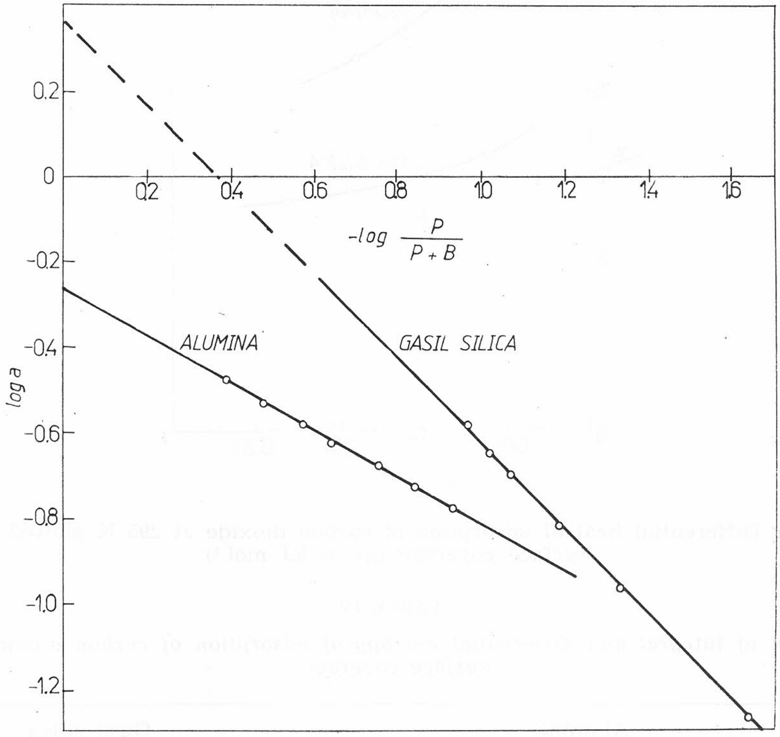

Figure 5. Sips plots for adsorption of carbon dioxide at 295 K (Alumina: $B = 70$; Gasil silica: $B = 400$).

TABLE V

Equilibrium adsorption data of carbon dioxide at 195 K

Alumina		Gasil silica	
$\frac{P}{\text{kPa}}$	$\frac{a}{\text{mol kg}^{-1}}$	$\frac{P}{\text{kPa}}$	$\frac{a}{\text{mol kg}^{-1}}$
7.48	0.8753	6.29	1.2684
12.48	0.9949	10.40	1.5365
17.05	1.0766	15.23	1.8033
23.41	1.1716	20.02	1.9863
29.32	1.2568	24.96	2.1607
		29.22	2.3061
		34.78	2.4632
		42.38	2.6479
		51.26	2.8460

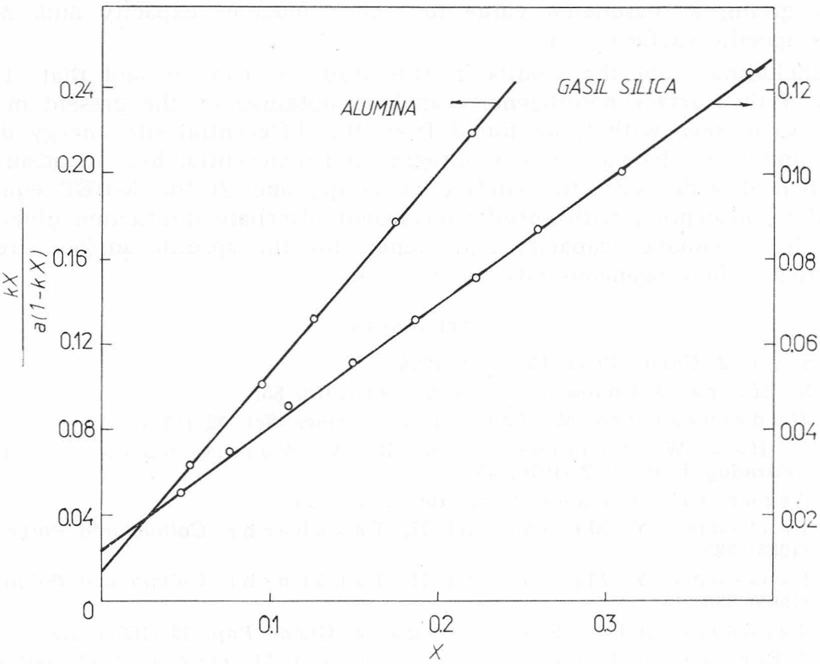

Figure 6. k-BET plots for adsorption of carbon dioxide at 195 K (Alumina: $k = 0.99$; Gasil silica: $k = 0.70$).

TABLE VI

B *and* k *constants and specific surface area of adsorbents*

Adsorbent	B	k	S CO_2 295 K Sips	S CO_2 195 K k-BET	S N_2 78 K BET
Alumina	70	0.99	$0.78\ 10^5$	$1.27\ 10^5$	$1.30\ 10^5$
Gasil silica	400	0.70	$3.06\ 10^5$	$2.79\ 10^5$	$2.87\ 10^5$

(S in $m^2\ kg^{-1}$)

Since the k constant is a measure of the attractive force field of adsorbent, its values are in correlation with the heats of adsorption. For comparison, the adsorbent specific surface areas determined from nitrogen adsorption isotherms, using the standard BET method, are listed in the last column of Table VI. The results show that the values of specific surface area are in agreement with those determined from nitrogen adsorption isotherms, except for the value for alumina at 295 K. The difference in specific surface area for alumina is due to the fact that the area occupied by one adsorbate molecule on adsorbent surface at local adsorption and in low surface coverage region depends on the distribution of more active adsorption sites. The molecules of carbon dioxide adsorbed on alumina at 195 K, however, are close packed giving a reasonable value for the monolayer capacity and, hence, for the specific surface area.

Concluding from the results in this study, it can be said that: 1) the results of the surface heterogeneity analysis obtained by the present method are in accordance with those found from the differential site energy distribution and from the variation of integral and differential heat of adsorption of carbon dioxide with the surface coverage, and 2) the k-BET equation applied to adsorption with specific adsorbent/adsorbate interaction gives real values for monolayer capacity and, hence, for the specific surface area of energetically heterogeneous adsorbents.

REFERENCES

1. R. Sips, *J. Chem. Phys.* **18** (1950) 1024.
2. D. N. Misra, *J. Colloid Interface Sci.* **43** (1973) 85.
3. W. Rudzinski and M. Jaroniec, *Surface Sci.* **42** (1974) 552.
4. C. C. Hsu, W. Rudzinski, and B. W. Wojciechowski, *J. Chem. Soc., Faraday Trans. I* **2** (1976) 453.
5. M. Jaroniec, *Thin Solid Films* **100** (1983) 325.
6. K. Tsutsumi, Y. Mitani, and H. Takahashi, *Colloid and Polym. Sci.* **263** (1985) 832.
7. K. Tsutsumi, Y. Mitani, and H. Takahashi, *Colloid and Polym. Sci.* **263** (1985) 838.
8. M. Jaroniec and J. Piotrowska, *J. Chem. Pap.* **40** (1986) 339.
9. A. Adamson, I. Ling, L. Dormant, and M. Orem, *J. Colloid Interface Sci.* **21** (1966) 445.
10. L. Dormant and A. Adamson, *J. Colloid Interface Sci.* **38** (1972) 285.
11. M. Dubinin and V. Astakhov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1** (1971) 5.
12. M. Dubinin and V. Astakhov, *Adv. Chem. Series* **102** (1971) 69.
13. D. Burevski, *Colloid and Polym. Sci.* **260** (1982) 623.
14. D. Burevski, *Croat. Chem. Acta* **60** (1987) 649.
15. S. Brunauer, J. Skalny, and E. Bodor, *J. Colloid Interface Sci.* **30** (1969) 546.
16. D. Burevski, *Ph. D. Thesis,* Univ. of Bradford, England (1975).
17. T. Allen and D. Burevski, *Powder Technology* **17** (1977) 265.

IZVOD

Adsorpcija ugljen-dioksida na energetski heterogene adsorbense

D. Burevski

Određivane su adsorpcijske izoterme ugljen dioksida na 295 K i 195 K na dva adsorbensa (aluminium-oksid i gasil silika), sa različitim stepenom površinske heterogenosti. Površinska heterogenost procenjena je preko diferencijalne distribucije molarnog rada adsorpcije, određena jednačinom Dubinin-Astakhova. Rezultati analize prirode površine adsorbensa potvrđeni su diferencijalnom distribucijom energije adsorpcijskih mesta i podatcima o diferencijalnoj toplini adsorpcije.

Adsorpcijske izoterme analizirane su jednačinom Sips-a i tri parametarskom BET (k-BET) jednačinom. Specifična površina adsorbensa preračunata iz monoslojnog kapaciteta, određenog pomoću grafičkog prikaza jednačina, promatrana je s obzirom na međusobno djelovanje adsorbens-adsorbat.