DETERMINATION OF THE SPECIFIC SURFACE AREA OF ANATASE BY PHYSICAL ADSORPTION OF NOBLE GASES

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Specific surface area of titanium dioxide was determined by means of the physical adsorption of argon, krypton, and xenon. The DKR and BET methods were used to evaluate the adsorption data. The specific surface area was also calculated from the data supplied by electron microscopy and X-ray diffraction. Possible reasons are discussed of differences in the values of the specific surface area as determined by the methods employed.

An important quantity characterizing solid substances in the dispersed state is their specific surface area, *i.e.* the surface of a weight unit of the solid substance. Many methods have been developed to measure the specific surface area. The most important and most frequently used methods are based on the physical adsorption of gases[1,2]. By analyzing the adsorption isotherm the number of moles of the adsorbate can be determined necessary to form a monolayer on the surface of the solid substance, N_1 (mol/g). The area is given by

$$S = N_1 N_A \omega 10^{-20} , \tag{1}$$

Here, S (m²/g) is the specific surface area of the adsorbent, N_A is the Avogadro constant, and $\omega(\text{Å}^2)$ is the effective adsorption cross section of a molecule of the adsorbate. Thus, in order to calculate the specific surface area, the values of N_1 and ω must be known. Because many theories exist to describe adsorption equilibria, there are also many methods to determine the value of N_1 from adsorption data. Recently, the method has been more and more used which is based on the theory of Dubinin and Raduškevič[3]. The method was first used by Kaganer[4] to determine the specific surface area of several adsorbents and it is usually called the DKR method.

According to Dubinin and Raduškevič, the adsorbed amount N_s can be expressed as a function of the relative pressure p/p_0 through the relation

$$\ln N_s = \ln N_1 - B(-RT \ln p/p_0)^2 = \ln N_1 - B\varepsilon^2 , \tag{2}$$

where B (mol² cal⁻²) is a constant, R is the gas constant, $T(K)$ is the temperature, p is the equilibrium pressure of the adsorbate over the adsorbent, and p_0 is the vapour pressure of the adsorbate at the temperature T. The quantity ε is sometimes identified with the Polanyi's potential which has the meaning of the free enthalpy change upon transferring one mol of the adsorbate from the gaseous to the adsorbed state.

By extrapolating the dependence $\ln N_s$ *vs* $(RT \ln p/p_0)^2$ to $p/p_0 = 1$, the value of N_1 can be obtained, and from it, using equation (1), the specific surface area of the adsorbent, provided that ω for a given gas is known. In this case equation (2) serves a different purpose than that one for

which it was suggested originally[3]. At the present time, no statement can be made solely on the ground of theoretical considerations about the applicability of equation (2) to the accurate determination of the specific surface area. Neither the question is clear why equation (2), suggested originally to describe the adsorption equilibria on microporous adsorbents, suits in many cases even in the description of the adsorption equilibria of gaseous adsorbates over non-porous adsorbents in the region of submonomolecular surface coverage. Conclusions concerning the applicability of the DKR equation to the specific surface area determination can be at present made only by comparing the values measured with the values obtained by other methods. As a comparative method, *e.g.*, the classical BET method[1] can be used which is regarded as a standard method. However, even this procedure has a shortcoming, because in general the results obtained by the BET method cannot be always regarded as accurate.

It follows from the published data[4,5] that the differences between the values of specific surface areas determined by the DKR and the BET method are in some cases smaller than 6%. However, in the case of metals prepared by vacuum sublimation as thin films[6,7], the DKR method gave values of specific surface areas as much as 25% higher than the BET method. On the other hand, the BET method gave higher values for pyrex[8-10], porous silver[11], rhenium powder[12], and thin layers of alkali metal chlorides[13]. In the case of porous silver the BET value was by 36% higher than the DKR value. Possible reasons of these differences have not been so far discussed.

The DKR method has several advantages over the BET method, because the measurement of only a part of the adsorption isotherm in the region of submonomolecular coverage is sufficient to determine the specific surface area. Thus, the method is conveniently used in high-vacuum systems, where pressures higher than 10^{-3} Torr are not desirable, and also are difficult to measure accurately by ionization gauges usually used with this type of equipment.

In this contribution we report on results of measurements of the specific surface area of titanium dioxide (anatase) by means of the physical adsorption of argon, krypton, and xenon using both the DKR and BET method. The value of the specific surface area was also calculated from the mean size of particles, as determined both from the X-ray diffraction studies and from the electron microscope investigation of the adsorbent. The calculation of the specific surface area was carried out assuming spherical shape of the particles of anatase. Possible reasons of the difference in the specific surface area values as obtained by various methods, namely DKR and BET, are discussed, too.

EXPERIMENTAL

The adsorption measurements reported in this communication were carried out in a static vacuum volumetric apparatus described in detail earlier[14]. The over-all free volume of the measuring section was $761 \cdot 6$ cm^3; $520 \cdot 4$ cm^3 of it was the volume of the McLeod gauge used in pressure measurements. Before starting the adsorption measurements, the apparatus was pumped down to $p \leq 10^{-6}$ Torr and the adsorbent was simultaneously heated to about 600 K. The adsorption cell was connected with the apparatus through a trap cooled during the last period of evacuation and during the measurements to about 195 K. The trap prevented spoiling of the adsorbent by mercury vapours. During the measurements, the required temperatures of the adsorbent were achieved by cooling it by liquid nitrogen, liquid oxygen, or by the mixture of both. The temperature of the adsorbent was measured by a platinum resistance thermometer with an accuracy of 10^{-2} K. The temperature of the measuring section of the apparatus was kept constant during the

measurements at $300 \cdot 6 \pm 0 \cdot 1$ K. The values of the equilibrium pressures of the gas over the ad-sorbent were measured with a relative error of $0 \cdot 3 - 3\%$. (The size of the error is a function of the pressure; a larger error occurs at very low pressures, $p \approx 10^{-6}$ Torr, or at very high pressures, $p \approx 10$ Torr.) The maximum error in estimating the adsorbed amount was 5%. The values of the equilibrium pressures lower than 1 Torr were corrected on the effect of the thermal transpiration using the Liang equation in the Bennett–Tompkins modification[15]. The time necessary to reach the adsorption equilibrium varied between 30 and 120 minutes depending on the equilibrium pres-sure, temperature of the measurement, and kind of the gas used. The reversibility of the adsorption process was in some cases checked by measuring the desorption part of the adsorption isotherm.

The purity of titanium dioxide (BDH Chemicals, Ltd., England), as given by the producer, was $99 \cdot 95\%$. (The results of the spectral analysis showed only $10^{-2}\%$ silicon, $10^{-4}\%$ copper, and trace amounts of calcium and zinc.) The phase analysis by X-ray diffraction showed that the titanium dioxide was a tetragonal modification anatase without any measurable amounts of other modifications.

The gases used in the adsorption measurements were designed by the producer (Norsk Hydro EK Oslo, Norway) as spectrally pure. Nontheless, xenon which may contain small amounts of krypton[16] was purified additionally in the apparatus by multiple vacuum fractional distillation.

RESULTS AND DISCUSSION

The physical adsorption of argon was investigated at $77 \cdot 7$ K, that one of krypton at $77 \cdot 70$ K, $81 \cdot 15$ K, and $90 \cdot 20$ K, and that one of xenon at $77 \cdot 96$ K and $90 \cdot 20$ K. The adsorption isotherms obtained are shown in Fig. 1, the region of relative pressures p/p_0 over which the adsorption measurements were carried out is given in Table I. The adsorption data were processed using the DKR (equation (2)) and BET (ref.[15]) theories. The regions of relative pressures over which the DKR and BET isotherms were linear and which characterize the range of validity of these theories are summa-rized in Table II. The values of N_1 were determined from the linear parts of the DKR and BET isotherms, and from these then the values of the specific surface areas of anatase, S, were calculated with the use of equation (1). The values of N_1 and S obtained in this way are given in Table I. When the DKR theory was used, the adsorption data were processed by the least square method. The standard deviations of N_1 and S are given in Table I, too. When the BET method was used, the data were not processed by the least square method, because the linear parts of the BET isotherms did not usually contain more than six experimental points. Estimated relative errors in determining N_1 (BET) were about 5%.

In order to determine the mean size of particles from the X-ray diffraction, the diffraction pictures were obtained in a semi-focused chamber by the copper mono-chromatic radiation with the incidence angle of $70°$. The mean value of the particle diameter was calculated from the diffraction line broadening corrected to the in-strumental broadening with the use of the Debye–Scherrer relation[18], assuming the so called shape factor $k = 1$.

The mean value of the particle size thus obtained, calculated from the width of the last intense line 424, was 650 ± 150 Å. The specific surface area of anatase calculated

with the use of the above mentioned value of the mean particle size (assuming spherical shape of the particles and using the tabulated[17] value of the density of anatase, 3.84 g/cm^3) was 24 ± 4 m^2/g. Probable reasons of the significant difference between this calculated value and the values obtained from the adsorption measurements are the following: *1*) The presence of defects and mechanical strains in the crystal lattice of the anatase powder; *2*) Single particles may be formed by aggregates of microcrystals; *3*) The value of the shape factor k may not be unity. Besides that, it is known from literature that the determination of the specific surface area of powdered materials from the broadening of diffraction lines does not usually give very accurate values and the respective values are often regarded as approximate.

It was found in the investigation of anatase by the transmission method in the electron microscope that the size (diameter) of particles varied between 600 and 2300 Å. With regard to the distribution of the diameters the mean value was chosen at 1400 Å which leads — assuming spherical shape of the particles — to the specific surface area of 11·5 m^2/g. Moreover, electron microscope pictures showed that the assumption of the spherical shape of the particles was approximately correct in this case. This explains the reasonably good agreement between this calculated value of the specific surface area and the values obtained by the adsorption methods.

It is surprizing that the values of the specific surface area of anatase (Table I) obtained by adsorption methods — which were entirely different from the theoretical point of view — agreed reasonably well with each other. At the temperature of the measurements 77·70 K the best agreement between the DKR and BET values of the specific surface area was obtained when argon was used as the adsorbate (5·2%), while with krypton and xenon the difference was larger, 13·5% and 16·2%, respectively. It is interesting to note that in all the systems studied the DKR value was always
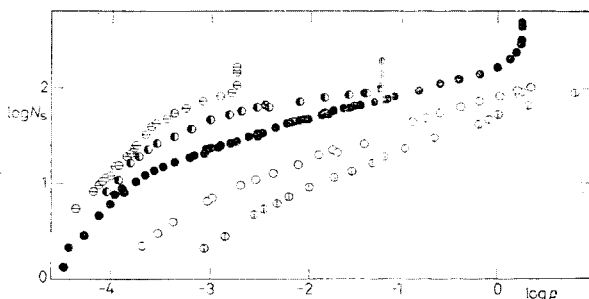

FIG. 1

Adsorption Isotherms Ar at 77·70 K (◐), Kr at 77·70 K (●), Kr at 90·20 K (○), Xe at 77·96 K (◔), and Xe at 90·20 K (◓)

N_s Adsorbed amount, μmol/g; p equilibrium pressure of adsorbate, Torr.

TABLE I
Results of Physical Adsorption Measurements of Argon, Krypton, and Xenon on Anatase Surface

Gas	T, K	Region p/p_0	N_1(DKR) μmol/g	N_1(BET) μmol/g	S(DKR)^a m²/g	S(BET) m²/g	p_0, Torr
Ar	77·70	$1\cdot03 \cdot 10^{-5} - 2\cdot56 \cdot 10^{-2}$	$104\cdot12 \pm 0\cdot55$	99·02	$10\cdot41 \pm 0\cdot06$	9·90	250^b
Kr	77·70	$1\cdot85 \cdot 10^{-5} - 1$	$98\cdot64 \pm 0\cdot13$	86·88	$12\cdot00 \pm 0\cdot02$	10·57	1·85
	81·15	$6\cdot80 \cdot 10^{-4} - 1$	$92\cdot64 \pm 1\cdot41$	85·24	$11\cdot27 \pm 0\cdot17$	10·37	4·27
	90·20	$9\cdot27 \cdot 10^{-6} - 1\cdot02 \cdot 10^{-1}$	$85\cdot90 \pm 0\cdot43$	83·92	$10\cdot45 \pm 0\cdot05$	10·21	$21\cdot40^b$
Xe	77·96	$1\cdot77 \cdot 10^{-2} - 1$	$87\cdot89 \pm 1\cdot62$	75·63	$9\cdot95 \pm 0\cdot17$	8·56	$1\cdot87 \cdot 10^{-3}$
	90·20	$1\cdot17 \cdot 10^{-3} - 1$	$89\cdot12 \pm 1\cdot64$	—	$10\cdot09 \pm 0\cdot19$	—	$6\cdot11 \cdot 10^{-2}$

^{a} Values S calculated from N_1 using the following values of ω: Ar 16·6 Å², Kr 20·2 Å², Xe 18·8 Å² (from ref.[1,2]); ^{b} see ref.[17].

TABLE II
Range of Applicability of DKR and BET Method

Gas	T, K	p/p_0(DKR)	p/p_0(BET)
Ar	77·70	$1\cdot03 \cdot 10^{-5} - 5\cdot89 \cdot 10^{-3}$	$2\cdot57 \cdot 10^{-3} - 2\cdot56 \cdot 10^{-2}$
	77·70	$6\cdot67 \cdot 10^{-5} - 7\cdot25 \cdot 10^{-2}$	$1\cdot20 \cdot 10^{-2} - 3\cdot72 \cdot 10^{-1}$
Kr	81·15	$6\cdot80 \cdot 10^{-5} - 4\cdot56 \cdot 10^{-2}$	$1\cdot20 \cdot 10^{-2} - 2\cdot02 \cdot 10^{-1}$
	90·20	$1\cdot62 \cdot 10^{-4} - 1\cdot32 \cdot 10^{-2}$	$1\cdot20 \cdot 10^{-2} - 1\cdot47 \cdot 10^{-1}$
Xe	77·96	$1\cdot77 \cdot 10^{-2} - 9\cdot50 \cdot 10^{-1}$	$1\cdot86 \cdot 10^{-1} - 5\cdot26 \cdot 10^{-1}$
	90·20	$1\cdot17 \cdot 10^{-3} - 9\cdot35 \cdot 10^{-1}$	—

larger than the BET value. Similar results with other adsorbents were obtained by other authors, too[6,7].

It follows from equation (l) that the specific surface area of the adsorbent depends on the values of ω and N_1. The numerical value of ω depends on the nature of the adsorbate gas, and on the way adsorbed molecules are arranged in the monolayer. In the case of localized adsorption and assuming the distance between two vicinal adsorption sites is not smaller than the diameter of the adsorbed molecule, the value of the effective adsorption cross-section ω is determined by the dimensions of the surface crystal lattice and depends, therefore, on the chemical composition and on the crystal structure of the adsorbent. In the case of mobile adsorption, the value of ω depends mainly on the dimensions of the adsorbed molecules, if non-spherical molecules are involved also on their orientation with respect to the surface. With energetically heterogeneous surface the situation is even more complicated, because the adsorption cross-section may be a complicated function of the extent of the surface coverage. As no model of physical adsorption so far available takes quantitatively into consideration the above mentioned facts, a suitable choice of a numerical value of ω is rather difficult. Indeed, various authors report widely different values of the effective adsorption cross-section for the same adsorbate[1,2,10-12,15].

In view of the uncertainty in choosing the value of the effective adsorption cross-section, it appears more suitable — in comparing various adsorption methods applied to the same adsorption system — to use the values N_1, *i.e.* the number of moles of the adsorbate necessary to form a monolayer. The correctness of the estimated value of N_1 depends on the correctness of the theoretical expression used in describing the adsorption equilibrium, and — of course — on the accuracy of measuring and evaluating the adsorption data. Because of the reasons stated above, it is in general very difficult to verify the correctness of the theoretical isotherm used. Both theories of physical adsorption used in this study represent in effect a way of linearizing the adsorption isotherm or its part. The derivation of them is based on assumptions which do not have to be fulfilled, and in the given case the assumptions of one theory contradict the assumptions of the other one. Thus, *e.g.*, the BET theory assumes the adsorption process to occur over an energetically homogeneous surface, the DKR theory is derived under the assumption of the validity of a special distribution function for the adsorption energy on various adsorption sites[2]. All these shortcomings, including the fact that both theories do not consider mutual interactions between the adsorbed molecules, may in principle lead to different values of N_1 depending on the method used.

In this regard the finding of this study is of interest (Table I) that, within the framework of each of the methods used, the value of N_1 decreases linearly in dependence on the atomic number of the gaseous adsorbate. As the value of N_1 also decreases linearly with the increasing collison cross-section of the molecule, calculated[19] from the critical temperature and the critical pressure of the gas, as well as

with the increasing polarizability of the molecule, the observed decrease of the value of N_1 with the increasing atomic number of the adsorbate molecules can be explained in two ways: *1*) With the increasing cross-section of the molecule the number of molecules necessary to form a monolayer on a surface unit area decreases (assuming a close packing of the adsorbed layer). *2*) With the increasing polarizability of the adsorbed molecules the separation between molecules increases as a result of the repulsive dipole–dipole interactions, and thus also the number of molecules needed to form a monolayer decreases.

A more probable appears to be the second explanation which is also supported by the fact that the decrease of the adsorption heat as a function of the surface coverage is most pronounced for xenon and least pronounced for argon adsorption[14].

Furthermore, it follows from Table I that for a given adsorbate the value of N_1 is always larger when determined by means of the DKR method than when determined by the BET method. The above mentioned explanation can be used to account for this fact, too. The value N_1 from the DKR method is obtained by extrapolating the part of the isotherm measured over the region of small surface coverage, *i.e.* over the region where interactions between the adsorbed molecules cannot play a substantial role. On the other hand, the BET method used data obtained in the region of a nearly complete monomolecular surface coverage. Therefore, it may be expected that the higher the differences between the specific surface areas obtained by the two methods will be, the larger the strength of the surface electrostatic field leading to the polarization of the adsorbate molecules will be. In this way one can explain large differences in the values of specific surface areas obtained by the DKR and BET method in studying the adsorption of krypton over the alkali halide surfaces[13] and in studying the adsorption of ammonia over the anatas surface[14], where the value N_1 (DKR) is by 65% higher than the value N_1 (BET).

A reasonable agreement between the values of the specific surface areas obtained by the two adsorption methods and the applicability of equation (2) to the description of the part of the adsorption isotherm over the region of submonomolecular surface coverage cannot be regarded in any case as a confirmation of the assumptions under which equation (2) was derived. Also, the explanation offered to describe the differences between the two methods can be regarded as a qualitative one. In order to make further conclusions, it would be useful to use other known methods[1,2,20-22] to evaluate the adsorption data and to obtain the value of N_1. Interesting results can be expected from the application of the very general method[23] by Kindl and Wojciechowski which respects in a satisfactory way the heterogeneity of real surfaces of some solid substances.

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