The Molecular Cross-sectional Areas for the Determination of Specific Surface Areas of Solids. II. Titania and Silica

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As for the determination of the specific surface areas of solids by the B.E.T. method[1], it is generally experienced that the values obtained by different adsorbate gases do not always coincide among themselves. In the preceding paper[2], specific surface areas of carbon blacks were estimated by means of the B.E.T. method using several gases, and by comparing them with those from electron microscopy, the molecular cross-sectional areas of the gases which would give the consistent surface areas with different gases and also with those from electron microscopy were determined. In this paper, similar studies with titania and silica as adsorbents will be mentioned.

Experimental Method and Results

A series of ten commercial titania samples and five silica samples listed in column 2 of Table I were used. Nitrogen, argon, oxygen, carbon dioxide and *n*-butane were chosen as adsorbate gases, and the adsorption isotherms were measured as in the preceding paper. B.E.T. plots obtained from the isotherms are classified in four types from I to IV as shown in the preceding paper, in which, curves I and III are similar in form excepting that the former has a longer linear portion that the latter, curve II is a normal form with a length of linear portion being intermediate between I and III, and curve IV has a special form with shortest linear part. In Table I, types of isotherms are listed together with the appearance of the hysteresis in the measured pressure range, where "?" shows that the existence of hysteresis is not clear because the desorption isotherm was not measured in these cases. Estimated specific surface areas from the isotherms using the molecular cross-sectional areas[3] listed in column 4 of Table V, i.e. the values calculated from the densities of liquid state, are shown in Table II. Values under S_{N_2}/S in the table are ratios between the surface areas estimated by nitrogen and by other gases. Surface areas* calculated from $d_3=K\sum nd^3/\sum nd^2$ determined by electron microscopy by Suito and Arakawa[4] are also listed in the table**. It should be noted that in the calculation an equation $S=6/d_3\rho$ was used. This can be applied only for spherical or cubic particles. In this equation, S represents the specific surface area and ρ the specific gravity of the sample. Values of ρ used were 3.9 for anatase, 4.2 for rutile and 2.0 for silica.

In order to study the effect of the degree of crystallization or other surface states of the sample, surface areas of ten titania samples specially prepared under different conditions were measured by nitrogen, argon, oxygen and carbon dioxide, and the results are given in Table III. These samples were prepared by Kennedy's method[5], namely, titanium dioxide precipitated by hydrolysis of titanium tetrachloride was dried for five hr. at 100°C and then heated at different temperatures under the current of various gases***.

Discussion

From Table I, it is seen that the isotherms to which the B.E.T. equation can be applied most satisfactorily are those obtained by argon and oxygen, and then those by nitrogen and carbon dioxide; but for *n*-butane, about half of the isotherms are of special types. As in the case of carbon black in the preceding paper, the isotherms of nitrogen and argon generally show no hysteresis, whereas by other gases, hystereses of isotherms are seen in nearly half of the cases.

As are shown in Table II, the average values of S_{N_2}/S for argon at two temperatures are 1.26 and 1.25 and their standard deviations are small. For oxygen, the deviation is also small despite the rather great value for the carbon black but those for *n*-butane and carbon dioxide are great. In these the ratios in parentheses were excluded from the average. This

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[1] S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

[2] K. Kodera and Y. Onishi, This Bulletin, **32**, 356 (1959).

[3] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 1553 (1937).

* Ti-8, 9, 10 were measured by the present authors.

** '*d*' represents the particle diameter measured on an electron micrograph.

[4] E. Suito and M. Arakawa, unpublished.

[5] D. R. Kennedy, M. Ritchie and J. Mackenzie, *Trans. Faraday Soc.*, **54**, 119 (1958).

*** These samples have been prepared by Prof. I. Uei and Prof. F. Mashio of Kyoto Technical University.

TABLE I. TYPES OF B.E.T. CURVES

No.	Samples	N_2(−196°C)		Ar(−196°C)		Ar(−183°C)		O_2(−183°C)		CO_2(−78°C)		n-C_4H_{10}(0°C)	
		Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst.
Ti- 1	Ishihara A-100	I	−	II	−	II	−	II	−	III	−	II	+
〃 2	Ishihara R-810	I	−	I	−	II	−	II	−	II	−	II	−
〃 3	Tochigi TP-53	III	−	I	−	I	−	II	−	III	−	I	−
〃 4	Tochigi TP-53C	III	+	II	+	I	+	II	+	III	+	IV	+
〃 5	Furukawa Anatase-F	II	−	II	−	II	−	II	+	III	−	II	−
〃 6	Furukawa Rutile-F	II	−	II	−	II	−	II	+	II	−	II	+
〃 7	Chitan-kogyo Cronos	II	−	II	−	II	−	II	−	III	−	II	−
〃 8	TFM	II	?	II	?	II	?	II	?	III	+	—	—
〃 9	Titanox RA-Nc	II	?	II	?	II	?	II	?	III	?	—	—
〃 10	Unitane O-220	II	?	II	?	II	?	II	?	III	−	—	—
Si- 1	Hisil-101	III	−	II	−	II	−	II	?	III	−	IV	?
〃 2	Aerosil	III	−	II	−	II	−	II	?	III	+	IV	?
〃 3	Carplex 1120	III	+	II	−	II	−	II	?	III	+	IV	?
〃 4	Microsil B-55	III	−	II	−	II	−	II	?	III	+	IV	?
〃 5	Nisil F-1	III	−	II	−	II	−	II	?	II	+	IV	?

TABLE II. SPECIFIC SURFACE AREAS MEASURED BY VARIOUS GASES

No.	N_2(−196°C) S_{N_2} m^2/g.	Ar(−196°C)		Ar(−183°C)		O_2(−183°C)		CO_2(−78°C)		n-C_4H_{10}(0°C)		Electron microscope m^2/g.
		S, m^2/g.	S_{N_2}/S	S, m^2/g.	S_{N_2}/S	S, m^2/g.	S_{N_2}/S	S, m^2/g.	S_{N_2}/S	S, m^2/g.	S_{N_2}/S	
Ti- 1	9.48	7.60	1.25	7.71	1.23	8.06	1.17	6.95	1.36	7.18	1.32	8.93
2	6.41	5.32	1.21	5.32	1.21	5.45	1.18	4.29	1.49	4.33	1.48	3.40
3	8.14	6.47	1.26	6.57	1.24	7.09	1.15	6.28	1.30	5.91	1.38	8.58
4	7.61	5.90	1.29	5.91	1.29	6.31	1.21	4.90	1.55	5.27	1.45	8.67
5	10.97	8.60	1.28	8.90	1.23	9.22	1.19	6.13	1.79	7.70	1.43	8.82
6	8.57	6.88	1.25	7.21	1.19	7.20	1.19	3.87	(2.21)	5.48	1.56	6.53
7	9.88	7.88	1.25	7.99	1.24	7.97	1.24	5.69	1.74	7.02	1.41	8.82
8	16.90	13.70	1.23	13.55	1.25	13.70	1.23	9.78	1.73	—	—	9.50
9	8.89	7.03	1.26	7.06	1.26	7.00	1.27	6.21	1.43	—	—	6.14
10	8.50	6.68	1.27	6.80	1.25	6.84	1.24	4.71	1.81	—	—	6.14
Si- 1	93.3	73.9	1.26	73.9	1.26	79.4	1.18	68.7	1.36	61.6	1.51	100.0
2	118.7	92.7	1.28	94.0	1.26	97.3	1.22	82.8	1.44	88.2	1.35	77.3
3	86.0	67.8	1.27	69.0	1.25	73.4	1.17	65.3	1.32	55.6	1.55	126.4
4	117.8	91.0	1.29	91.4	1.29	97.4	1.21	87.9	1.34	74.0	1.59	64.9
5	24.7	19.3	1.28	19.9	1.24	20.2	1.22	8.5	(2.91)	15.6	1.58	—
Average			1.26		1.25		1.21		1.51		1.47	
Standard deviation			0.02		0.03		0.03		0.17		0.08	

TABLE III. SURFACE AREAS OF SPECIALLY PREPARED TiO_2

Heat treatments of samples			N_2(−196°C) m²/g.	Ar(−183°C)		O_2(−183°C)		CO_2(−78°C)	
				m²/g.	S_{N_2}/S_{Ar}	m²/g.	S_{N_2}/S_{O_2}	m²/g.	S_{N_2}/S_{CO_2}
Vacuum	200°C	5 hr.	59.3	47.2	1.26	49.5	1.20	49.1	1.21
O_2	385	5	31.4	25.3	1.24	26.6	1.18	34.3	0.92
O_2	585	5	12.80	10.34	1.24	10.55	1.21	14.5	0.88
O_2	790	5	4.30	3.42	1.26	3.52	1.22	3.65	1.18
O_2	1000	3	2.82	2.29	1.23	2.46	1.15	2.15	1.31
N_2	900	3	6.85	5.48	1.25	5.70	1.20	—	—
N_2	1000	3	4.29	3.47	1.24	3.55	1.21	3.81	1.13
N_2-O_2(1:1)	1000	3	4.70	3.88	1.21	3.97	1.18	—	—
N_2-O_2(4:1)	1000	3	4.55	3.66	1.24	3.74	1.22	—	—
N_2-O_2(9:1)	1000	3	3.96	3.08	1.29	3.25	1.22	—	—
				Average	1.25		1.20	—	—

TABLE IVa. COMPARISON OF SURFACE AREAS FROM THE B.E.T. METHOD AND ELECTRON MICROSCOPY

Ratio of area by B.E.T. to area by electron microscopy

No.	N_2	Ar(−196°C)	Ar(−183°C)	O_2	CO_2	n-C_4H_{10}
Ti-1	1.06	0.85	0.86	0.90	0.78	0.81
2	(1.89)	(1.57)	(1.57)	(1.61)	(1.26)	(1.27)
3	0.95	0.75	0.77	0.83	0.73	0.69
4	0.88	0.68	0.68	0.73	0.57	0.61
5	1.25	0.98	1.01	1.05	0.70	0.87
6	1.31	1.05	1.10	1.10	0.59	0.84
7	1.12	0.89	0.91	0.90	0.65	0.80
8	1.77	1.44	1.43	1.44	1.03	—
9	1.45	1.15	1.15	1.14	1.01	—
10	1.39	1.09	1.11	1.11	0.77	—
Average	1.24	0.99	1.00	1.02	0.76	0.77
Molecular cross-section	13.1	13.9	14.4	13.8	22.4	41.7 Å²

TABLE IVb.

Si- 1	0.93	0.74	0.74	0.79	0.69	0.62
2	1.54	1.20	1.22	1.26	1.07	1.14
3	0.68	0.54	0.55	0.58	0.52	0.44
4	1.82	1.40	1.41	1.50	1.35	1.14
Average	1.24	0.97	0.98	1.03	0.91	0.84

anomaly for carbon dioxide has been observed also for the carbon black. From the comparison with the preceding paper, it is seen that the ratio in Table II is 7∼11% greater than those for carbon black; therefore, the discrepancy between surface areas by nitrogen and those by other gases increased further.

With the titanias prepared under various conditions shown in Table III, nitrogen, argon, and oxygen give surface areas parallel to each other, i.e. the area ratios S_{N_2}/S are nearly constant, and equal to the values in Table II. This fact suggests that these gases give reliable areas despite the difference in the surface state of the samples. For carbon dioxide, however, ratios vary considerably, and in a few cases give values smaller than 1. Such deviations of ratios by carbon dioxide have been observed also for samples of carbon black, silica and other solids in our laboratory. It seems, therefore, that the adsorptions of carbon dioxide change considerably by some slight change in the surface state of the solid, thus, it is concluded that this gas is not suitable for use in the B.E.T. method.

For the reason mentioned above and for the same reason as in the preceding paper, argon may be taken as the standard gas. To determine the molecular cross-sectional areas of the standard gas and of the other gases, the specific surface areas estimated by the B.E.T. method, were compared with those from electron microscopy, the

TABLE V. MOLECULAR CROSS-SECTIONAL AREAS

Gas	Temp.	Van der Waals' const.	From liquid density	Livingston's	Present authors'		
					TiO_2, SiO_2	Carbon black[2]	Average
N_2	−196°C	15.4 Å²	16.2 Å²	15.4 Å²	12.9 Å²	14.2 Å²	—
Ar	−196	13.6	13.8	14.6	13.8	13.8	13.8 Å²
Ar	−183	13.6	14.4	15.5	14.3	14.4	14.4
O_2	−183	13.5	14.1	14.6	13.5	13.5	13.5
CO_2	− 78	16.5	17.0	19.5	20.4	20.8	20.6
n-C_4H_{10}	0	33.0	32.1	44.6	37.4	38.6	38.0

TABLE VI. MOLECULAR CROSS-SECTIONS CALCULATED FROM THE COMPARISON WITH THE ABSOLUTE METHOD

Gas	Temp.	Molecular cross-sections		Ratio	Literature
		From the liquid dens.	From the absolute method		
N_2	−196°C	16.2 Å²	16.2 Å² 16.27	1.00 1.00	6, 7, 8 9
Ar	−196	13.8	16.6 16.88	1.20 1.22	8 9
Ar	−183	14.4	18.19	1.26	9
O_2	−196	13.2	17.5	1.33	7
Kr	−196	15.3	19.5 21.78	1.28 1.42	6 9
CO_2	− 78	17.0	24.39	1.43	9

method independent of the former. The results are shown in Tables IVa and IVb, where figures represent ratios of surface areas estimated by the B.E.T. method and by electron microscopy. In the table, values of Ti-2 were excluded from the average, because it contained needle-like parallel piped particles. Since only a few samples of silica have been measured and the values in the table scatter rather badly, they were used only to verify those with the titanias. These scattered values for the silicas may be explained by the fact that they consist of far smaller particles than the titanias, so that the measurement of the particle diameters on an electron micrograph would yield more series errors. The values shown in the lowest part of Table IVa are obtained by dividing the molecular cross-sections from the liquid densities (column 4, Table V) by respective average ratios in the table. These values should give the consistent surface areas with those from electron microscopy. Since the molecular cross-sections of argon at −196°C thus obtained agree fairly well with both van der Waals' constant and that from liquid density, the value 13.8 Å² from the liquid density was employed as the standard as in the preceding paper. Molecular cross-sections for the other gases are calculated from this value and the values of S_{N_2}/S in Table II, and are shown in column 6 of Table V. From Table IVb it is seen that these values might be applied for silica as well. Since these values, except for that for nitrogen, agree very well with those for the carbon black, average values for both adsorbents can be used for both solids and are shown in the last column. It is seen that these values agree very well with those in Table IV. Agreement with those from the liquid densities also are fairly good, and the value for oxygen agrees with van der Waals' constant. The value for nitrogen, 12.9 Å², however, is considerably smaller than that for the carbon black, 14.2 Å², and deviation from the widely used value, 16.2 Å², from the liquid density is even greater. This deviation amounts to 26% and will be discussed below.

Beebe[6], Arnold[7], Corrin[8], and Pickering et al.[9] determined the molecular cross-sections of several gases for use in the surface area measurement by the B.E.T. method. In their studies, anatase used by Harkins and Jura[10] and determined to

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[6] R. A. Beebe, J. B. Beckwith and J. M. Honig, *J. Am. Chem. Soc.*, **67**, 1554 (1945).

[7] J. R. Arnold, ibid., **71**, 104 (1949).

[8] M. L. Corrin, ibid., **73**, 4061 (1951).

[9] H. L. Pickering and H. C. Eckstrom, ibid., **74**, 4775 (1952).

[10] W. D. Harkins and G. Jura, ibid., **66**, 1362 (1944).

TABLE VII. SPECIFIC SURFACE AREAS

No.	N_2 m²/g.	Ar(−196°C) m²/g.	Ar(−183°C) m²/g.	O_2 m²/g.	CO_2 m²/g.	n-C_4H_{10} m²/g.	B.E.T. mean m²/g.	Elec. micro. m²/g.
Ti- 1	7.55	7.60	7.71	7.72	8.42	8.50	7.92	8.93
2	5.10	5.32	5.32	5.22	5.20	5.12	5.21	3.40
3	6.48	6.47	6.57	6.79	7.61	7.00	6.82	8.58
4	6.06	5.90	5.91	6.04	5.94	6.24	6.02	8.67
5	8.74	8.60	8.90	8.83	7.43	9.11	8.60	8.82
6	6.83	6.88	7.21	6.89	(4.69)	6.49	6.86	6.53
7	7.87	7.88	7.99	7.63	6.89	8.31	7.76	8.82
8	13.45	13.70	13.55	13.12	11.85	—	13.13	9.50
9	7.08	7.03	7.06	6.70	7.52	—	7.08	6.14
10	6.77	6.68	6.80	6.55	5.71	—	6.50	6.14
Si- 1	74.3	73.9	73.9	76.0	83.2	73.0	75.7	100.0
2	94.5	92.7	94.0	93.1	100.3	104.3	96.5	77.3
3	68.5	67.8	69.0	70.2	79.1	65.8	70.1	126.1
4	93.8	91.0	91.4	93.2	106.5	87.6	93.9	64.9
5	19.7	19.3	19.9	19.3	(10.3)	18.5	19.3	—

have the specific surface area of 13.8 m²/g.**** by their absolute method was chosen as a standard solid of the known surface area. They measured adsorption isotherms on this sample by several adsorbates, and calculated V_m by the B.E.T. equation. Dividing 13.8 m² by V_m they determined the cross-sectional area of adsorbate gas molecule. Areas thus obtained for various adsorbate gases are shown in Table VI together with the respective ratios to the areas from the liquid densities. These cross-sections have been proved by the above authors to give consistent surface areas for various solids examined, which include carbon black, rouge, rutile, etc. As are shown in column 5, the ratio of nitrogen is naturally 1, but all other values are greater than 1, i.e. from 1.20 to 1.43. From these ratios it is clear that, except for carbon dioxide and one of kryptons, the deviations of 26% for nitrogen mentioned above will nearly compensate deviations indicated by the ratios in the table, if 12.9 Å² were used for the cross-section of nitrogen. Moreover, ratios of the cross-sections of argon at two temperatures and carbon dioxide to that of nitrogen are 1.04, 1.12, and 1.50, respectively, by Pickering et al.⁹⁾, and 1.07, 1.12, and 1.58, respectively, by the present study. This fact also shows the agreement of the relative molecular cross-sections between both cases. Alexander et al.¹¹⁾ measured surface area of six silica samples by the B.E.T. method, and determined their mean volume surface diameters (d_3) from electron microscopy. The ratios of the specific surface areas by nitrogen adsorption given in Table II in their paper and those calculated from d_3 in the same table give 1.27 on an average. Therefore, if the areas by electron microscopy are correct, the cross-section of nitrogen must be larger by 27% and agrees with the present study again.

From those discussed above the relative values of the molecular cross-sections estimated by the present authors are in fair agreement with those by the others, but from comparison with electron microscopy 16.2 Å² for nitrogen at −196°C seems to be too great and better agreement might be attained by choosing argon as a standard and giving 13.8 Å² for its cross-section at −196°C.

The specific surface areas of all the samples calculated by the cross-sections shown in column 8, Table V, are shown in Table VIII. The average value for each sample together with that from electron microscopy are also listed. In general, the surface areas from the different gases and from electron microscopy are in fair agreement with each other, except for a few cases which are shown in parentheses under carbon dioxide and excluded from the average. Especially for samples of titania, the agreement is satisfactory. Anomalous results obtained by carbon dioxide in certain cases may be explained by some difference in the surface state as in the case of the carbon black. Anomalous ratios in Table III for carbon dioxide are also explained similarly as was discussed above.

**** The same sample gave 13.9 m²/g. by the B. E. T. method using nitrogen as the adsorbate and by assuming 16.2 Å² for its molecular cross-section.

11) G. B. Alexander and R. K. Iler, *J. Phys. Chem.*, 57, 932 (1953).

Conclusion

For the estimation of the specific surface areas of titania and silica, argon, nitrogen, and oxygen are suitable for adsorbate gases and *n*-butane may also be available, but carbon dioxide must be used carefully as it gives unreliable results in some cases. The molecular cross-sectional areas given in Table V, column 6, are in fair agreement with those obtained for the carbon black except for that of nitrogen. The discrepancy by nitrogen would need further investigation, but for other gases, average values shown in column 8 may be expected to give consistent surface areas for many kinds of solids by different gases.

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