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THERMAL TREATMENT OF NON-POROUS SILICA, LIMITED CHANGES IN THE MAGNITUDE OF THE BET-C CONSTANT AND THEIR INFLUENCE ON ADSORPTION: REFERENCE DATA FOR BENZENE ADSORPTION

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ABSTRACT

The surface chemistry of Degussa aerosil TK800 is investigated by means of nitrogen adsorption at liquid nitrogen temperature and benzene adsorption at 35°C. Samples are dehydrated at temperatures in the range 20—900°C and subsequent changes in water content (and/or hydroxyl group content) significantly alter the extent of interaction at the surface—adsorbate interface which is shown as a change in magnitude of the BET-C constant.

Based on adsorption measurements, non-porous samples are used to construct reference V/V_m, P/P_0 curves which show variable changes in the BET-C constant, namely to 6—35, 40—50 and infinity. Reference curves for benzene adsorption are presented and discussed.

INTRODUCTION

Various reference standards for nitrogen adsorption have been reported by Cranston and Inkley [1], Lippens et al. [2], and Carruthers et al. [3]; different Degussa aerosils were used in all cases. A marked increase in the reduced adsorption value, V/V_m, has been found to accompany the increase in BET-C constant. The adsorption process is therefore monitored by the changes in the free energy of adsorption (BET-C constant); the higher the value of BET-C, the greater the amount of gas adsorbed.

Reference data have already been published [4] for the adsorption of a number of organic vapors on different non-porous samples, special attention being paid to Degussa aerosil TK800. The adsorption of benzene will be considered in this paper. Attention will be focussed on changes in BET-C, from which three reference n_R, P/P_0 curves are established. These n_R, P/P_0 curves show relatively smaller changes in BET-C, namely to 6—35, 40—50 and infinity, compared to the results of an earlier investigation [4].

The mechanism necessary for the establishment of three n_R, P/P_0 curves has been considered, and conclusions are presented here.

EXPERIMENTAL

Samples of silica aerosil TK800 were thermally dehydrated in a vacuum for 4 h at several temperatures, 20, 110, 200, 290, 380, 480, 510 and 900°C, which are identical to the values used previously [5,6]. The samples are designated as T(20), T(110), T(200), T(290), T(380), T(480), T(510) and T(900), respectively.

Heating was done in a small electrical tubular furnace at a rate of 2.5—3.0°C min^{-1}. Both adsorption of nitrogen at liquid nitrogen temperature [7] and benzene adsorption at 35°C [8] were investigated with a conventional volumetric apparatus.

RESULTS AND DISCUSSION

Nitrogen specific surface areas, S^{N_2}, were calculated by applying the BET method to the nitrogen adsorption isotherms in the range 0.05—0.35 P/P_0, and adopting a value of 16.2 $Å^2$ for the cross-sectional area of the nitrogen molecule [9]; the adsorption data were taken from an earlier investigation [5].

Benzene specific surface areas, S^B, were also derived by applying the BET method to the adsorption isotherms, but in the range 0.05—0.25 P/P_0. A value of 42 $Å^2$ was adopted for the cross-sectional area of the benzene molecule [10].

All the adsorption isotherms were type II of Brunauer's classification [11]. As mentioned earlier [5], nitrogen adsorption isotherms shows no detectable hysteresis effects on heating to >110°C; it was therefore anticipated that benzene adsorption isotherms for samples preheated at >110°C would also show no hysteresis effects. It became evident, however, that benzene isotherms in fact exhibit high-pressure hysteresis loops which end at 0.70—0.80 P/P_0. Based on experience, the occurrence of such high-pressure hysteresis indicates marked intergranular capillary condensation rather than detectable porosity characteristics.

Surface areas, S^B, BET-C values, and values of S_t are listed in Table 1; the S_t values were calculated by applying the V_l—t method [2] with data from ref. 4: BET-C $\simeq$ 4—58 was used as the reference standard, which covers the subsequent changes in magnitude of BET-C, and satisfies the criteria for meaningful analysis [2,12]. The agreement between S^B, and S_t is taken as sufficient evidence for the correct choice of reference data [4].

As reported earlier by Brunauer [12], the appropriate t curve should not

TABLE 1

Some surface characteristics of benzene adsorption on TK800

Sample	BET—C	S^B (m^2 g^{-1})	S_t (m^2 g^{-1})
T (200)	48—49	111.3	150
T (290)	8—9	90.7	90
T (380)	7—8	87.3	87
T (480)	42—43	61.4	87
T (510)	6—7	96.7	90
T (900)	∞	37.2	—

be chosen on the basis of chemical similarity of adsorbent surface, but rather on the magnitude of heat of adsorption. The value of BET-C is frequently adequate to test the appropriateness of the *t* curve, but a more reliable check is the measure of agreement between S_{BET} and S_t. In addition, Brunauer [12] has pointed out that BET-C is directly related to the free energy of adsorption (or change in chemical potential) rather than heat of adsorption, thus the magnitude of the BET-C also depends on the range of linearity of P/P_0 in the BET plot.

V/V_m, P/P_0 curves for selected samples T(380) with BET-C $\simeq$ 7, and T(290) with BET-C $\simeq$ 8—9, as well as reference data [4] are shown in Fig. 1. The curves are initially superimposed, from low pressures to $P/P_0 = 0.55$. At relatively high pressures ($P/P_0 > 0.55$), measurable differences in V/V_m were noted.

It is evident from Fig. 1 that T(200) has lowest V/V_m values at relatively high pressures ($P/P_0 > 0.70$), indicating a less dominant contribution from intergranular capillary condensation in this region, compared both to the reference data [4] and TK800. At some intermediate and high relative pressures ($P/P_0 > 0.55$), the reference data [4] show fairly high V/V_m values compared to T(290) and T(380). This is usually taken as evidence for the dominant contribution of multi-molecular adsorption and intergranular capillary condensation.

With regard to sample T(380): BET-C $\simeq$ 7 (see Table 1) and was previously considered as a reference standard for nitrogen adsorption measurements [5] with BET-C $\simeq$ 110, in agreement with another report [3]. Evidently, at $P/P_0 > 0.85$, considerable interparticle condensation of adsorbed nitrogen occurs in reference standard T(380).

The good agreement between S^B and S_t, as shown by Table 1, indicates

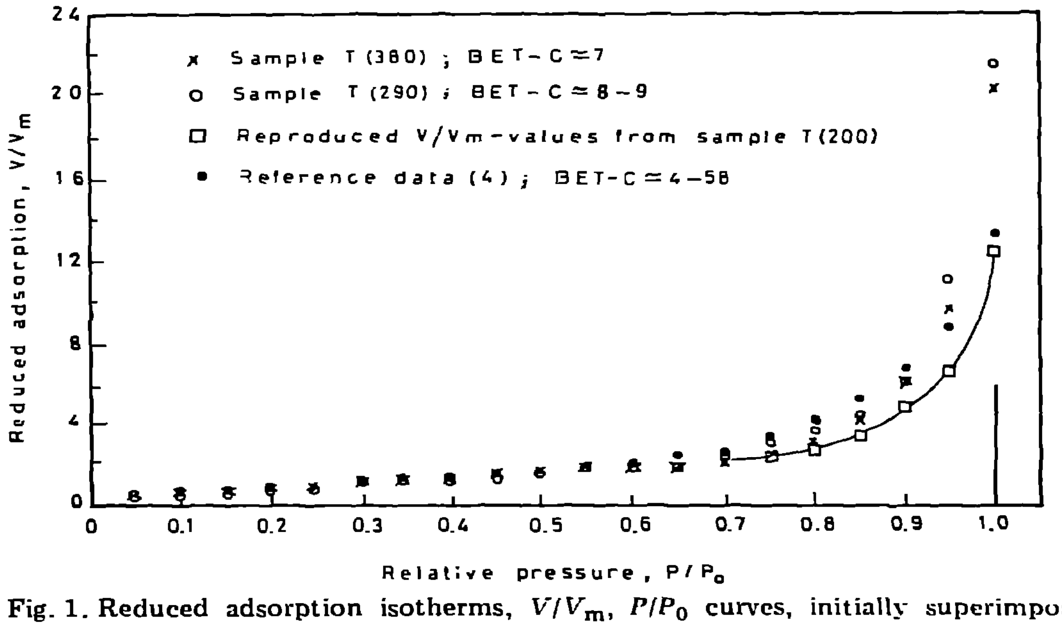

Fig. 1. Reduced adsorption isotherms, V/V_m, P/P_0 curves, initially superimposed, for some samples.

the correct choice of reference data [4] in the low BET-C values as satisfying the criterion for meaningful analysis [2,12]; however, the reference data [4] seems to contain (at $P/P_0 > 0.55$) measurable contributions from multi-layer adsorption and significant capillary condensation. The reference material [4] has high V/V_m values even compared with pre-characterized sample T(290), which has some limited porosity [5]. Naturally, the reference material [4] must have some porous character, because it contains some wide- and/or meso-pores.

The V/V_m values for T(290), T(380) and T(510), together with the reference data [4], are listed in Table 2. In practice T(510) with BET-C $\simeq$ 6—7 at $P/P_0 < 0.65$ gives a V/V_m, P/P_0 curve which is directly superimposed on the V/V_m, P/P_0 curves for T(290) with BET-C $\simeq$ 8—9 and T(380) with BET-C $\simeq$ 7, in agreement with the results of a previously reported investigation [13].

The various V/V_m, P/P_0 curves for selected samples of T(200), T(480) and T(900), together with the reference data [4], are shown in Fig. 2. As already noted, a general increase in V/V_m values was found to follow the increase in BET-C, in agreement with conclusions reported earlier [1—3].

Sample T(200) with BET-C $\simeq$ 48—49 shows an increase in the statistical number of monolayers V/V_m with increase of relative pressure P/P_0.

TABLE 2

Reduced adsorption values of benzene on various TK800 samples

Relative pressure P/P_0	V/V_m			
	Sample T (290) BET—C$\simeq$8—9	Sample T (380) BET—C$\simeq$7	Sample T (510) BET—C$\simeq$6—7	Reference data [4] BET—C$\simeq$4—58
0.05	0.36	0.37	0.33	0.49
0.10	0.54	0.56	0.42	0.63
0.15	0.63	0.65	0.57	0.72
0.20	0.80	0.74	0.67	0.82
0.25	0.89	0.93	0.84	0.91
0.30	1.07	1.11	1.01	1.05
0.35	1.21	1.21	1.17	1.21
0.40	1.25	1.24	1.26	1.30
0.45	1.43	1.48	1.42	1.49
0.50	1.52	1.52	1.51	1.66
0.55	1.61	1.67	1.59	1.88
0.60	1.79	1.76	1.68	2.10
0.65	(1.96) *	1.85	1.72	2.36
0.70	(2.32)	2.04	1.76 **	2.71
0.75	(2.95)	2.41	2.01 **	3.26
0.80	(3.57)	3.97 **	2.85 **	4.11
0.85	(4.37)	4.08 **	4.36 **	5.31
0.90	(6.16)	6.18 **	7.54 **	6.72
0.95	(11.07)	9.64 **	14.24 **	8.73
1.00	(19.64)	20.39 **	—	13.54

* Values in parentheses involve measurable multi-molecular adsorption and capillary condensation effects.

** V/V_m values involving measurable intergranular capillary condensation.

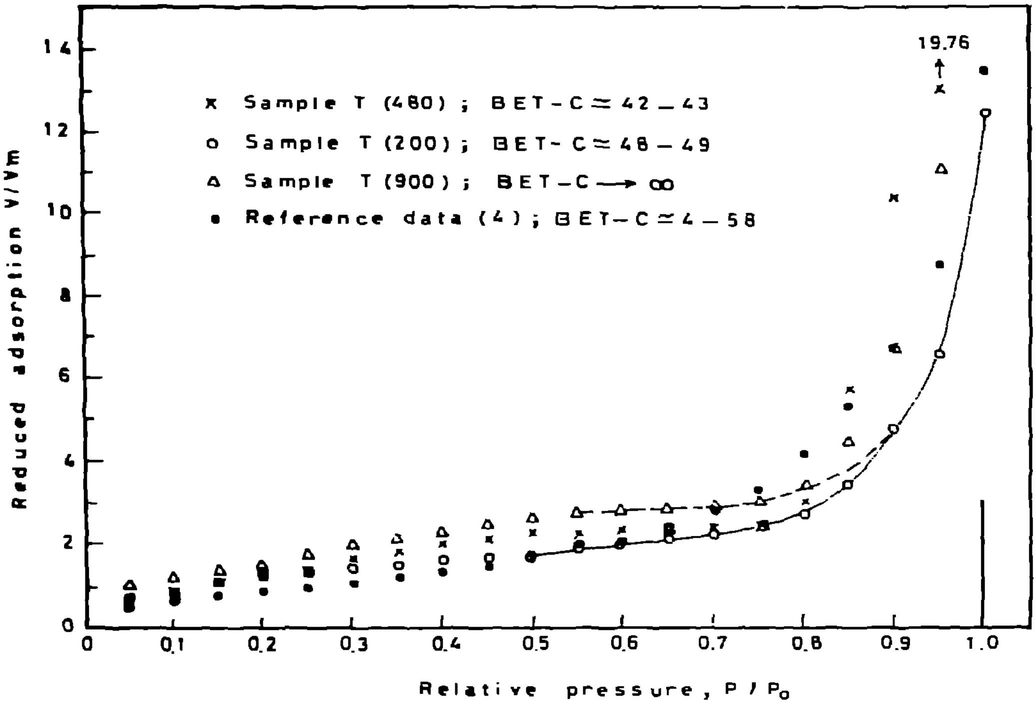

Fig. 2. The marked increase in reduced adsorption, V/V_m, following increase of BET-C.

However, above $P/P_0 = 0.50$ the sample has the lowest V/V_m values of all the samples examined, including the reference data [4]. This indicates that there is little or no capillary condensation effect here. Low V/V_m values at intermediate and high relative pressures ($P/P_0 > 0.50$) might be thought, by comparison with other samples, to characterize the later stages of adsorption up to saturation pressure. Adsorption isotherms for materials which differ significantly in chemical nature have been reported earlier [2,12], and reference curves for water adsorption have been given by Hagymassy et al. [14].

T(900) has an infinitely large value of BET-C and consequently the highest V/V_m values are at low and intermediate relative pressures; more gas adheres to the surface as the value of free energy of adsorption increases. As shown in Fig. 2, the V/V_m values at $P/P_0 > 0.75$ seem to indicate significant interparticle capillary condensation. At higher relative pressures, values of V/V_m are the same as those for T(200) [2,14].

It is evident from Fig. 2 that the V/V_m, P/P_0 curve for the reference data [4] shows the lowest V/V_m values when compared with all the other samples examined; this is especially so for T(480) with BET-C ≃ 42—43 and T(200) with BET-C ≃ 48—49.

Based on the implications of Fig. 1, the reference data [4] fits the criteria for correct analysis [2,12] in the case of low BET-C values only [6—8]; from the results of the present work it is suggested that analysis of the reference data [4] should be limited to the BET-C range of 4—35, and outside this range another n_R, P/P_0 curve should be used.

The V/V_m values for sample T(200) with BET-C ≃ 48—49, together with some initial V/V_m values ($P/P_0 < 0.25$) for sample T(480) at BET-C ≃ 42—

43, are considered [13] to cover the range BET-C $\simeq$ 40—50.

Sample T(480) with BET-C $\simeq$ 42—43 gives a V/V_m, P/P_0 curve which is initially superimposed on the V/V_m, P/P_0 curve of T(200); thus situation continues to $P/P_0 = 0.30$. At higher relative pressures an increased number of monolayers was noted, despite the non-porous nature of T(480), as derived from nitrogen adsorption measurements [5].

The increased adsorption values, V/V_m, at relative pressures $P/P_0 > 0.30$, might be related to the formation of benzene clusters. According to spectroscopic studies of Tursi and Nixon [15], Si—OH (silanol) bond acts as a donor for hydrogen bonding to other hydroxyl adsorbates like methanol. Similarly, silanol groups readily react with the π-bonds of aromatic substances, giving rise to specific interaction; details are reported elsewhere [16,17]. Such a mode of interaction predominates at low relative pressures ($P/P_0 < 0.25$) on a nearly clean surface. The reaction between surface silanol groups and adsorbate molecules continues until about 50% of the hydroxyl groups are consumed, and then benzene molecules tend to form clusters before the rest of the silanol groups are utilized. Formation of clusters is initiated by a relatively high heat of liquification compared to the limited interaction of a single silanol group (as present on a non-porous and partially hy-

TABLE 3

Reduced adsorption values of benzene on various TK800 samples

Relative pressure P/P_0	V/V_m			
	Reference data [4]	Sample T (480) BET—C$\simeq$42—43	Sample T (200) BET—C$\simeq$48—49	Sample T (900) BET—C $\rightarrow \infty$
0.05	0.49	0.64	0.73	0.96
0.10	0.63	0.79	0.87	1.22
0.15	0.72	1.05	1.02	1.31
0.20	0.82	1.19	1.16	1.39
0.25	0.91	1.32	1.31	1.65
0.30	1.05	(1.58) *	1.38	1.91
0.35	1.21	(1.85)	1.46	2.05
0.40	1.30	(1.98)	1.53	2.26
0.45	1.49	(2.11)	1.60	2.48
0.50	1.66	(2.24)	1.67	2.61
0.55	1.88	(2.24)	1.82	2.70
0.60	2.10	(2.24)	1.89	2.74
0.65	2.36	(2.24)	2.04	2.79
0.70	2.71	(2.24)	2.18	2.87
0.75	3.26	(2.37)	2.33	2.92
0.80	4.11	(2.90)	2.69	3.30
0.85	5.31	(5.67)	3.42	3.75
0.90	6.72	(10.28)	4.73	6.61 **
0.95	8.73	(19.76)	6.55	11.05 **
1.00	13.45	(44.27)	12.37	21.84 **

* Parentheses indicate increased adsorption values, V/V_m, at intermediate and high relative pressures; formation of benzene clusters.

** V/V_m values involving intergranular capillary condensation.

drophobic surface) with a single adsorbate molecule. It has been reported by Klier et al. [18], because of the low heat of adsorption, that each silanol group is bonded to one molecule of adsorbate. An increased probability exists for interaction of more than one surface silanol group with one molecule of adsorbate when the surface is porous and/or increasingly hydroxylated. Therefore, further adsorbate molecules cluster on the silanol groups which have already reacted and consequently this increases V/V_m at moderate and high relative pressures, $P/P_0 > 0.30$. The various V/V_m values are listed in Table 3.

In practice, the measure of agreement between the BET surface areas of nitrogen [5] and benzene may be considered indicative of surface hydroxylation. In the present case the adsorbents possess a smaller area for benzene adsorption (reported to the area for nitrogen); the surface is considered composite (hydrophilic/hydrophobic) in nature.

As shown in Fig. 1, the V/V_m values for T(380) with BET-C $\simeq$ 7 represent the BET-C range 6—35. The initial V/V_m values ($P/P_0 < 0.25$) were averaged [13] for samples T(290) and T(510), see Table 2, and then the values of V/V_m at intermediate pressures ($P/P_0 < 0.55$) were averaged for sample T(510) only. V/V_m values for the discrete samples are listed in Table 2 and the composite n_R, P/P_0 curve is shown in Fig. 3; various n_R values for the composite behaviour are shown in the second column of Table 4.

TABLE 4

Reference n_R values for benzene adsorption measurements

Relative pressure P/P_0	n_R		
	BET—C$\simeq$6—35 Samples T (380), T (510), T (290)	BET—C$\simeq$40—50 Samples T (200), T (480)	BET—C $\rightarrow \infty$ Sample T (900)
0.05	0.37	0.69	0.96
0.10	0.55	0.83	1.22
0.15	0.64	1.04	1.31
0.20	0.77	1.18	1.39
0.25	0.91	1.32	1.65
0.30	1.09	1.38	1.91
0.35	1.21	1.46	2.05
0.40	1.25	1.53	2.26
0.45	1.46	1.60	2.48
0.50	1.52	1.67	2.61
0.55	1.64	1.82	2.70
0.60	1.78	1.89	2.74
0.65	1.90	2.04	2.79
0.70	2.04	2.18	2.87
0.75	2.37	2.33	2.92
0.80	2.69	2.69	3.30
0.85	3.42	3.42	3.75
0.90	4.73	4.72	4.73
0.95	6.55	6.55	6.55
1.00	12.37	12.37	12.37

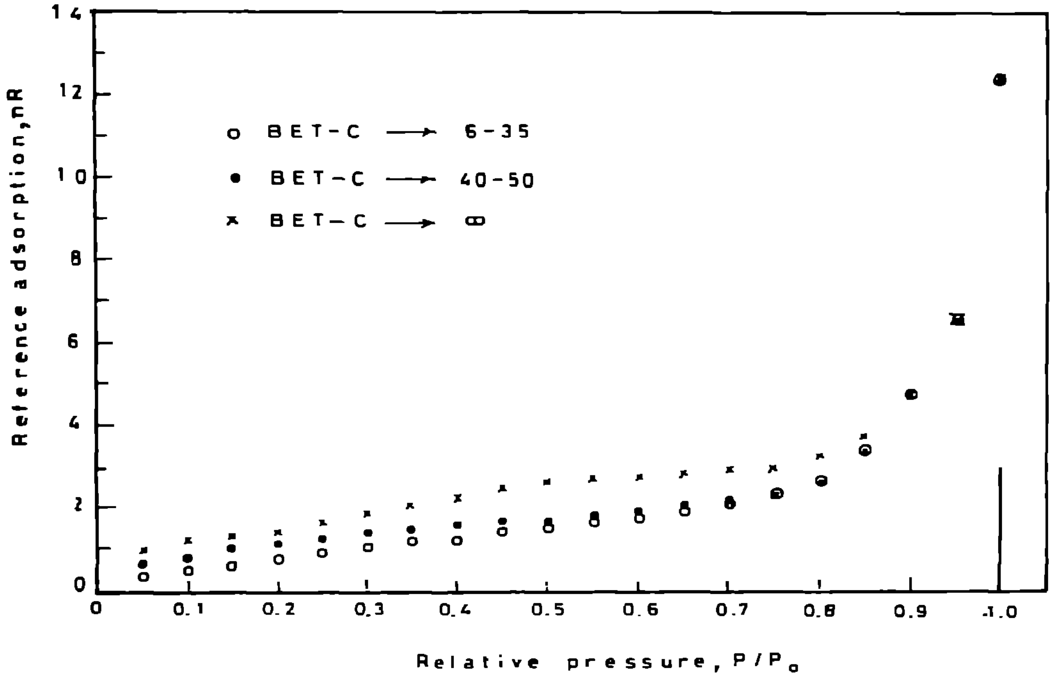

Fig. 3. Reference standard curves for benzene adsorption.

On comparing the composite set of n_R values (Table 4, column 2) with the reference data [4] (Table 3, column 2), the present results show relatively lower initial n_R values up to $P/P_0 = 0.25$, although some are almost comparable. At intermediate pressures, 0.50—0.75 P/P_0, the present work gives markedly lower V/V_m values, which situation continues to the saturation pressure, $P/P_0 = 1.0$.

Sample T(200) has a n_R, P/P_0 curve which represents the BET-C range 40—50; initial n_R values ($P/P_0 < 0.25$) were averaged [13] using sample T(480).

Only T(900) shows infinite interaction of benzene with the surface (BET-C → ∞); the adsorption values, V/V_m at relative pressures $P/P_0 > 0.80$ were initially taken to be those of sample T(200).

The three n_R, P/P_0 curves are listed in Table 4 and graphically represented in Fig. 3. The t curves can be basically calculated by multiplying the statistical number of monolayers, n_R, by the unilayer thickness t_m.

Application of the reference data was initially checked by the V_l—t method. From the results it was ascertained that S_t values had been reliably evaluated, with good agreement for the BET values of surface area as determined from benzene adsorption measurements.

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