

## THERMAL TREATMENT OF NON-POROUS SILICA. THE POROSITY CHARACTERISTICS OF SILICA AEROSIL TK800 INDUCED BY TRIMETHYLCHLOROSILANE TREATMENT

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### ABSTRACT

The surface chemistry of the dehydrated parent and silanized TK800 samples were investigated by low temperature ( $-195.6^{\circ}\text{C}$ ) nitrogen adsorption. For silica aerosil TK800 samples dehydrated at various temperatures, the water content, average pore radii and number of surface hydroxyls were calculated, and the percentage conversion of surface silanols for various dehydrated samples was estimated.

As is evident, the availability of surface hydroxyls seems to play a major role in controlling the conversion rates, together with the minor role played by the average pore radius. In general, the conversion of surface silanols is responsible not only for determining the extent of uni- and multi-molecular adsorption, but may also be responsible for some of the observed porosity characteristics.

### INTRODUCTION

The physical structure of the silica surface may be readily modified by changing the nature of some surface chemical constituents, e.g. the vapor phase reaction of some organo-silanes with surface silanols in silicas, such as trimethylchlorosilane (TMCS) and hexamethyldisilazine (HMDS). Such a reaction may dissolve or react with some surface constituents leaving a porous sample, which might markedly differ in porosity characteristics when compared with the parent non-porous TK800 samples. Furthermore, these surface reactions increase the surface hydrophobicity, since there is chemical substitution of the surface hydrophilic sites ( $\text{Si}^{\text{S}}\text{-OH}$ ) by other hydrophobic centres.

As stated earlier [1], the thermal dehydration of aerosil TK800 at low temperature ( $<110^{\circ}\text{C}$ ), in the presence of its own water induces the creation of a secondary pore structure, which has already been shown [1] to contain some wide- and/or meso-pores.

The induced surface porosity is increased by the subsequent increase in extent of the surface reaction. This can be attained through decreasing particle size or increasing the extent of hydroxyl population, as well as by varying the availability of these surface hydroxyls for chemical reaction or exchange. According to Babkin [2] the conversion rate of surface hydroxyls is increased by preliminary hydroxylation of the parent surface, as well as

increasing its ability to form hydrogen bonds [3]. Recently, it was reported by Snyder and Ward [4] that reactive hydroxyls react more rapidly with  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_2\text{SiCl}_2$ , such reactive hydroxyls appearing to consist of an adjacent pair of strongly hydrogen-bonded surface hydroxyls, which have already been denoted by Armistead [5] as B-sites.

In the present communication the system of TK800 + trimethylchlorosilane (TMCS) was investigated at different water contents, which were primarily controlled by thermal treatment. The hydroxyl contents ( $N_{\text{OH}}/100 \text{ \AA}^2$ ), availability of surface silanols to reaction (percentage conversion), average pore radius, together with the development of induced surface porosities were studied and inter-related.

## EXPERIMENTAL

Silica aerosil TK800 was thermally dehydrated in vacuo for 4 h at temperatures of 20, 110, 200, 290, 380, 480 and 510°C, in accordance with relevant details from previous reports [1,6]. The samples were designated as  $T(20)$ ,  $T(110)$ ,  $T(200)$ ,  $T(290)$ ,  $T(380)$ ,  $T(480)$  and  $T(510)$ , respectively.

The silanized samples were prepared from the thermally dehydrated parent samples: at the same temperatures, then at room temperature, the samples were exposed to trimethylchlorosilane vapor kept at 22°C ( $P \approx 210$  mmHg) for 20 min, and left in contact with its own vapor for 12 h, which certainly appears to be a sufficient period for completing the reaction [7]. Chemically modified samples were designated as  $T^-(200)$ ,  $T^-(290)$ ,  $T^-(380)$ ,  $T^-(480)$  and  $T^-(510)$  for the preheating temperatures indicated in parentheses. The choice of the samples thermally dehydrated above 110°C is discussed later.

Heating was carried out using a small electrical tubular furnace programmed at a rate of 2.5–3.0°C min<sup>-1</sup>. Adsorption of nitrogen, at liquid-nitrogen temperature, was carried out using a volumetric apparatus of conventional design [8].

Water losses of the various parent samples were accurately estimated, and, based on an assumption of complete water loss at 900°C, the number of surface silanols ( $N_{\text{OH}}/100 \text{ \AA}^2$ ) were readily calculated [9]. The values of water loss of  $N_{\text{OH}}/100 \text{ \AA}^2$  are listed in Table 1, the adsorption data for the parent samples being taken from an earlier investigation [1].

For the silanized samples, the respective uptake of trimethylchlorosilane (calculated per one gram of dry sample), percentage conversion of surface silanols, together with the surface characteristics of the treated samples are listed in Table 2.

## RESULTS AND DISCUSSION

Based on earlier investigations [1,10], the oxide surface structure of TK800 was considered composite (hydrophilic/hydrophobic) in nature.

Evidently, the disappearance of hysteresis effects in nitrogen adsorption

TABLE 1

Some surface characteristics of parent TK800 samples using nitrogen adsorption

Sample	Water loss ( $\mu\text{H}_2\text{O}/\text{g} \times 10^2$ )	Water content ( $\text{g H}_2\text{O}/\text{g} \times 10^2$ )	BET-C constant	$V_m$ ( $\text{cm}^3 \text{g}^{-1}$ )	$N_2$ $S_{N_2/T}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_t$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p$ ( $\text{ml g}^{-1}$ )	$F(\lambda)$	$N_{OH}/$ $100 \text{ \AA}^2$
T(20)	2.10	2.51	12	50.78	220.9	225	0.370	33.8	(7.57)*
T(110)	2.64	1.97	74	39.06	170.0	170	0.480	56.8	(7.73)*
T(200)	3.36	1.25	38	44.25	192.6	215	0.280	19.0	4.38
T(290)	3.48	1.13	6	34.19	148.8	161	0.290	38.7	5.06
T(380)	3.73	0.88	110	36.86	158.2	163	0.196	24.8	3.71
T(480)	3.99	0.62	17	22.00	95.8	100	0.140	28.2	4.32
T(510)	4.09	0.52	29	45.98	200.1	210	0.280	120.0	1.73

\* The number of silanol groups calculated on the basis of the "total" water loss including surface adsorbed water.

TABLE 2

Some surface characteristics of silanized TK800 samples using nitrogen adsorption

Sample	Uptake/ dry weight ( $\times 100$ )	Percentage conversion	BET-C constant	$V_m$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{N_2/T}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_t$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p$ ( $\text{ml g}^{-1}$ )	$F(\lambda)$
T <sup>-</sup> (200)	9.44	0.63	18	40.98	178.5	195	0.49	54.9
T <sup>-</sup> (290)	17.43	1.29	9	85.59	155.0	165	0.40	51.6
T <sup>-</sup> (380)	7.83	0.74	6	117.65	512.5	495	0.88	34.3
T <sup>-</sup> (480)	33.94	4.55	138	32.03	139.5	145	0.47	66.9
T <sup>-</sup> (510)	19.59	2.18	7	99.50	433.1	425	0.81	38.8

isotherms [1] obtained above 110°C indicate that the various samples (preheated above 110°C) were essentially treated as non-porous in nature, with the only exception being that sample T(290) seems to possess some limited hysteresis effect which ends at  $P/P_0 = 0.65$ , which might act as evidence for the limited porosity of the sample.

For parent samples dehydrated at low temperatures (20 and 110°C), the number of surface silanols,  $N_{OH}/100 \text{ \AA}^2$ , were higher than those calculated based on some crystallographic studies [11,12]. This indicates that the surface is densely populated with molecular water rather than surface silanols. As reported by Zhdanov [12] for fully hydroxylated silicas, the number of silanol groups ( $N_{OH}/100 \text{ \AA}^2$ ) will not exceed the number of silicon atoms per unit area ( $100 \text{ \AA}^2$ ), as calculated on the basis of crystallographic data [11,12]. By assuming that each silicon atom coming to the surface binds only one hydroxyl group, therefore, the minimum values obtained for different crystalline and amorphous silicas are 4.2–5.7 OH groups/ $100 \text{ \AA}^2$ , further details being reported elsewhere [13].

As is evident from the tenth column of Table 1, the number of surface silanols above 110°C is smaller than that postulated on a crystallographic basis [11,12]. Therefore, the surface was predominantly occupied by surface silanols with no residual molecular water. According to Babkin [2], the extent of interaction in the system silica aerosil + trimethylchlorosilane was found to be increased by preliminary hydration (and/or hydroxylation) of the surface. If there is some molecular water, additional trimethylchlorosilane molecules will be consumed in the reaction with molecular water.

As indicated earlier, the precharacterized samples (>110°C) were carefully selected, and will represent the subject of this investigation.

The reaction of trimethylchlorosilane with surface silanols primarily depends on:

*1. The hydroxyl content.* The presence of more surface silanols enhances the occurrence of further reactions, as well as the availability of these silanols for exchange; in the view of Folman and Yates [3], the perturbation and availability (to exchange) of surface silanols increases because of the enhanced ability to form hydrogen bonds, in accordance with some recent reports from Snyder and Ward [4].

As shown in Fig. 1, the maximum exchange rate (percentage conversion) was observed at 480°C, which indicates the dominant reaction with the already hydrogen-bonded hydroxyls, which were denoted later by Armistead [5] as B-sites. On thermal dehydration at higher temperatures (>500°C), the formation of isolated and unperturbed hydroxyls (A-sites) is evident, which seems to reflect a lower conversion rate, due to the decreased availability [4] of the *sole* silanols for the reaction.

*2. Size of entry group.* Treatment of a silica surface with methanol at elevated temperatures of up to 470°C, leads to an increase in the degree of methylation. However it is impossible to replace all surface hydroxyls by methyl groups; no more than about 30% of the hydroxyl content is methylated, partially due to the occurrence of steric hindrance [14]. The methyl

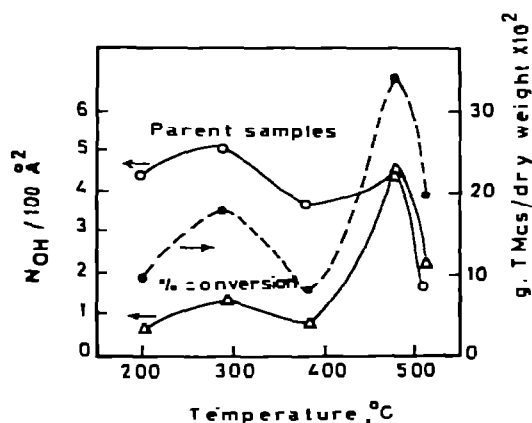


Fig. 1. Variations of number of surface silanols, uptake of trimethyl chlorosilane ( $\text{g g}^{-1}$ ) and percentage conversion of surface silanols as functions of the pretreatment temperature.

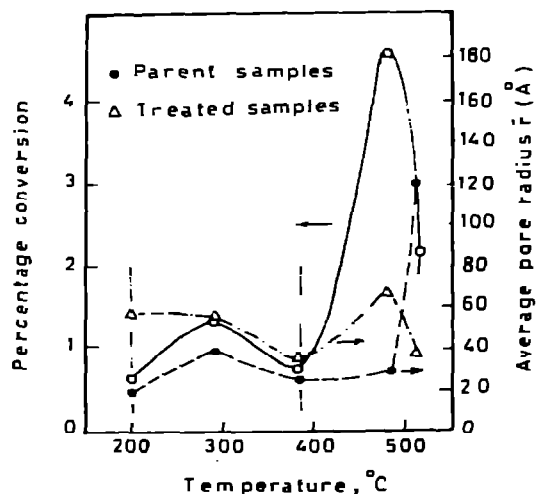


Fig. 2. Variations of the percentage conversion and the average pore radii as functions of the pretreatment temperature.

groups on top of the surface silanols reflect some thermal stability even at  $400^\circ\text{C}$  since the reverse reaction is very slow [14,15].

The reaction of bulkier molecules, e.g.  $(\text{CH}_3)_3\text{N}$ : and  $(\text{CH}_3)_3\text{SiCl}$ , were almost identical in their occupation of about  $40 \text{ \AA}^2$ /one ligand group, on top of the surface silanols. Based on the wide differences in molecular size of methanol and  $(\text{CH}_3)_3\text{SiCl}$ , one can satisfactorily interpret the small uptakes (column 2, Table 2) and the finite conversion rates (column 3, Table 2) as well.

As shown in this discussion, the occupation of 2.45 ligand groups/ $100 \text{ \AA}^2$  is considered indicative of 100% exchange.

In this context, the nature of these surface reactions was found to be dependent on the following:

(a) The rate constant for the reaction, kinetic factors involved in the sample preparation, as well as the concentration of chemical constituents, possibly as Si—OH groups in silicas, and also the presence of some molecular water.

(b) The temperature of preparation, which might widely alter the previous parameters.

(c) The physical structure (as a surface property) of the parent material.

Figure 1 illustrates the variations in the number of silanol groups ( $N_{OH}/100 \text{ \AA}^2$ ) for parent samples, uptake of trimethylchlorosilane and the percentage conversion of silanol groups, all as functions of the pretreatment temperature. The changes in uptake of TMCS ( $\text{g g}^{-1}$ ), and the percentage conversion seem to run in harmony with the following change in the number of silanol groups,  $N_{OH}/100 \text{ \AA}^2$ . An increase in the extent of conversion of surface silanols was noted as the hydroxyl content increased, in accordance

with some of Babkin's view [2]. The harmonic changes of the three parameters over the temperature range studied (200–510°C), indicates the major role displayed by surface silanols in the exchange reactions.

Figure 2 illustrates the variations in percentage conversion of surface silanols and the average pore radii for parent and silanized samples, all as functions of the pretreatment temperature. Evidently, in the limited range 200–380°C, the harmonic changes in percentage conversion and average pore radius,  $\bar{r}$  (Å), for parent samples reflects a less significant role displayed in such exchange reactions.

The silanized samples possess larger average pore radii; the general widening of pores seems to be more significant in the case of thermal dehydration above 380°C. According to Armistead [5], the B-sites of reactive hydroxyls readily form hydrogen bonds above 380°C, easily interact with trimethylchlorosilane molecules [3], and this in turn induces higher conversion rates, as well as measurable widening of the pores. The less significant effect noted at 510°C is partially attributed to the decreased ability of *isolated and unperturbed silanols* [3,5], formed on thermal dehydration at 510°C, to react with trimethylchlorosilane.

The porous character of the thermally dehydrated parent and silanized samples was detected by both the  $t$ -method [16] and the  $n_S-n_R$  method, recently developed by Mikhail and Cadenhead [17] and both essentially lead to the same conclusions.

The application of the  $t$ -method on parent samples has already been discussed in a previous communication [1], and the  $t$ -method was applied to silanized samples using the  $t$ -curves [18,19] as a *reference standard*. The applicability of the criteria for a correct analysis [16,20] was considered so that the heat of adsorption for both the reference and the investigated sample was comparable. The magnitude of BET-C constant (fourth column of Table 2) is considered an adequate measure for the free-energy change accompanying adsorption [20].

A more reliable check is the measure of agreement between BET-surface areas and  $S_t$  ( $\text{m}^2 \text{g}^{-1}$ ). The good agreement between BET-surface areas (sixth column of Table 2) and  $S_t$  (seventh column of Table 2) was considered primarily as evidence for the suitability of the  $t$ -curves [18,19] for the proposed analysis.

For silanized silica samples dehydrated in the range 200–380°C, the  $V_1-t$  plots show an initial straight-line portion representing  $S_t$  ( $\text{m}^2 \text{g}^{-1}$ ), which continues to about  $t = 8 \text{ \AA}$  (in  $P/P_0$  range of 0.65–0.75), followed by a continuous decrease in slope up till the saturation pressure,  $P/P_0 = 1.0$ .

As is evident from the  $V_1-t$  plot of sample  $T^-(480)$ , the initial straight-line portion ( $S_t$ ,  $\text{m}^2 \text{g}^{-1}$ ) continues to  $t = 6 \text{ \AA}$  ( $P/P_0 = 0.40$ ), then deviates upwards with increasing slope to  $t = 10 \text{ \AA}$  ( $P/P_0 = 0.75$ ), then the slope decreases until the saturation pressure is reached.

From the  $V_1-t$  plot of sample  $T^-(510)$ , the initial straight-line portion represents  $S_t$  ( $\text{m}^2 \text{g}^{-1}$ ) continues to  $t = 5 \text{ \AA}$  ( $P/P_0 = 0.40$ ) after which the slope increases, continuing up to the saturation pressure,  $P/P_0 = 1.0$ .

As is evident from the  $V_1-t$  analysis, at temperatures above 380°C, the silanized samples contained some wide- and/or meso-pores with marked dif-

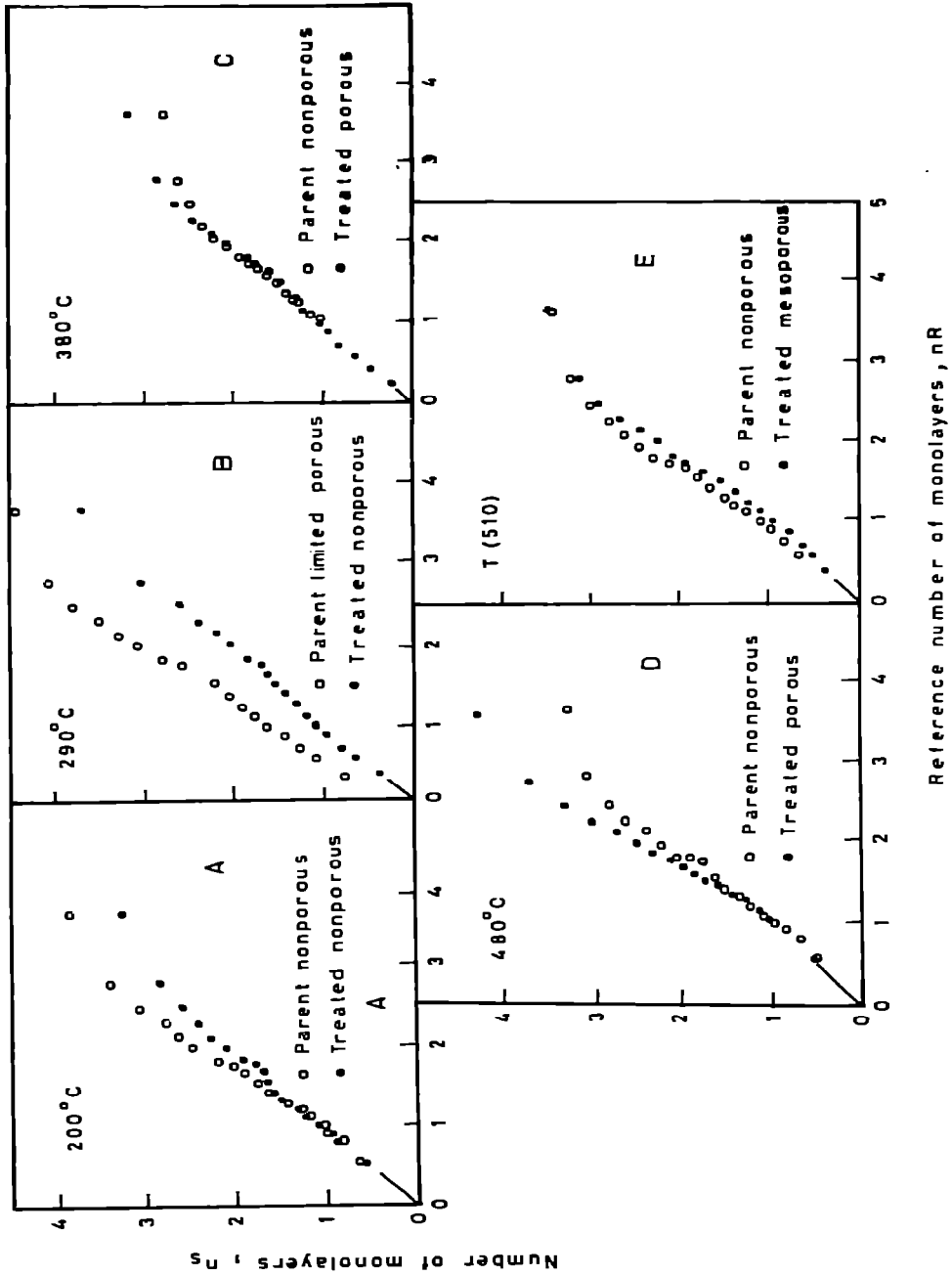


Fig. 3.  $n_5-n_R$  curves for various parent and silanized TK800 samples.

ferences in the uni- and multi-layer adsorption. The subject is suitably illustrated based on the  $n_S-n_R$  method [17].

Figure 3 illustrates the comparative study of  $n_S-n_R$  curves for the parent and silanized samples and in this context certain comments arise, which might be summarized in the following:

*Samples dehydrated at 200°C.* The silanized sample possesses a smaller BET-C constant with no detectable change in the BET-surface area (cf. the fourth and sixth columns of Tables 1 and 2).

As shown in Fig. 3A, the chemical treatment was accompanied by a decrease in the extent of multimolecular adsorption. The natural decrease in nitrogen quadrupole interaction with surface silanols [21] has led to a decrease in the extent of multimolecular adsorption. The limited layer-by-layer building following silanization was recently reported by Zettlemoyer [7].

Both samples were of the same BET-nitrogen area, which indicates that nitrogen molecules are readily adsorbed on surface sites underlying the bulky interacting ligand groups  $(\text{CH}_3)_3\text{Si}-$ ; both parent and the silanized samples were treated as totally *non-porous* in nature.

*Samples dehydrated at 290°C.* The silanized sample was precharacterized by a general decrease in uni- and multi-molecular adsorption, starting from the early low pressures and continuing up to the saturation pressure; cf. Fig. 3B.

The higher  $n_S-n_R$  curve for the parent sample is attributed mainly to the higher nitrogen interaction with surface silanols [21] besides the limited porosity of sample *T*(290), which might enhance the reduced adsorption,  $n_S$ , at the early low and intermediate relative pressures.

*Samples dehydrated at 380°C.* The silanized silica sample was of a lower BET-C constant despite the fact that the BET-surface area is higher (cf. Tables 1 and 2; fourth and sixth columns). The growth of surface porosity — induced by silanizing the parent sample — appears as a hysteresis loop in the adsorption isotherm, and effectively interprets the enhanced  $n_S-n_R$  curve at high relative pressures, cf. Fig. 3C.

*Samples dehydrated at 480°C.* The developed surface porosity induced by silanization appears to play a dominant role, due to the maximum conversion rate at 480°C (cf. Fig. 1). Therefore, the parameters of porosity characteristics, together with surface constitution, are directly related to the magnitude of the BET-C constant, and accordingly an enhanced  $n_S-n_R$  curve was noted (cf. Fig. 3D).

*Samples dehydrated at 510°C.* Evidently, the silanized sample possesses a smaller BET-C constant (cf. Tables 1 and 2, fourth column), despite the development of some wide and/or mesopores, which appear markedly as a hysteresis effect in the adsorption isotherm, but are still reflected in a lower  $n_S-n_R$  curve (cf. Fig. 3E).

The development of surface porosity was quantitatively traced in terms of



relative surface area (R.S.A.), as well as relative BET-C constant (R. BET-C).

$$\text{R.S.A.} = \frac{\text{BET-surface area of the silanized silica}}{\text{BET-surface area of the parent silica}}, \text{ and}$$

$$\text{R. BET-C} = \frac{\text{magnitude of the BET-C for silanized silica}}{\text{magnitude of the BET-C for parent silica}}$$

The changes in these parameters, together with the percentage conversion of silanols all as functions of the pretreatment temperature are listed in Table 3, and graphically represented in Fig. 4.

The variation of relative BET-C constant (R. BET-C) and percentage conversion of surface silanols as functions of the pretreatment temperature are shown in Fig. 4A. The harmonic changes of both parameters reflect the effect of the availability of surface hydroxyls on both the heat of adsorption [21], and the extent of hydroxyl conversion [2-4].

Figure 4B illustrates the change in relative surface area (R.S.A.) as a function of the pretreatment temperature. At low dehydration temperatures (<290°C), both parent and silanized samples were of nearly identical surface areas (R.S.A.  $\approx$  1), which might give rise to the conclusion that nitrogen molecules are readily adsorbed on surface sites underlying silanized surface hydroxyls, with no measurable pore size restrictions. At higher dehydration

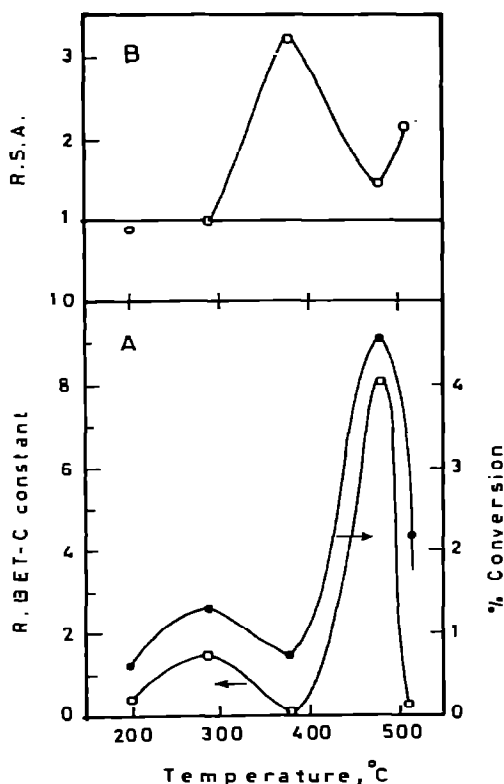


Fig. 4.A, Variation of relative BET-C constant and percentage conversion, as functions of the pretreatment temperature. B, Change in relative surface area as a function of the pretreatment temperature.

TABLE 3

Relative BET—C constant, relative surface areas and percentage conversion of surface silanols

Temperature	R. BET—C	R.S.A.	Percentage conversion
200	0.474	0.926	0.63
290	1.500	1.042	1.29
380	0.055	3.240	0.74
480	8.120	1.457	4.55
510	0.240	2.166	2.18

temperatures ( $>290^{\circ}\text{C}$ ), the silanized samples possess relatively higher BET-surface areas (R.S.A.  $\gg 1$ ), which indicate the development (or creation) of measurable porosity characteristics accompanying the partial silanization of the surface.

Not only was the chemical modification of surface silanols induced by trimethylchlorosilane treatment, but they may also be responsible for some of the porosity characteristics discussed in this paper.

#### REFERENCES

- 1 A.M. Khalil, *J. Colloid Interface Sci.*, **66** (1978) 509.
- 2 I.Yu. Babkin, A.V. Kiselev and A.Ya. Korolev, *Dokl. Akad. Nauk SSSR*, **136** (1961) 373.
- 3 M. Folman and D.I.C. Yates, *Proc. R. Soc. London, Ser. A*, **246** (1958) 32.
- 4 L.R. Snyder and J.W. Ward, *J. Phys. Chem.* **70** (1966) 3941.
- 5 C.G. Armistead, A.J. Tyler, F.H. Hambleton, S.A. Mitchell and J.A. Hockey, *J. Phys. Chem.*, **73** (1969) 3947.
- 6 E. Koberstein and M. Voll, *Phys. Chem., N.F.*, **71** (1970) 275.
- 7 A.C. Zettlemyer and H.H. Hsing, *J. Colloid Interface Sci.*, **58** (1977) 263.
- 8 D.L. Kantro, S. Brunauer and L.E. Copeland, in A. Flood (Ed.), *The Solid—Gas Interface*, Marcel Dekker, New York, 1967, Part 1, Chap. 12.
- 9 J.H. de Boer and J.M. Vleeskens, *Proc. K. Ned. Akad. Wet., Ser. B*, **60** (1957) 24, 45, 57; **61** (1958) 58.
- 10 A.M. Khalil, *J. Colloid Interface Sci.*, **68** (1979) 357.
- 11 W. Stobber, *Kolloid. Z.*, **17** (1956) 17.
- 12 S.P. Zhdanov and A.V. Kiselev, *Zh. Fiz. Khim.*, **31** (1956) 2213.
- 13 L.T. Zhurlev and A.V. Kiselev, in D.H. Everett and R.H. Ottewill (Eds.), *Surface Area Determination*, Butterworths, London, 1970, p. 155.
- 14 R.M. Donald, *J. Am. Chem. Soc.*, **79** (1957) 850.
- 15 A.I. Nikitin, A.N. Sidorov and A.V. Karykin, *Zh. Fiz. Khim.*, **30** (1956) 177.
- 16 B.C. Lippens, B.G. Linsen and J.H. de Boer, *J. Catal.*, **3** (1964) 32. J.H. de Boer, B.G. Linsen and Th.J. Osinga, *J. Catal.*, **4** (1965) 643.
- 17 R.Sh. Mikhail and D.A. Cadenhead, *J. Colloid Interface Sci.*, **55** (1976) 462.
- 18 R.Sh. Mikhail, N.M. Guindy and S. Hanifi, *Egypt. J. Chem., ARE, Special Issue "Tourky"*, (1973) 55.
- 19 J.D. Carruthers, P.A. Cutting, R.E. Day, M.R. Harris, S.A. Mitchell and K.S.W. Sing, *Chem. Ind. (London)*, (1968) 1772.
- 20 S. Brunauer, in D.H. Everett and R.H. Ottewill (Eds.), *Surface Area Determination*, Butterworths, London, 1970, p. 63.
- 21 M.R. Harris and K.S.W. Sing, *Chem. Ind. (London)*, (1967) 757.