Colloid Polym Sci (2004) 282: 1049–1053
DOI 10.1007/s00396-003-1029-4

SHORT COMMUNICATION

M. S. Nadiye-Tabbiruka

Characterisation of porous silica. 2. CPG-10 (VYCOR)

Received: 14 August 2003
Accepted: 5 October 2003

M. S. Nadiye-Tabbiruka
Department of Chemistry,
University of Botswana,
Private bag 0704, Gaborone,
Botswana
e-mail: nadiyemst@yahoo.com

Abstract Porous silica CPG-10 has been characterised by adsorption of benzene before and after modification with trimethylchlorosilane. The Brunauer–Emmet–Teller (BET) specific surface areas were determined where possible. Modification of CPG-10 reduces its adsorption for benzene and hence reduces the BET specific surface area, with the extent of reduction depending on the extent of modification. For a fully modified sample with the highest surface concentration of trimethylsilyl groups, the adsorption isotherm changes from type IV of the unmodified sample to type V. The hysteresis loop size and position are also altered. A mechanism for multilayer adsorption and capillary condensation in modified porous silica is proposed.

Keywords Silylated vycor · Characterisation · Absorption of benzene

Introduction

Trimethylchlorosilane (TMCS) is often used to modify the surfaces of siliceous materials in order to alter their surface properties, including their polarity and their adsorption of other molecules. It has been shown for nonporous silica aerosil [1] that these properties depend on the type, concentration and availability of surface silanols. Silylating of a surface that has a high concentration of surface silanols results in a high concentration of surface silyl groups. Such surfaces give large contact angles and low adsorption with various adsorbates [2]. Work on aerosil has shown that surfaces with intermediate properties can be prepared by silylating with larger molecules, which leave a large number of silanols at the surface [1]. This can also be achieved by partially silylating the surface with TMCS, resulting in this intermediate behaviour [1]. It would be interesting to investigate the effect on the surface properties of silylating porous silica of different pretreatment with TMCS. The question that requires a clear answer is how does the variation of compaction of the trimethylsilyl (TMS) groups affect adsorption of benzene, specific surface area and the porosity of CPG-10 porous glass? This paper reports results from this investigation.

Isotherms for adsorption of benzene were measured on porous glass CPG-10 before and after treatment with TMCS. In these physical adsorption experiments, benzene was chosen as a nonpolar adsorptive in order to reveal unambiguously changes occurring in the pore structure. This is because the same small contact angle of nearly zero degrees is, to a reasonable extent, maintained on both untreated and treated surfaces. Measurements of contact angles on glass slides treated in a similar way to the adsorbents have shown that the contact angle hardly changes [2].

The suitability of benzene as an adsorbate used for the determination of the specific surface area of silicates by the Brunauer–Emmett–Teller (BET) method has been discussed in detail in an earlier paper on aerosil [1]. The concentration of silanols as well as the concentration of the grafted groups from the various modifiers were also discussed in great detail in the same paper.

Experimental

In principle, degree of adsorption of benzene is obtained by measuring the change in mass at equilibrium of a pretreated powdered sample of CPG-10 of known initial weight, using a vacuum microbalance, after every dose of the adsorbate until saturation is reached. The apparatus used in this work was described in detail in an earlier paper [1].

Materials

CPG-10 porous glass

The samples used in this work were obtained from earlier experiments in which kinetics of the silylation reaction was investigated [3]. Detailed specifications of the original porous glass samples together with details of methods of preparation and conditions of modifications are given in earlier work [3].

Benzene

Benzene of analytical quality (BDH Chemicals), was used as the adsorbate. It was distilled and dried using molecular sieves. It was degassed in situ by the freeze–thaw procedure and then redistilled in a reservoir bulb. It was then frozen using liquid nitrogen and out-gassed with the rest of the apparatus.

Procedure

A small glass bucket of known weight was filled with about 200 mg of the appropriate powdered sample of modified CPG-10 porous glass and suspended on one arm of the electronic vacuum microbalance [1]. Details of the electronic microbalance have been given elsewhere [4]. A counterweight, which was made from a solid glass rod, equal in weight to the combined weight of the bucket and the sample, was suspended on the other arm. Details of the rest of the experimental procedure have been given elsewhere [1].

Results and discussion

Benzene adsorption isotherms

Adsorption isotherms for benzene on the CPG-10 porous glass series are given in Figs. 1, 2, 3 and 4.

The specific surface areas were determined by the BET method [1]. The values obtained in this work are given in Table 1. They were determined using data from smooth isotherm curves fitted by hand to the experimental data. A Fortran 77 line-fitting program, based on the least-squares procedure, was used to determine the BET areas. The relative pressure range used was between 0.05 and 0.38. The BET surface areas for benzene were determined using a value for the cross-sectional area of an adsorbed benzene molecule of 0.423 nm^2, a value determined by Hsing and Wade [5] for benzene on α-alumina. It compares quite well with the value of 0.408 nm^2 calculated from liquid densities. The Hsing and Wade value was determined by adjustments to give results consistent with those obtained by using the value of 0.162 nm^2 for nitrogen on alumina.

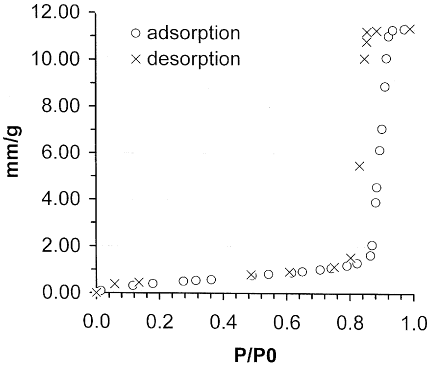

Fig. 1 Adsorption of benzene at 293 K on unsilylated CPG-10 (average pore diameter 17.5 nm) evacuated at 673 K

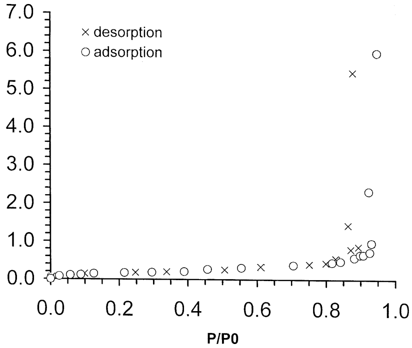

Fig. 2 Adsorption of benzene at 293 K on partially trimethylchlorosilane (*TMCS*) treated CPG-10 (one-quarter treated, average pore diameter 17.5 nm)

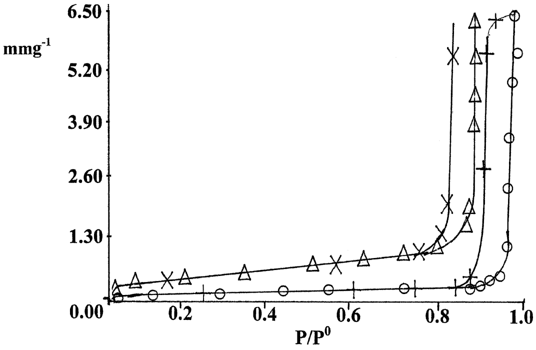

Fig. 3 Adsorption of benzene at 293 K on untreated and TMCS-treated CPG-10 (average pore diameter 17.5 nm). Untreated: adsorption (*circles*), desorption (*pluses*). Fully treated: adsorption (*triangles*), desorption (*crosses*)

The BET surface area (for benzene) of the sample of untreated CPG-10 of pore diameter 12.5 nm (using the molecular cross-sectional area of 0.423 nm^2) is 84.5 m^2 g^{-1}. This value agrees quite well with the value

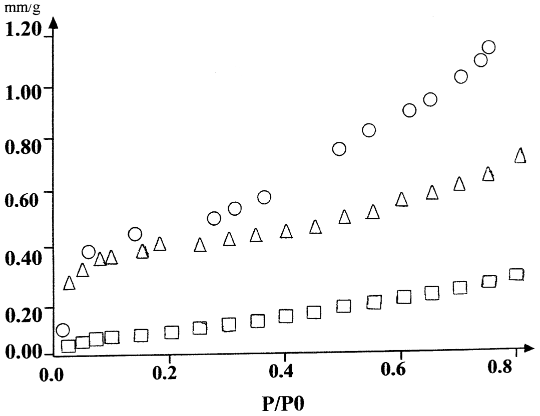

Fig. 4 Adsorption of benzene at 293 K on CPG-10 of varying modification (average pore-diameter 17.5 nm). Untreated (*circles*), one-quarter TMCS-treated (*triangles*), fully TMCS treated (*squares*)

Table 1 Measured surface areas of pretreated CPG-10. The value in *parentheses* is for CPG-10 of diameter 12.5 nm

Silane modifier/T/K	Area/m^{2}g^{-1}
None/673	(66.1) 84.5
1/4 TMCS/673/673	31.0
TMCS/673/653	21.4
TMCS/598/598	Type V

of 120 m^2 g^{-1} determined by Morgan using the same adsorptive [6], but applying the value of the cross-sectional area for benzene, of 0.57 nm^2, obtained by McClellan and Harnsberger [7]. If the BET surface area is divided by the corresponding molecular cross-sectional area, the first set (84.5/0.423) yields a value of 200; the second set (120/0.57) yields a value of 210. These two values are related to the monolayer coverage and, as can be seen, they are within 5% of each other. This is good agreement considering the shortcomings of the BET model [1].

Effect of modification on the adsorption of benzene

As discussed in an earlier paper [1], modification of the silica surface reduces adsorption for benzene. This reduced adsorption can be attributed to the reduction of the adsorption potential, caused by the increased distance from the surface and the shielding effect of the modifier layer. The decrease in the adsorption of benzene for CPG-10 at a relative pressure of 0.4, corresponding to the various conditions of pretreatment, is shown in Table 2.

Table 2 Decrease in adsorption for benzene (on CPG-10 of pore diameter 17.5 nm) due to treatment with silanes. Adsorption at $P/P_0 = 0.4$

Pretreatment T/K	Modifier	Adsorption (mmol g^{-1}) ± 0.005	(Treated/ untreated) %
	None	0.670	100.00
673/653	TMCS	0.136	20.30
673/598	1/4 TMCS	0.45	67.55
673/673	TMCS	0.130	20.90

It has already been shown that modified aerosil adsorbs less benzene than unmodified samples [1]; however, Table 2 shows that in porous samples modification has less effect on the adsorption of benzene than with nonporous samples. This is probably because the silanols in porous glass are less accessible to the silane molecules than in aerosil probably owing to the narrower entrances to the blind pores [8, 9, 10, 11, 12, 13, 14, 15, 16] or owing to the repulsive as well as steric interactions at these entrances resulting from adsorption of TMS groups at the entrances or owing to the curvature in the pores.

Figure 4 is a multiplot showing the relative effect of modification on the adsorption of benzene on CPG-10 of average pore diameter 17.5 nm. Isotherm cross-plots against the isotherm of the untreated sample are given in Fig. 5. They were obtained by plotting the quantity adsorbed by the unmodified adsorbent sample at a given partial pressure against the quantity adsorbed by a modified sample at the same pressure.

The figure also shows the expected cross-plot (a line of slope 1) for two systems with equivalent adsorption. For CPG-10 modified by TMCS, after a short initial proportionate adsorption (with the modified sample adsorbing a lot less), a break at A leads to an increase in adsorption on the modified samples. This is followed by a second break, at B, at a slightly higher partial pressure, which is followed by lower adsorption.

It is believed that the initial proportionate adsorption occurs on the remaining specific sites (the silanols) [1] in the modifier defects on the surface and in the pores inaccessible to silane molecules, forming small clusters

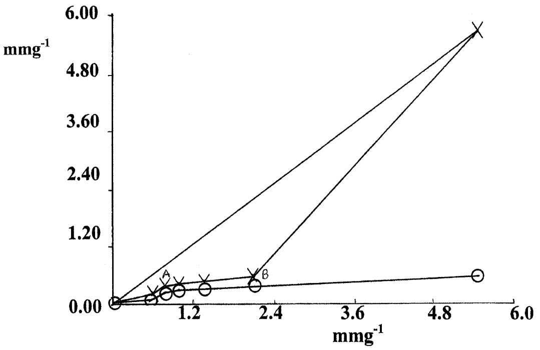

Fig. 5 Cross-plots between the adsorption of benzene at 293 K on unmodified and TMCS-modified CPG-10 of varying pretreatment. x-axis unmodified CPG-10, y-axis TMCS-treated CPG-10. One-quarter TMCS-treated (*crosses*), fully TMCS treated (*circles*)

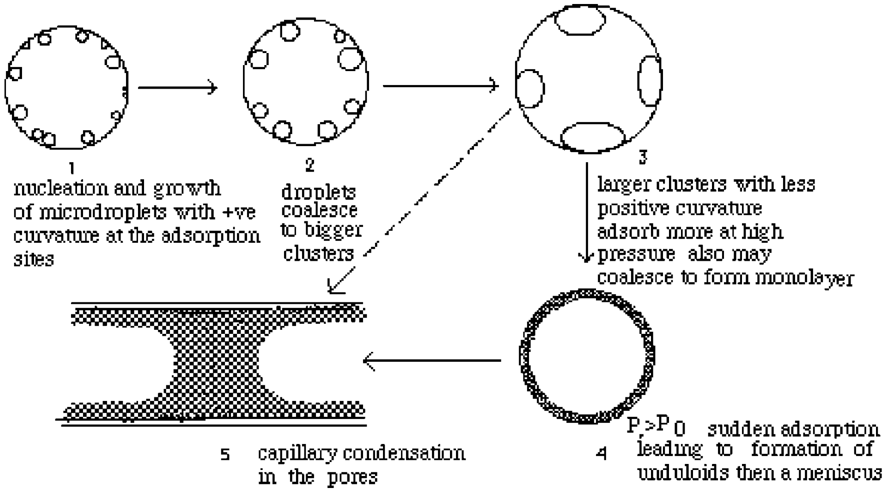

Fig. 6 Proposed mechanism for multilayer adsorption and capillary condensation in modified porous silica

as a result of the higher potential for adsorption at these sites [17, 18]. As the pressure is increased, the clusters grow by adsorption through lateral interaction with the adsorbed molecules. At or near the adsorption sites, the clusters grow thicker through piling up on top of the first layers of adsorbed molecules. However, the total quantity adsorbed remains lower because the adsorption sites remaining on the modified sample are much fewer. Around saturation, these clusters have a positive curvature; therefore, further adsorption onto them would require much higher pressure than the saturation vapour pressure. As the pressure is increased further, these microdroplets continue to grow in size through adsorption, whilst their curvature becomes less positive during the process. At the same time, neighbouring clusters coalesce to form larger clusters, which also have a less positive curvature owing to the increased width and owing to distortion from adsorption potential effects from the solid, which is still very close. Since at this moment $P > P_0$,fast adsorption occurs, leading to more coalescence which, through a series of similar cycles, may develop into a multilayer; the pressure is also reduced to P_0 during these last stages of the process. Therefore, the first break probably represents the coalescence of large clusters to form multilayers.

Inside the pores, the fast adsorption may lead to the formation of a hemispherical lens directly or through the formation of multilayers as already described. The lens so formed then initiates capillary condensation (Fig. 5, line segment AB). The second break, at B, probably represents the end of capillary condensation in the modified pores and the continuation of capillary condensation in the unmodified pores, which is then followed by adsorption on the external surface of the adsorbent. A suggested pictorial sequence of events inside the pores from multilayer adsorption to capillary condensation is given in Fig. 6.

Effects of a modification on capillary condensation

The capillary condensation region of isotherms for untreated and TMCS-treated CPG-10 is shown in Fig. 3. For the TMCS-treated CPG-10 both the adsorption and desorption branches shifted to the higher-pressure end, representing a delay in capillary condensation. This can be attributed to a larger Kelvin radius for a given relative pressure, either owing to the reduced multilayer adsorption [17, 18, 19] or to the increased contact angle or both. In the present work, the change in contact angle is very small and was assumed to be negligible. Adsorption of large organic groups such as TMCS physically reduces the pore volume by reducing the pore radius. It is thought that the small increase in contact angle is probably enough to be responsible for the delay in capillary condensation, leading to a shift of the whole hysteresis to the higher relative pressure end.(Fig. 6)

Acknowledgements I am grateful to the British Commonwealth Scholarship Committee for financial support for this research and to the School of Chemistry of the University of Bristol in the United Kingdom for the help given during the course of this research.

References

1. Nadiye-Tabbiruka MS (2003) Colloid Polym Sci 281:36
2. Nadiye-Tabbiruka MS (1991) PhD thesis. University of Bristol
3. Nadiye-Tabbiruka MS (2000) Colloid Polym Sci 278:677
4. Nadiye-Tabbiruka MS, Haynes JM (1994) Colloid Polym Sci 272:1601
5. Hsing HH, Wade WH (1974) J Colloid Interface Sci 47:490
6. Morgan JC (1976) PhD thesis. University of Bristol
7. McLellan AL, Harnsberger HF (1967) J Colloid Interface Sci 23:577
8. Barrer RM Gabor T (1959) Proc R Soc Lond Ser A 51:353
9. Vaughan MF (1962) Nature 195:801
10. Venzel BI, Zhdanov SP, Koromal DEV (1975) Kolloidn Zh 37:1053
11. Janowski VF, Heyer W (1979) Z Chem 91:1
12. Liabastre AA, Orr C (1978) J Colloid Interface Sci 64:1
13. Barrer RM, Barrie JA (1952) Proc R Soc Lond Ser A 213:250
14. Amberg CH, McIntosh R (1952) Can J Chem 30:1012
15. Schechter S, Wade WH, Wingrave JA (1977) J Colloid Interface Sci 59:7
16. McCaffery FC, Haynes JM (1977) J Colloid Interface Sci 59:24
17. Bangham DH, Saweris W (1952) Trans Faraday Soc 48:749
18. Derjaguin BV, Zorin ZM (1957) Proc 2nd Int Conf Surf Activity 11:145
19. Balyakova LA, Varvarin A M (1999) Colloids Surf 154:285