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SHORT COMMUNICATION

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The kinetics of silylation of hydroxylated silica II CPG-10 porous glasses

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Abstract The kinetics of chemisorption of trimethylchlorosilane, trimethylbromosilane, and triethylchlorosilane on samples of porous silica, CPG-10 porous glasses, of varying pore diameter were investigated and found to follow a first-order kinetics law in which the reaction is retarded by one of its products. At constant temperature, the rate was found to increase with increasing diameter of the pores in the range used. Increasing the molecular cross-sectional area of the adsorptive, the silane molecule, in the range 0.35–0.465 nm^2 decreased the rate of reaction.

Introduction

The surface properties of porous hydroxylated adsorbents are altered by the chemisorption of silanes. As an example, the wettability of these adsorbents can be manipulated by stepwise fractional hydrophobisation by partial adsorption of silanes. This alters their adsorptive properties, capillary condensation behaviour and contact angles with various adsorbates [1]. Because of the consequent variable surface properties, these modified adsorbents are finding increasing applications in chromatography, as standards for evaluating pore parameters, as well as for standardising techniques such as mercury porosimetry [2, 3].

Although much work has been done on the silylation of silica, porous samples have rarely been used. The present note reports investigations of the kinetics of silylation of these porous adsorbents by studying the effect of pores of the adsorbent as well as the effect of the diameter of the silane molecule on the kinetics of silylation of porous silica, a CPG-10 series of glasses similar to Vycor.

The rate of a surface reaction is dependent on the flux, J, to the surface of the reactant molecules. In porous solids, the flux is affected by the diffusion of reactants from the bulk phase to the inner surface. The effective diffusion coefficient, D_{eff}, for solute i is given by

$$D_{\mathrm{eff}} = \frac{\varepsilon_{\mathrm{p}} D_i}{\tau} \ , \tag{1}$$

where D_i is the diffusivity in the bulk phase, ε_{p} is the proportionality factor, which represents the internal porosity and τ is the tortuosity, which represents the increased diffusion path length due to the winding nature of the pores. In addition to the mean diameter of the pores, D, the molecular diameter, d_i, also affects diffusion in porous solids. Three broad regimes can be identified [4]. These are

1. $D \gg d_i$: diffusion is similar to bulk diffusion and is proportional to D.
2. If D is only a few times larger than d_i, then $D_{\mathrm{eff}} \propto D^{-1}$ and in this case adsorption is enhanced by adjacent walls.
3. If D is of the order of d_i, then repulsion forces dominate and diffusion is then activated.

If the vapour pressure is high and the pores are large ($D > 100$ nm) then the diffusion process is that of the bulk-diffusion type. If small pores are present and the vapour pressure is low Knudsen diffusion dominates, resulting in a small effective diffusivity,

$D_{\mathrm{eff}(i)}$,

$$D_{\mathrm{eff}(i)} = \varepsilon_{\mathrm{p}} D_i^k / \tau \ . \qquad (2)$$

In this case, the mean free path, λ_i, is larger than D. In broad terms, if $\lambda/D > 10$ Knudsen diffusion dominates, if $0.1 < \lambda/D < 10$ a transition mechanism operates, and if $\lambda/D < 0.1$ bulk diffusion dominates.

Experimental

Materials

CPG-10 porous glass (Vycor)

Granules of CPG-10 glass (BDH Chemicals, Poole) in the range of pore diameters from 12.5 to 200.0 nm were used as the porous glass samples. These were supplied as granules of 120–200-mesh size. More detailed specifications are given in Table 1.

The porous silica material is of general composition 96% SiO_2, 3% B_2O_3, and 0.4% Al_2O_3. It has a refractive index of 1.458, a density of 3.18 kg/dm^3, and a controlled and narrow pore size distribution [5, 6]. It has a continuous interconnected system of pores, with more or less cylindrical channels punctuated with well-distributed enlargements which tend to act as "blind-pores" [3, 7–11].

CPG- 10 porous glasses, such as Vycor, are quite stable to heat and chemical action [13]. The possibility of predetermined alterations to their pore sizes, pore size distribution, surface chemistry [17], and surface area makes them versatile materials [13] for use as a pore structural model standard [2], as well as for use as a stationary phase support in chromatography and as a support for catalysts [5].

Preparation of Vycor

The physical structure of CPG-10 porous glasses, such as Vycor, and, to a lesser extent, their surface properties originate from the method of their preparation. They are prepared using the Vycor process patented by Nordberg and Hood [14] in 1934. SiO_2 B_2O_3 and Na_2O are mixed in their formula mass ratios [4] and heated to melting point. The molten mixture is cooled to temperatures only slightly above the annealing point (avoiding serious deformations) and then annealed to induce phase-separation. Two intermingled phases result: one which is silica-rich and soluble in alkali and another which is boric oxide rich and soluble in hot dilute acid. This selective solubility of the phases enables alterations to surface structure and properties. Leaching with acid removes the boric oxide phases, leaving a cellular rigid structure similar to the original shape but containing a network of interconnected pores and capillaries. The pore sizes and pore size distributions of the products are determined by carefully controlling the phase-separation process [14] and the extent of leaching [17]. Heating Vycor to temperature of 673 K or higher, in addition to removing surface silanols, causes rearrangements of its structure [18], with the migration of boron to the surface. Rehydration of this surface results in the formation of very reactive hydroxyl groups attached to boron atoms [18].

Table 1 Corning controlled-pore glasses, CPG-10 series

Product specifications [12]				
Nominal pore size (nm)	12.5	17.5	37.0	200.0
Maximum variation in pore size from nominal value	20%	15%		
Minimum pore volume (cm^3 gm^{-1})	0.5	0.7		
Maximum variation in pore size ± from average pore diameter	10%	10%		
Batch specifications				
Average pore diameter (nm)	12.0	17.6	41.2	180.5
Diameter distribution % ±	10	7.9	9.2	7.5
Pore volume (cm^3 gm^{-1})	0.59	1.07	0.9	0.73

The samples used in the present work were those of mean pore diameters of 200.0, 37.0, 17.5, and 12.5 nm and whose specific surface areas, calculated from the adsorption of benzene, are 23.0, 71.0, 135.0, and 90.0 m^2 g^{-1}, respectively. In the present work, the benzene-specific surface areas were preferred to the nitrogen-specific surface areas because the cross-sectional area of 0.423 nm^2 for the benzene molecule is quite close to the cross-sectional area of 0.37 nm^2 of the silyl group. Therefore, the two molecules have comparable penetrations of the adsorbent. The samples were pretreated and reacted under similar conditions as given in Table 2.

Reagents

Trimethylchlorosilane (TMCS), trimethylbromosilane (TMBS), triethylchlorosilane (TECS), and triphenylchlorosilane (TPCS), all from BDH Chemicals, Poole, of 99.99% purity were chosen as the organosilanes for the study. They were transferred directly to the samples reservoirs. The liquid silanes were purified by using the freeze-thaw procedure described in an earlier article [20]. These silanes were chosen so that in addition to investigating the effect of the size of the pores on the kinetics molecular size effects could also be studied.

Apparatus

A schematic diagram of the apparatus used for the silylation of Vycor is given in Fig. 1; an outline of its mode of operation together with the method used to follow the reaction are given next. Details were described in an earlier article [20]. A mercury diffusion pump backed by a rotary pump was used to achieve a vacuum of about 10^{-5} torr as checked with a Mcleod gauge. The pressure in the apparatus was followed using a calibrated pressure transducer,

Table 2 Silylation runs. Reaction temperature of 653 K, pretreatment temperature of 673 K, vapour pressure for triethylchlorosilane (*TECS*) of 6.5 mm, for trimethylchlorosilane (*TMCS*), and trimethylbromosilane (*TMBS*) of 60 mm Hg. All runs were performed up to infinity, i.e. until no further change in mass occurred

Silane /run		Pore diameter, D, (nm)	rate coefficient k ± 5%	Path lenth, λ, (nm)	λ/D
TMCS					
	1	200.0	2.2×10^{-5}	2161	11.4
	2	37.0	1.5×10^{-5}	2285	61.8
	3	17.5	1.1×10^{-5}	2285	130.6
TMBS					
	4	17.5	5.6×10^{-5}	2285	130.6
	5	12.5	1.5×10^{-5}	2285	182.8
TECS					
	6	17.5	4.1×10^{-7}	15,875	907.1

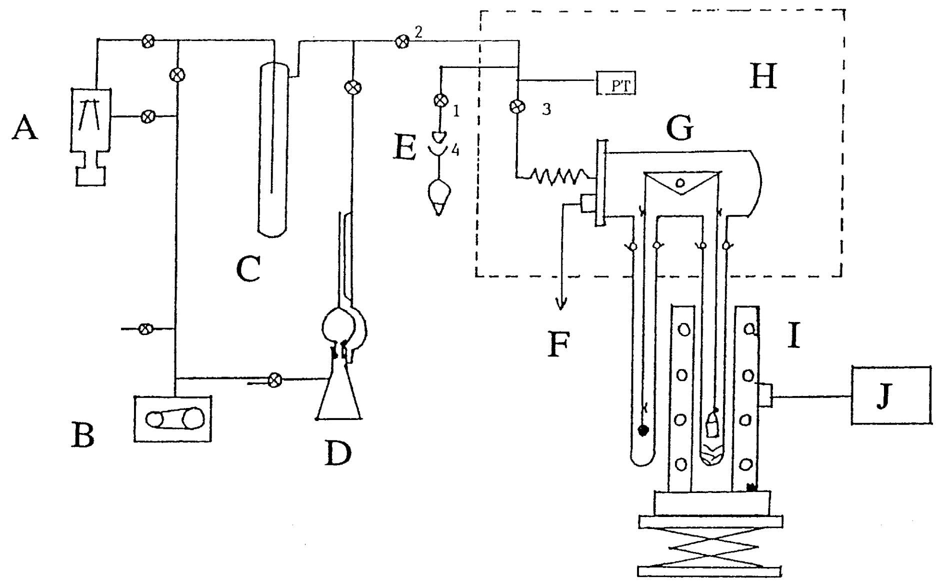

Fig. 1 The apparatus used for the study of the kinetics of silylation of hydroxylated silica CPG-10 porous glasses. *A*, mercury diffusion pump; *B*, rotary pump; *C*, cold trap; *D*, McLeod gauge; *E*, silane sample bottle; *F*, voltage output; *G*, microforce balance; *H*, air thermostat; *I*, furnace; *J*, electronic control unit

whose output (in millivolts) was assumed to remain linear with respect to pressure in the pressure range 0–760 torr.

The extent of silylation was followed gravimetrically using a vacuum electronic microbalance connected to the vacuum frame using a brass flange and flexible metal bellows (C.I. Electronics, Salisbury). Details of the balance and its mode of operation have been described elsewhere [21]. The details of the conditions of the silylation reaction are given in Table 2.

Procedure

A known quantity of CPG-10 porous glass powder (about 200 mg) was loaded into a silica bucket. In order to minimise spluttering of the powder, the bucket was plugged with glass wool which had earlier been fully silylated to ensure that only changes in mass due to the silylation of Vycor were measured during the experiment. The bucket was then suspended from a microbalance, which had been calibrated prior to loading. The sample were evacuated at room temperature, very slowly initially, in order to avoid losing the powder through spluttering. It was then evacuated to a pressure of 10^{-5} torr or lower at a temperature of 100 °C for a total period of 24 h or until the sample had reached a constant weight. The sample was then pumped at the required temperature for a further 4 h and then rehydrated overnight using a water vapour pressure of about 10 cm Hg. Excess water vapour was pumped off at the appropriate temperature; the sample was then gradually brought to the reaction temperature. With the reaction chamber isolated, the large volume of the apparatus was filled with the appropriate silane at a predetermined pressure. As the silane vapour was allowed into the reaction chamber, the calibrated chart recorder was started. The reaction was continued until there was no further increase in weight as shown by a straight flat trace on the chart recorder.

Results and discussion

The details of the experimental runs and the conditions used are shown in Table 2. The vapour pressure of TMCS used in this work were very high (60 cm Hg in a volume of 2 l Table 2). The reservoir of TECS, which is a liquid of low vapour pressure at room temperature, was open to the reaction mixture during the experiment to ensure constant vapour pressures throughout the run. Therefore, a type of bulk diffusion was in operation and the rate of adsorption should increase with increasing pore diameter.

The results obtained are given in Fig. 2 as a plot of mass of adsorbate per unit area of adsorbent against reaction time. The total uptake of trimethylsilyl groups has the trend Vycor of diameter 200 nm (v200) > v17.5 > 12.5 and aerosil > v37.0. With the

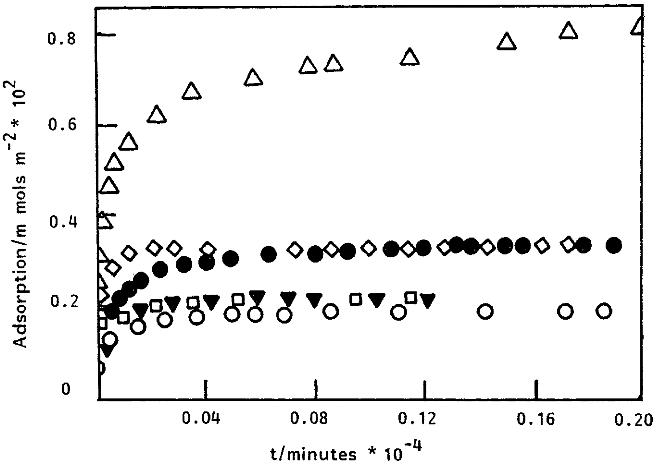

Fig. 2 Chemisorption of silanes at 653 K by CPG-10 porous glass samples of varying pore diameter pretreated at 673 K. (◇) trimethylbromosilane (*TMBS*) on Vycor of 17.5 nm diameter (v17.5 nm), (□) trimethylchlorosilane (*TMCS*) on Aerosil, (●) TMCS on v17.5 nm, (○) TMCS on v37.5 nm, (▼) TMBS on v12.5 nm, (△) TMCS on v200.0 nm

exception of v200 and Aerosil, the trend follows the specific surface area trend of 23 $m^2\,g^{-1}$ for v200, 135 $m^2\,g^{-1}$ for v17.5, 90 $m^2\,g^{-1}$ for v12.5, 200 $m^2\,g^{-1}$ for aerosil, and 71 $m^2\,g^{-1}$ for v37, respectively, as measured using a benzene molecule of cross-sectional area 0.423 nm^2. The unexpected large uptake by v200 is rather surprising in view of its very small specific surface area. It is though to originate from the more easily accessible silanols in the interior due to the wider necks of the large pores. This is probably augmented by a higher chemisorption force field in the anterior due to the presence of large quantities of very reactive hydroxyl groups attached to boron atoms, which migrated to the surface during annealing (see preparation of Vycor). This force field would enable deeper penetration by the silane molecules compared to benzene molecules, which are only physisorbed. This is also reflected qualitatively in Fig. 2 by the higher initial rate by v200 compared to the other samples.

Figure 3 shows the results fitted to the retarded reaction model (derived in earlier work [20]) assuming diffusion does not limit the reaction. According to this model, the reaction follows the law

$$\left[\frac{1+b}{t}\right]\ln\left\{\frac{M_\infty}{M_\infty - M_t}\right\} - \frac{M_t b}{M_\infty t} = k_{a1} \ , \tag{3}$$

where k_{a1} is a rate coefficient, b is a composite coefficient [20], M_t is the mass adsorbed at any time t, and M_∞ is the final mass adsorbed.

The results are fitted on the model by plotting (M_t/t) against $(1/t)\ln\{M_\infty/(M_\infty - M_t)\}$, which should give a straight line whose slope yields $[M_\infty(1+b)/b]$ and an intercept which yields $((-M_\infty/b)k_{a1})$.

According to this model, the rate coefficients obtained for TMCS and TMBS show that the rate of reaction increases with increasing pore diameter. They also show that the rate decreases with increasing molecular diameter (Table 2). The good fit of the results to the model, except in the case of TMBS at this temperature (Fig. 4), should be understood bearing in mind that in the presence of narrow pores and at low vapour pressure diffusion is activated, just like the chemical reaction.

Furthermore, while the pore diameters may appear large (12.5–200.0 nm) compared to the molecular diameters (0.67–0.77 nm) they are just averages and are obtained by assuming a pore model, which is idealistic. They may represent the diameters of the larger cavities present in CPG-10 porous glass (Vycor) and not the narrow entrances to these cavities. In this case, it is important to consider the pore size distribution from the adsorption branch, which represents the large internal cavities, as well as from the desorption branch, which represents the narrow entrances. Both parameters have a role to play in influencing diffusion and, hence, the rate of chemisorption.

The effect of the molecular diameter on the reaction kinetics is also shown in Table 2. The rate constant for the reaction using TMCS is larger than that for the reaction using a larger molecule, TECS, for CPG-10 porous glass of the same pore diameter of 17.5 nm. This indicates that the reaction rate decreases with increasing diameter of the reactant molecule. An attempt to use TPCS yielded poor results because of the very large molecular diameter involved in this case. It is thought that the TPCS could not enter the pores of Vycor. Good results have been obtained with this adsorptive on nonporous Aerosil [21].

A study of diffusion in CPG-10 glass is essential at the reaction temperatures using a wide range of pressures of an inert adsorptive of similar molecular structure to the silanes. This would clarify the effect of diffusion an the reaction at the reaction temperatures and pressures. Useful information may also be obtained

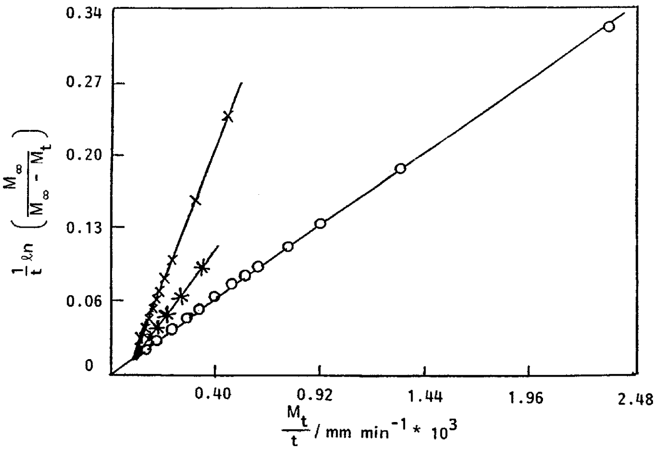

Fig. 3 The effect of the pore diameter on the kinetics of the TMCS silylation of CPG-10 porous glasses using the retarded reaction model. Diameter 200.0 nm (○), diameter 37.1 nm (×), diameter 17.5 nm (*)

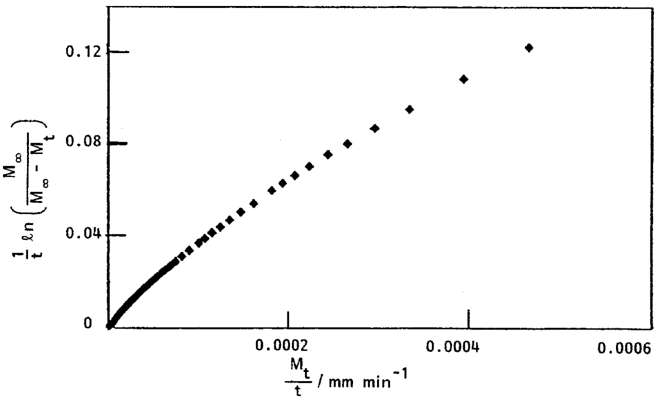

Fig. 4 Kinetics of the TMBS silylation reaction at 653 K on CPG-10 porous glass (diameter of 17.5 nm) pretreated at 673 K

by silylating porous silica samples of various pore diameters in the narrow-neck range and of fairly uniform pore cross-section (i.e. without large cavities and narrow necks) with a narrow pore size distribution. This should show the effect of the necks on the silylation reaction on CPG-10 porous glasses.

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