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Preparation of glass and fused-silica capillary columns coated with immobilized XE-60

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The modification of deionized silica surfaces by persilylation with monofunctional silylating agents[1] results, in addition to increasing inertness, in a decreased surface energy. Consequently, subsequent coating is successful only with more or less apolar phases the surface tension of which allows a sufficiently homogeneous spreading on the modified support surface.

Procedures have been described[2] which to increase the surface energy by introducing dipoles, while preserving the inertness. Our attemps to use the recommended cyanopropylmethylcyclosiloxanes for the persilylation of glass capillaries led to pyrolysis of the cyclosiloxanes, resulting in dark brown deposits whenever the reaction was carried out at 350°C for several hours.

In order to interpret this observation, we have to start with the assumption that a cyclic siloxane is attacked by a surface silanol group (*cf.*, Fig. 1), resulting in ring opening. The linear siloxane produced is bonded to the former surface silanol, while a new silanol group is formed at the free end of the siloxane. Further reaction with a second surface silanol group to build a bridge over a section of the surface, *i.e.*, to regenerate a cyclosiloxane, would be the most desirable outcome (Fig. 1a). However, we expect the probability of this reaction to be relatively low, particularly on a strongly hydroxylated surface (as is that of leached glass), and with a siloxane containing sterically hindering groups such as phenyl. The only alternative would seem to be attack of terminal silanol groups on other siloxane molecules (cyclic and/or linear). At the high temperature used for persilylation, this type of reaction will occur very rapidly, and result in continued opening and closing of rings of different sizes, and in lengthening and shortening of linear chains; the average size of the rings and chains will rapidly approach the equilibrium size typical for the given temperature, or the chemical nature of the chosen cyclosiloxane, respectively.

We believe the modest thermal stability of the system (insoluble, brown deposits formed) to be explained best by assuming unknown side reactions to occur during the silanol/siloxane reactions. Accordingly, end capping the linear siloxanes is expected to hinder the side reactions (Fig. 1b). However, the end-capping agent has to be sufficiently sterically hindered so as not to compete with the cyclosiloxane
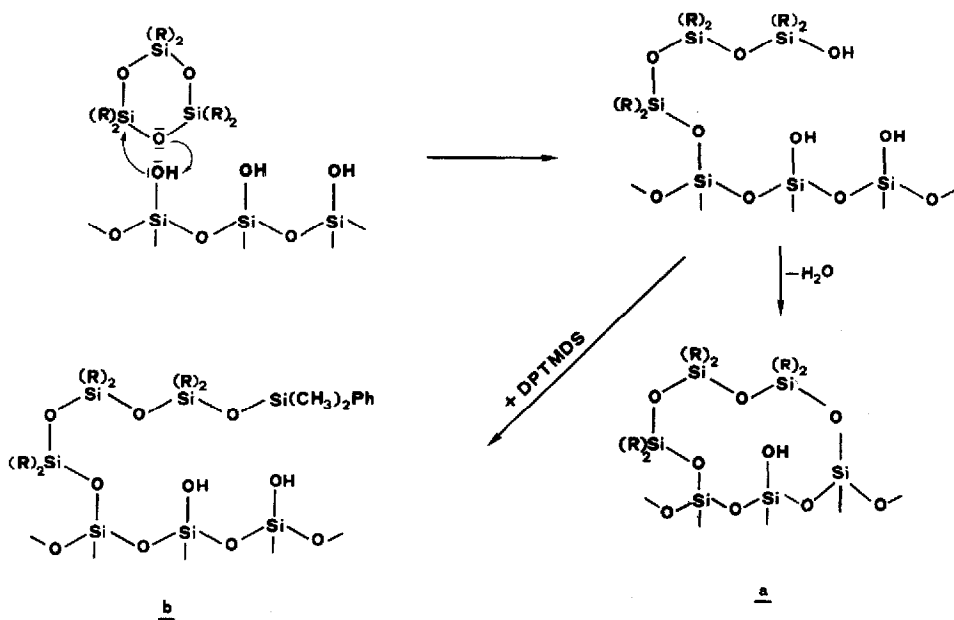
Fig. 1. Tentative mechanism for the reaction of a cyclic siloxane with a hydroxylated silica surface. (a) Double condensation (recyclization) on the silica surface; (b) Monofunctional reaction with the silica surface, followed by end capping with DPTMDS.

for reaction with the surface silanols. For instance, the common monofunctional silylating agent hexamethyldisilazane produces a primarily trimethylsilylated silica surface with little increase in surface energy.

In fact, persilylation with a mixture of bis(cyanopropyl)hexamethylcyclotetrasiloxane and diphenyltetramethyldisilazane (DPTMDS) could be carried out at 370°C for 8 h without any evidence of pyrolysis. The added monofunctional agent clearly increased the thermostability of the reacting system while not hindering the increase in surface energy.

A successful persilylation based on thermal degradation of polysiloxane phases has been described by Schomburg et al.[3]. It is known that, at temperatures above 300°C, linear polysiloxanes release cyclic ethers of various ring sizes[4,5]. We believe, therefore, that persilylation with cyclic siloxanes, and with the degradation products of linear polysiloxanes, are based on the same mechanisms. Thus, there should be no disadvantage in replacing an individually synthesized, non-commercially available, cyclosiloxane[2] by a common stationary phase of corresponding structure.

The procedure we describe here is based on the use of a mixture of the traditional stationary phase XF-1150 (polysiloxane with 50% each of cyanoethyl and methyl groups) and DPTMDS. The deactivated silica surface obtained can successfully be coated with stationary phases of medium polarity.

EXPERIMENTAL

Leaching

Glass (Duran) and fused-silica capillaries (20 m × 0.3 mm) were used. The Duran capillaries were filled with 20% hydrochloric acid to 92% of their volume. After sealing under vacuum, leaching was carried out at 180°C for 12 h[1]. The fused-silica capillaries were rinsed with 3% hydrochloric acid, immediately sealed and kept at 220°C for 7 h[6]. All capillaries were then rinsed with twice their volume of 1% hydrochloric acid, and dried with both ends connected to a vacuum. The drying conditions were 280°C for 2 h for Duran, and 240°C for 1 h for fused-silica, capillaries.

Persilylation

The silylating mixture consisted of two volume of XF-1150 (Alltech/Socolabo, Pully-Lausanne, Switzerland) and one volume of DPTMDS (Fluka, Buchs, Switzerland). One volume of this mixture was diluted in four volumes of methylene chloride. The solution was sucked into the capillaries so as to fill 15% of their length. The plug was moved with nitrogen at a rate of 4 cm/s. When the solution left the capillary (without a buffer column), the carrier connection was immediately switched to the exit end, and the bulk of solvent was evaporated by a stream of nitrogen at a pressure of 0.5 bar for 10 min. Complete evaporation of methylene chloride was assured by keeping the capillaries for 10 min in a gas chromatograph at 80°C under 0.2 bar of hydrogen. Both ends were washed with methylene chloride, then connected to a vacuum for 15 min and flame-sealed under vacuum. The capillaries were kept at 360 ± 5°C for 7 h, the fused-silica capillaries at 330 ± 5°C for 12 h (the oven thermometer should be carefully calibrated). After cooling and opening, the capillaries were rinsed with toluene, methanol and diethyl ether, and dried under a stream of nitrogen.

Coating and immobilization

The coating solution contained 0.4% XE-60 and 1% of its weight of dicumyl peroxide (Elfa, Zürich, Switzerland) in pentane–methylene chloride (1:1, v/v). Static coating was carried out according to ref. 1. At the inlet end, 1.5 m were left uncoated as a retention gap[7]. Both ends of the coated columns were connected to a vacuum and flame-sealed. The columns were then heated to 160°C and the temperature was programmed at a rate of 0.5°C/min to 200°C. After opening, the immobilized columns were kept at 200°C for 6 h and at 240°C for 4 h under a flow of hydrogen, and were then tested.

RESULTS AND DISCUSSION

Typical test chromatograms for XE-60 coatings on Duran glass and fused silica are shown in Fig. 2.

Whereas the separation efficiency and inertness of the two types of column are comparable, the thermal stability of XE-60 on Duran is better than on fused silica (less baseline drift with Duran column heated beyond 230°C). We attribute this difference to the larger density of surface silanols on Duran available for condensation with residual terminal silanols of the polysiloxane phase, which stabilizes the coating.
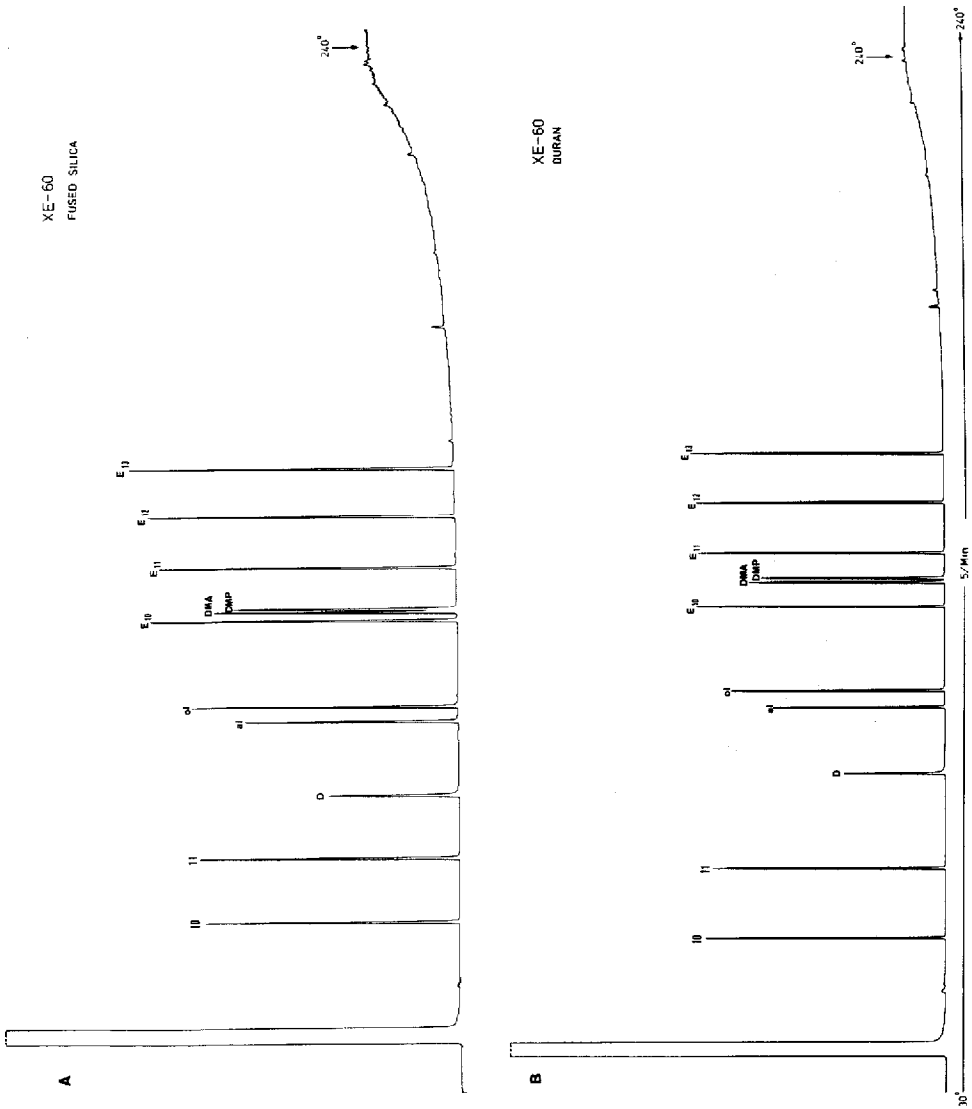
Fig. 2. Chromatograms obtained on identical coatings (XE-60) on identically persilylated surfaces: A, fused silica (18 m × 0.32 mm); B, Duran glass (20 m × 0.32 mm). Hydrogen flow-rate: 0.5 m/s. Temperature: 30–240°C, at an 5°C/min. Peaks: 10 = n-decane; 11 = n-undecane; D = 2,3-butanediol; al = nonanal; ol = octanol; E_{10} = methyldecanoate; E_{11} = methylundecanoate; DMA = 2,6-dimethylundecanoate; E_{12} = methyldodecanoate; E_{13} = methyltridecanoate. Note the smaller baseline drift and the increased polarity with Duran, probably due to residual surface silanols; there is virtually no difference in inertness.

We are aware of the very tentative character of our hypotheses concerning the functioning of a mono/bifunctional silylating agent. However, these ideas have provided a fruitful working model which is supported by various experimental evidence. Instead of reacting with the free ends of bonded polysiloxane sections, the end-capping agent will also compete with the siloxane for the surface silanols. However, we do not consider this competition to be serious, since XE-60 does not spread on a purely DPTMDS-persilylated surface of Duran or fused silica. Furthermore, our attempt to promote the competitiveness of the polysiloxane by increasing its relative concentration with respect to DPTMDS was unsuccessful. Lowering the proportion of the disilazane below the ratio indicated in Experimental resulted in a less thermally stable system, as shown by the partial pyrolysis which produced brown deposits. Similarly, the surface energy could not be increased by increasing the extent of phenyl substitution of the disilazanes[8].

Coating a polar phase on Duran requires less optimization than on fused silica. Whereas the deionization and dehydration of Duran occurred under the same conditions as described for the preparation of apolar columns[1], the treatment of fused silica differed from that applied for apolar coatings. Increasing the amount of dehydration beyond that indicated caused the method to fail, probably because small amounts of water are necessary for the production and the reaction of degradation products of the polysiloxane.

As a radical generator for the immobilization of XE-60, we prefer dicumyl peroxide because of its greater efficiency compared to an azo compound. As expected, the immobilization improved the thermal stability of the coating. We were unable to detect any evidence for an influence of the peroxide on the functional groups of the phase, as recently presumed[9].

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