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Studies on texture and properties of porous glass and silica gel used as supports for chemically bonded amino phases for high-performance liquid chromatography

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ABSTRACT

Two different types of siliceous materials, glass beads with a controlled porosity (PG) and silica gel (SG), were studied. One important difference between SG and PG is the presence of metal atoms in the PG surface and in the bulk. The surface concentration of these metals can be easily enhanced by appropriate secondary thermal treatment, thereby creating new adsorption sites in the PG surface. This thermal treatment results in migration of residual metal oxides such as boron, sodium or aluminium towards the PG surface, thereby forming highly active centres. The increase in the surface heterogeneity and the changes in the texture of PG subjected to secondary thermal treatment are responsible for the differing physico-chemical properties of such materials. SG and PG were modified with mono- and trifunctional 3-aminopropylsilanes. Before and after chemical modification all the materials were characterized by nitrogen sorption, Fourier transform IR spectroscopy, cross-polarization magic angle spinning NMR spectroscopy, secondary ion mass spectrometry and elemental analysis. The chromatographic properties of the modified PG phases were compared with those of the corresponding SG phases.

INTRODUCTION

Silica gel (SG) is the most commonly used support for chemically bonded phases (CBP), but porous glass (PG) also has promising properties for this application: porous glasses can be prepared with a highly controlled porosity and show relatively greater thermal, mechanical and solvolytic resistance [1–6].

PG is usually obtained from three-component glass melts in the Vycor glass region (typical composition: 40–85% silica, 4–15% sodium oxide, 18–40% boric oxide and about 10% other oxides [1–3,7]). This material is heated to about 700°C in order to bring about a phase separation into two continuous and immiscible phases: the silica phase, which is insoluble in acids, and the acid-solube alkali–borate phase [1–3,6,7]. The latter is removed by acid leaching, thereby forming a highly porous skeleton, consisting of SiO_2 (*ca.* 93–97%), B_2O_3 (*ca.* 3–6%) and other oxides (*ca.* 1%) [1,8–10].

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On the basis of recently published experimental investigations [11], we submitted PG material to a secondary thermal treatment (heating at 620°C for 50 h), thereby changing the PG texture in order to obtain a material with a strictly defined pore structure and an increased boron concentration at the surface. Boron atoms on diffusing to the PG surface react with the water present to form new active boranyl sites [3,11–13]. This effect must be taken into consideration when chemical modifications of the PG surface are carried out, because the reactivity and the adsorption properties of PG surfaces are governed mainly by silanol (SiOH) and boranyl (BOH) centres, the latter showing a significantly higher acidity and reactivity [1,3,9]. The new hydroxyl centres created by the secondary thermal treatment increase the surface heterogeneity and thereby may affect the mechanism of chemical reactions occurring on the surface [14].

In this work, particular attention was paid to the differences in the physico-chemical properties of PG and SG materials of similar porosity. Both siliceous materials were modified by 3-aminopropylsilanes with different functionality. The materials obtained were applied in the high-performance liquid chromatographic (HPLC) analysis of saccharides.

EXPERIMENTAL

Materials and reagents

Two types of siliceous materials, porous glass (PG) (Chemical Reagents Factory, Lublin, Poland) and Nucleosil-100 (SG) (Machery, Nagel & Co., Düren, F.R.G.) were used. Boron surface enrichment of the PG by secondary thermal treatment (PG_T) was carried out in a temperature gradient-free oven (Heraeus, Hanau, F.R.G.) at 620°C for 50 h. The physico-chemical characteristics of the materials used are given in Table I.

For chemical modification, 3-aminopropyltriethoxysilane (NH_2-T) and 3-aminopropyldimethylmethoxysilane (NH_2-M) (Fluka, Buchs, Switzerland) were used. All solvents, e.g., toluene, benzene, hexene, methanol, acetonitrile, dioxane and water (Merck, Darmstadt, F.R.G.), were of analytical-reagent grade.

Stainless-steel tubes (125 × 4.6 mm I.D.) were purchased from Grom and Stagroma (Herrenberg, F.R.G.).

TABLE I

PHYSICO-CHEMICAL PROPERTIES OF TWO TYPES OF SILICEOUS SUPPORTS

S = Spherical; I = irregular; d_p = mean particle size (μm); pH = for a 5% aqueous suspension; S_{BET} = specific surface area (m²/g).

No.	Type of support		Shape of particle	d_p	pH	Porosity		
						S_{BET}	D	V_p
1	Nucleosil-100	SG	S	7.0	6.15	345	9.8	1.01
2	Porous glass	PG_T	I	8.5	7.45	248	8.8	0.83
		PG			6.80[a]	332[a]	9.8[a]	0.99[a]

[a] Data before thermal treatment (620°C for 50 h).

Chemical bonding procedure

The chemical surface modification was carried out in glass reactors under a nitrogen atmosphere, carefully avoiding moisture [15]. The method and reaction conditions are described elsewhere [16].

Column packing

A slurry of 2 g of the prepared phases in 35 ml of dioxane–methanol (2:5, v/v) is placed in an ultrasonic bath for 5 min and then filled into the clumn using 50 ml acetonitrile as a packing solvent [16]. All columns were packed with a Shandon (Frankfurt, F.R.G.) packing pump under a constant pressure of 50 MPa.

Apparatus

The parameters characterizing the porosity, *i.e.*, specific surface area (S_{BET}), pore volume (V_P) and mean pore diameter (D), of the packings were determined by nitrogen sorption using a Model 1800 Sorptomatic instrument (Carlo Erba, Milan, Italy).

The particle shape and the mean particle size were determined by microscopic methods [15] using a Type MP-3 projective microscope (Polish Optical Factory, PZO, Warsaw, Poland).

The pH values of aqueous suspensions of both siliceous materials (5%, v/v) were determined with a Model PHM-84 pH-meter (Radiometer, Copenhagen, Denmark) according to Engelhardt and Müller [17].

Secondary ion mass spectrometry (SIMS) was carried out with Ar^+ primary ions (Telefocus Atomica, Munich, F.R.G.) with an acceleration voltage below 1.5 keV in order to minimize charging effects on the isolating samples. Spectra were recorded under "static" conditions (primary ion current < 5 nA). The poor conductivity of the samples necessitates charge compensation by low-energy electrons generated by a flood gun (Leybold, Cologne, F.R.G.). Experimental details have been given elsewhere [18].

Solid-state NMR measurements were performed on a Bruker (Rheinstetten, F.R.G.) MSL 200 spectrometer with samples of 200–300 mg in double-bearing rotors of zirconia. Magic angle spinning (MAS) was carried out at a spinning rate 4 kHz. ^{29}Si cross-polarization (CP) MAS-NMR spectra were recorded with a pulse length of 5 μs together with a contact time of 5 ms and a pulse repetition time of 2 s. All NMR spectra were externally referenced to liquid tetramethylsilane (TMS) and the chemical shifts are given in parts per milion (ppm).

Fourier transform (FT) IR spectra were recorded on a Model FS 48 instrument (Bruker) equipped with a TGS detector. The PG and SG samples were diluted 1:10 (w/w) in dry potassium bromide (Merck).

The surface concentration of the aminosilyl ligands (α_{RP}) on the prepared packing surfaces was calculated from carbon and nitrogen contents, determined with a Model 240 CHN analyser (Perkin-Elmer, Norwalk, CT, U.S.A.).

Chromatographic measurements were carried out on a Model LC-31 liquid chromatograph (Bruker) equipped with a Model 7121 sampling valve (Rheodyne, Berkeley, CA, U.S.A.) and a Model 3380A computing integrator (Hewlett-Packard, Karlsruhe, F.R.G.). Chromatograms were recorded with a refractive index detector.

RESULTS AND DISCUSSION

Table I gives the physico-chemical data for the investigated SG and PG materials prior to their modification with 3-aminopropylsilanes. It is apparent that the porosity data (S_{BET}, V_P and D) for the initial glass (PG) and SG are about the same. Secondary thermal treatment of the glass material, however, leads to a significant reduction in these values [11,14] (PG_T), thus indicating both a sealing process of small pores accompanied by the formation of a secondary silics subphase. In addition, the heat-induced migration of metal oxides towards the PG surface increases the surface heterogeneity by creating new active sites [1,3,7–14]. Information on the pore structure is obtained by nitrogen low-temperature adsorption–desorption isotherms and the pore-size distribution curves, both presented in Fig. 1.

The hysteresis curves indicate a cylindrical pore shape for all the materials investigated and that, in addition, secondary thermal treatment applied to PG brings about a 20% decrease in the pore volume, which is in good accord with the decrease found in S_{BET} (Table I). From the left part of the PG_T isotherm we conclude that the formation of smaller mesopores occurs as a consequence of the diffusion of metal oxides towards the PG_T surface during secondary thermal treatment [11,14]. This assumption is confirmed by the narrow pore distribution for PG and PG_T (Fig. 1). The distribution curves also confirm the formation of a secondary silica subphase with a controlled porosity [1,3,14,19].

In order to obtain direct information about the elemental composition of the substrate surface, "static" SIMS conditions (primary ion current <5 nA) were applied. Under such conditions the charging effects due to the isolating properties of the investigated siliceous materials are minimized but charge compensation with low-energy electrons is still required. Fig. 2 shows the "static" SIMS spectra of the three different materials.
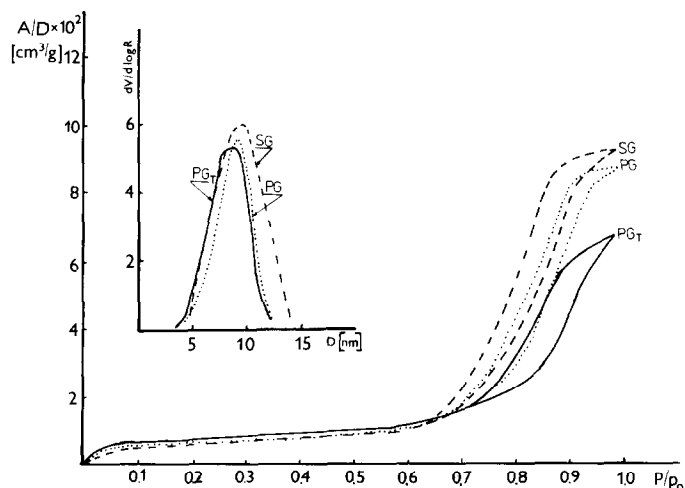

Fig. 1. Adsorption–desorption (A/D) isotherms of nitrogen and pore distribution curves. For notation, see text; p/p_0 is he relative pressure of the adsorbate.

The "static" SIMS spectra of SG (Fig. 2a) and PG (Fig. 2b and c) reflect their different chemical compositions. Whereas the SG (Nucleosil-100) is a highly pure siliceous material, porous glass is a polycomponent material, containing various metal oxides such as sodium, potassium, boron, aluminium oxides [1,6]. The increased
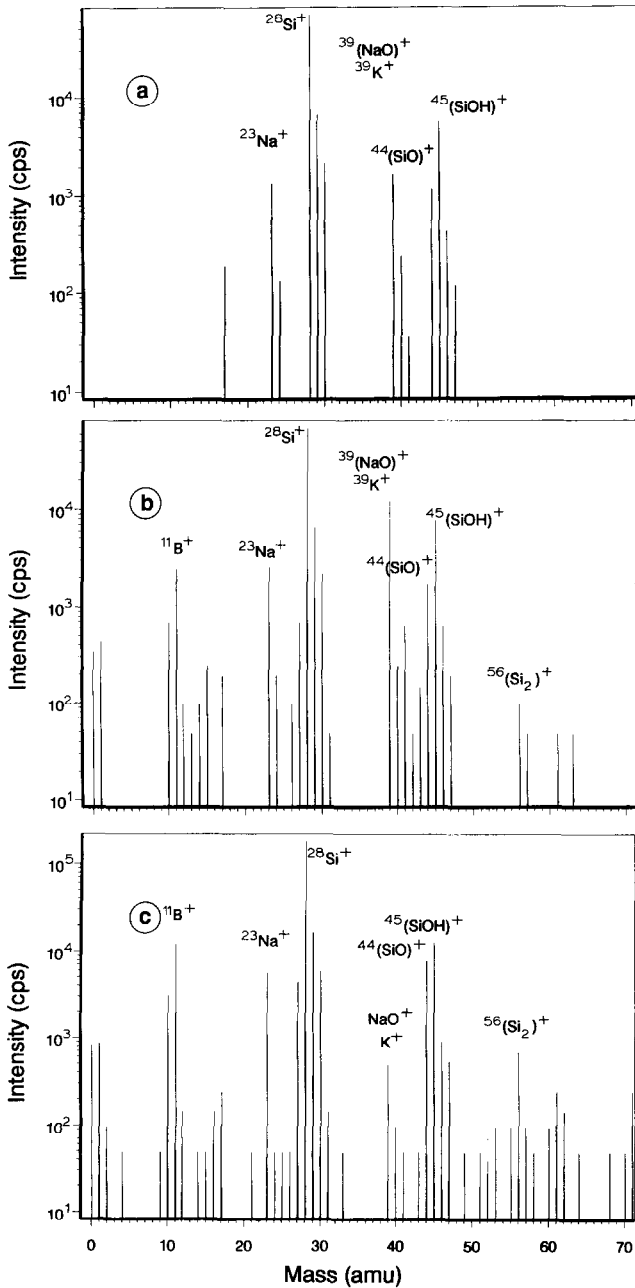

Fig. 2. Positive static SIMS spectra of the bare siliceous materials: (a) SG; (b) PG; (c) PG_T.

surface concentration of these elements effected by the secondary thermal treatment appears from the comparison of the "static" SIMS spectra of PG (Fig. 2b) and PG_T (Fig. 2c). In order to circumvent the quantification problems inherent in the SIMS method, the ^{28}Si surface concentration was considered to be constant throughout the secondary thermal treatment. Therefore, the ^{28}Si signal intensity can be used as an internal standard. The changes in the elemental composition of the substrate surfaces were evaluated from the SIMS signal intensities relative to the ^{28}Si signal. The increased pH of PG_T compared with the initial material (Table I) is a further indication for the increased sodium and potassium surface concentrations [14]. Our values for the changes in the boron surface concentration determined by this method are consistent with recently published data obtained by other methods [1,3,11,14,19].

In Fig. 3 the ^{29}Si CP-MAS-NMR spectra of the bare materials (SG, PG and PG_T) are presented. These spectra show the expected signals for Q_2 (geminal silanol groups, $\delta = -91$ ppm), Q_3 (vicinal and/or free silanol groups, $\delta = -100$ ppm) and Q_4 (siloxane groups, $\delta = -108$ ppm) [20]. No significant difference in the signal patterns between SG (Fig. 3a) and PG (Fig. 3b) is apparent. The secondary thermal treatment strongly affects the ^{29}Si spectrum of PG_T (Fig. 3c), mainly increasing the Q_3/Q_4 ratio and worsening the signal-to-noise ratio. The increase in the Q_3/Q_4 ratio is due to the fact that the cross-polarization efficiency is dependent on the Si–H distance. In the secondary thermal treatment, the dehydroxylation process that occurs reduces the number of protons in the PG_T surface [10,11]. This decrease in surface protons enlarges the average Si–H distance for those species which do not bear hydroxyl groups (Q_4), leading to a decrease in the signal intensity mainly for Si atoms involved in siloxane units (Q_4). The reduced proton concentration and thus reduced CP efficiency are also responsible for the overall low signal-to-noise ratio (Fig. 3c). Moreover, the increased boron and aluminium surface concentrations in the PG_T sample after secondary thermal treatment leads to an additional worsening of the signal-to-noise ratio and a slightly increased signal broadening of the $Q_3 + Q_4$ signal. Both effects are due to quadrupole coupling of the ^{29}Si ($I = 1/2$) with ^{10}B ($I = 3$), ^{11}B ($I = 3/2$) and ^{27}Al ($I = 5/2$), thereby disturbing the cross-polarization mechanism.

As reported in the literature [1–3], the degree of order in siliceous materials is proportional to the IR absorption band at 1100 cm^{-1}. Fig. 4 shows the FT-IR spectra of SG, PG and PG_T. The FT-IR spectrum of SG (Fig. 4a) shows a higher absorption intensity at 1100 cm^{-1} than that of PG (Fig. 4b), thus indicating a higher degree of order for SG materials, as has been reported previously [1,2]. The absorption band at 800 cm^{-1} can be ascribed to cyclic [SiO$_4$] tetrahedral structures. The intensity of this absorption band is increased by the secondary thermal treatment of the PG material (Fig. 4b and c).

The physico-chemically characterized SG and PG_T materials were used as supports for the preparation of chemically bonded amino phases with different structures.

In Table II the carbon and nitrogen contents and the surface concentration resulting from modifying the above-described materials with mono- and trifunctional 3-aminopropylsilanes are given. The highest surface concentration (α_{RP}) was obtained with trifunctional 3-aminopropylsilane as a modifier for SG and PG_T. It is interesting that SG/NH$_2$ yields a higher surface concentration than PG_T/NH$_2$. This effect can probably be explained by the greater heterogeneity and the greater surface energy of
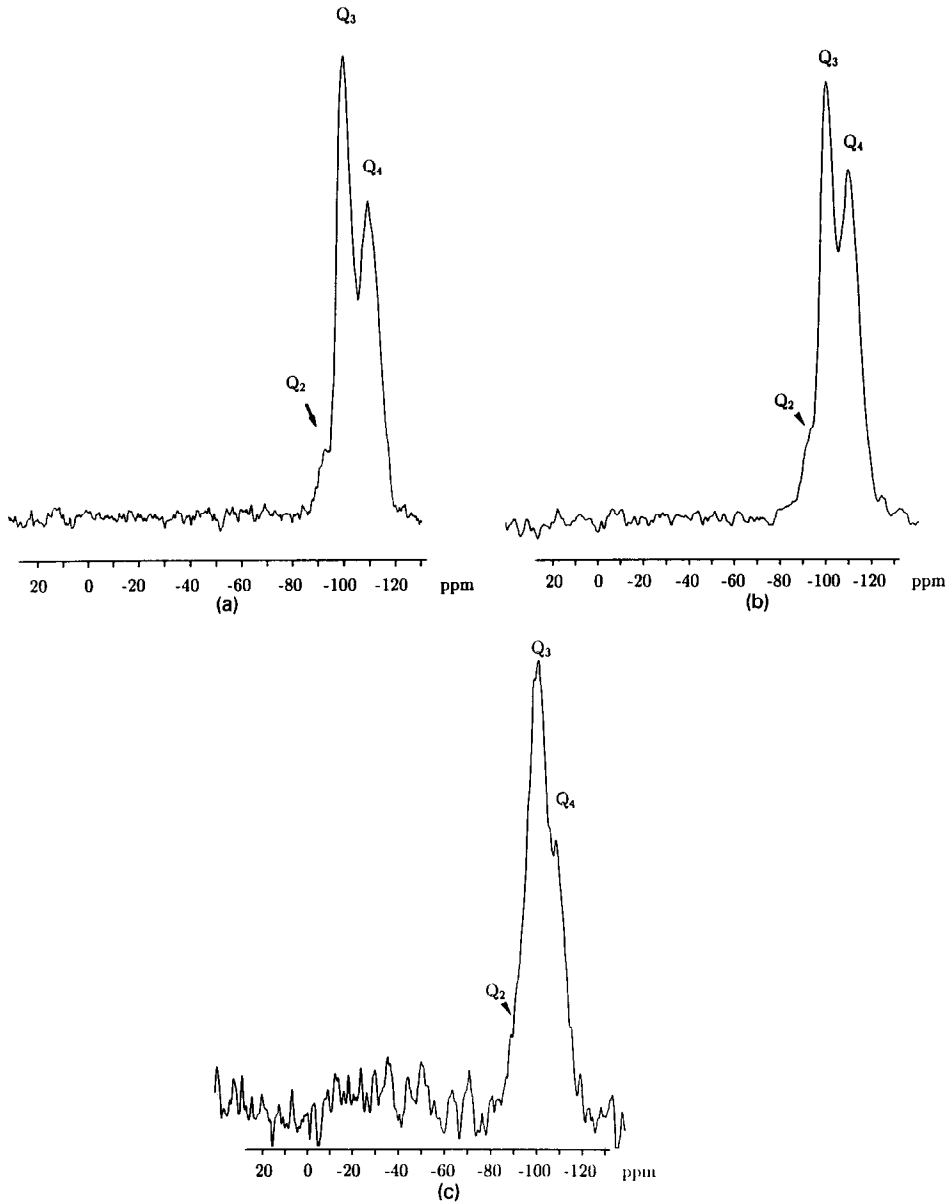
Fig. 3. ^{29}Si CP-MAS-NMR spectra of bare siliceous packings: (a) SG; (b) PG; (c) PG$_T$.

the PG$_T$ material affecting the pathway of the silylation reaction. We postulate that in a first step the highly polar 3-aminopropylsilane is physically adsorbed at the polar sites of the PG$_T$ surface, either by the polar amino group or by the ethoxy and/or methoxy group. Only those molecules adsorbed via the ethoxy or methoxy group can react in a second step to form the desired Si–O–Si bonds. With the PG$_T$ material,
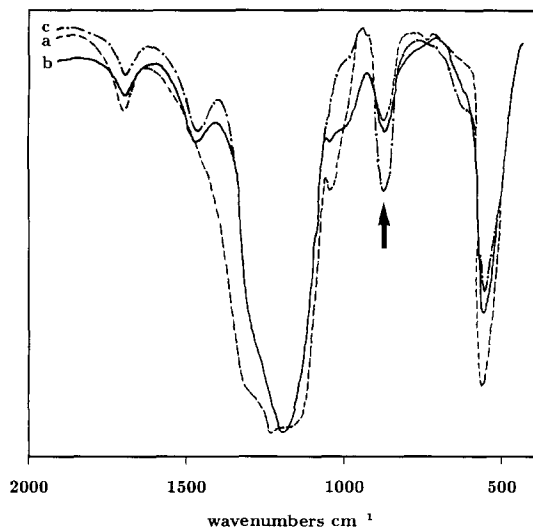
Fig. 4. FT-IR spectra of bare siliceous materials: (a) SG; (b) PG; (c) PG$_T$.

adsorption via amino groups is preferred as a consequence of the strong adsorption properties and the acidity of the boranyl sites present in the surface, thus the decreasing the yield of chemically bonded 3-aminopropylsilane [22].

All the packings prepared were characterized by ^{29}Si CP-MAS-NMR spectroscopy in order to obtain information about the different Si species formed on the modified surface. The possible Si species for materials modified with mono- and trifunctional silanes are shown in Fig. 5. The spectra of the investigated packings show the expected signals for monolayers for the monofunctional silane, as indicated by the signal at $\delta = +13$ ppm (M), and polymeric structures for the trifunctional silane, as indicated by the signals at $\delta = -60$ ppm ($T_3 + T'_3$) and $\delta = -66$ ppm ($T_4 + T'_4$) [21–23]. It is important to note that silanes bound to surface BOH groups cannot be distinguished from those bound to silanol groups by NMR techniques. In addition, the

TABLE II

CHARACTERIZATION OF SILICEOUS PACKINGS AFTER CHEMICAL MODIFICATION WITH AMINOSILANES

SG/NH$_2$-M and PG$_T$/NH$_2$-M are packings with monofunctional phase, SG/NH$_2$-T and PG$_T$/NH$_2$-T are packings with trifunctional phase. P_C = measured carbon percentage (%C); P_N = measured nitrogen percentage (%N); α_{RP} = concentration of aminosilyl ligands (μmol/m^2).

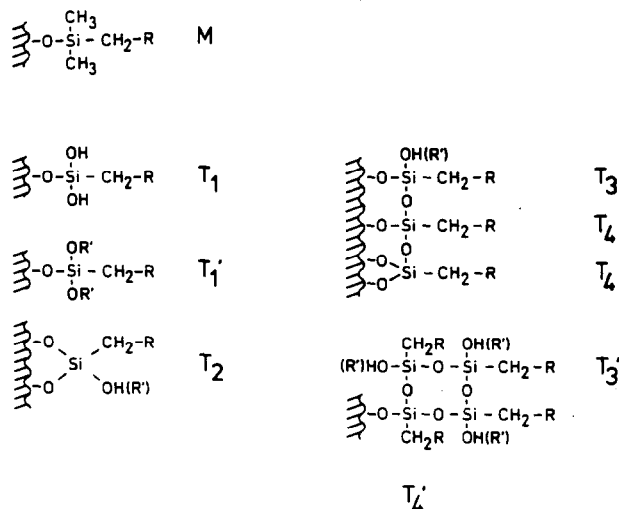| No.	Type of support	Type of phase	Surface concentration		
			P_C	P_N	α_{RP}
1	Nucleosil	SG/NH$_2$-M	4.63	0.97	2.48
2	Nucleosil	SG/NH$_2$-T	3.16	1.39	2.98
3	Porous glass	PG$_T$/NH$_2$-M	2.02	9.61	1.59
4	Porous glass	PG$_T$/NH$_2$-T	2.24	0.81	2.71

Fig. 5. Detectable Si surface species on siliceous supports after modification with monofunctional (M) and trifunctional (T) silanes.

phases were characterized by ^{13}C CP-MAS-NMR spectroscopy. Also in the ^{13}C CP-MAS-NMR spectra of the 3-aminopropyl-modified SG and PG materials it is possible to shift the signal of the C-2 atom of the 3-aminopropyl group between 27.16 and 21.12 ppm by changing the degree of protonation of the amino group [24,25]. More details will be reported later.

The materials prepared were tested in HPLC with a test mixture of saccharides (Fig. 6). The chromatograms show significantly better resolution for the materials prepared on the basis of SG (SG/NH$_2$-M, SG/NH$_2$-T; Fig. 6a and b) than for those with PG as a support (PG$_T$/NH$_2$-M, PG$_T$/NH$_2$-T; Fig. 6c and d). This is probably due to the different siliceous matrices of the two materials (SG, PG$_T$), which results in a higher peak capacity of the SG packings [14]. Moreover, the surface concentration (α_{RP}) and the structure of the CBP also affects the retention data (Table III). The best

TABLE III

k' AND α_{ij} VALUES OF SOME SACCHARIDES OBTAINED WITH ACETONITRILE–WATER (80:20, v/v)

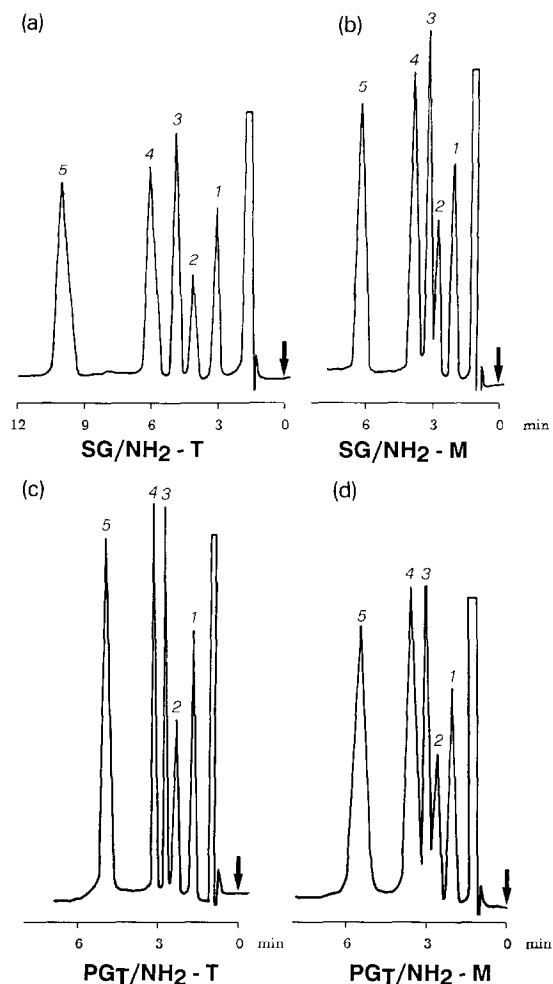| No.	Solute	SG/NH$_2$-M		SG/NH$_2$-T		PG$_T$/NH$_2$-M		PG$_T$/NH$_2$-T	
		k'	α_{ij}	k'	α_{ij}	k'	α_{ij}	k'	α_{ij}
1	Ramnose	1.19		1.29		1.14		1.03	
2	Arabinose	1.88	1.58	2.16	1.67	1.75	1.53	1.65	1.60
3	Fructose	2.32	1.88	2.74	1.26	2.22	1.75	2.23	1.35
4	Glucose	3.00	1.29	3.69	1.35	2.86	1.28	2.65	1.19
5	Saccharose	5.48	1.83	6.71	1.82	4.87	1.70	4.60	1.74

Fig. 6. Separation of some saccharides (1, ramnose; 2, arabinose; 3, fructose; 4, glucose; 5, saccharose) on the modified column packings: (a) SG/NH_2-T; (b) SG/NH_2-M; (c) PG_T/NH_2-T; (d) PG_T/NH_2-M. Chromatographic conditions: detector, refractive index; mobile phase, acetonitrile–water (80:20, v/v); flow-rate, 1 ml/min.

selectivity (α_{ij}) is shown by SG/NH_2-M, but the retention times are relatively long (Fig. 6b, Table III). The PG_T/NH_2-T show small differences in selectivity but shorter retention times and sharper peak shapes (Fig. 6d, Table III). The different chromatographic behaviour of the PG phases compared with the corresponding SG phases is a consequence of the different textures and surface properties of the two siliceous materials.

ACKNOWLEDGEMENTS

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