

Effect of silanol groups on heat-treated silicas by calcination and retention behaviour in high-performance liquid chromatography

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ABSTRACT

The effect of silanol groups on heat-treated silicas by calcination has been studied by high-performance liquid chromatography. After heat-treating at various temperatures, the silicas were used for the measurement of physical parameters and chemical analysis. From elemental analysis data for carbon and hydrogen, the reactive silanol group concentrations, $\alpha_{\text{OH}(s)}$, were determined to be 2.3% from C or 2.9% from H for 180°C-treated silica, and 1.6% from C or 1.6% from H for 950°C-treated silica (original silica: mean pore diameter 11.6 nm, specific surface area 298 m²/g, pore volume 1.22 ml/g, particle size 5.0 μm). The capacity factors of dioctylphthalate, dibutylphthalate and dimethylphthalate generally increased with increasing-heat treatment from 180 to 950°C, using methanol-hexane mixtures as the eluent. On the basis of the physico-chemical and chromatographic data the heat-treated silicas by calcination have been compared.

INTRODUCTION

Chemically modified phases are used mostly in high-performance liquid chromatography (HPLC). Thus, it is very important to investigate the mechanical, thermal and solvolytic resistance of these phases. Up to now silicas have been used preferentially as supports for chemically bonded phases. These materials consist of organic functional groups, such as octadecyl, octyl, ethyl and phenyl groups, bonded to silicas. In previous papers [1–8], we have suggested that the important parameters of silica with respect to the number of accessible alkylamino or phenyl groups per 100 Å^2 (1 nm²) are the pore diameter and the specific surface area. On the other hand, with respect to the surface hydroxyl group concentration, $\alpha_{\text{OH}(s)}$, there have been few reports of HPLC analyses on heat-treated silica by calcination in physical and chemical research [9]. Therefore we studied the effect of silanol groups on heat-treated silicas by calcination and the retention behaviour in HPLC.

EXPERIMENTAL

Reagent

Hexamethyldisilazane (HMDS) was obtained from Petrarch Systems (Bristol, PA, USA). Benzene, dioctylphthalate (DOP), dibutylphthalate (DBP) and dimethylphthalate (DMP) were obtained from Wako (Osaka, Japan). Porous silicas (Table I) were prepared in our laboratories. The other reagents and organic solvents were of analytical-reagent grade.

TABLE I
CHARACTERISTICS OF ORIGINAL SILICA

Sample ^a	Mean particle size (μm)	Mean pore diameter (nm)	Specific surface area (m^2/g)	Pore volume (ml/g)
Silica	5.0	11.6	298	1.22

^a The designation is for convenience and has no commercial significance.

Apparatus

The HPLC measurements were carried out on a Twinkle instrument (Jasco, Tokyo, Japan), equipped with a Uvidec-100IV variable-wavelength detector (Jasco) and a column of 250×4.6 mm I.D., packed with heat-treated silicas by calcination.

Stationary phase and elemental analysis

Porous silicas (Table I) were heated for 12 h at the required temperature (Table II). Then, according to the method of Buszewski [10], after 7 g of dried silica-180, silica-300, silica-500, silica-700 or silica-950 had been added to 70 ml of toluene and 4 ml of HMDS, silica-180-T, silica-300-T, silica-500-T, silica-700-T and Silica-950-T (which are listed in Table III) were prepared. Hereafter, silica-180-T to silica-950-T will be abbreviated to "column gel". The characteristics of these materials are also given in Tables II and III. The carbon and hydrogen contents of the treated silicas were de-

TABLE II
CHARACTERISTICS OF HEAT-TREATED SILICAS BY CALCINATION

DOP = Dioctylphthalate; DBP = dibutylphthalate; DMP = dimethylphthalate.

Treated gel ^a	Specific surface area (m^2/g)	Total silanol group concentration, $\alpha_{\text{OH(s)}}$	Capacity factor, k'		
			DOP	DBP	DMP
Silica-180	298	9.1	0.16	0.38	1.03
Silica-300	285	9.4	0.17	0.38	1.03
Silica-500	301	7.3	0.19	0.43	1.14
Silica-700	306	3.9	0.24	0.56	1.38
Silica-950	257	1.9	0.27	0.65	1.60

^a The number indicates the heat-treatment temperature.

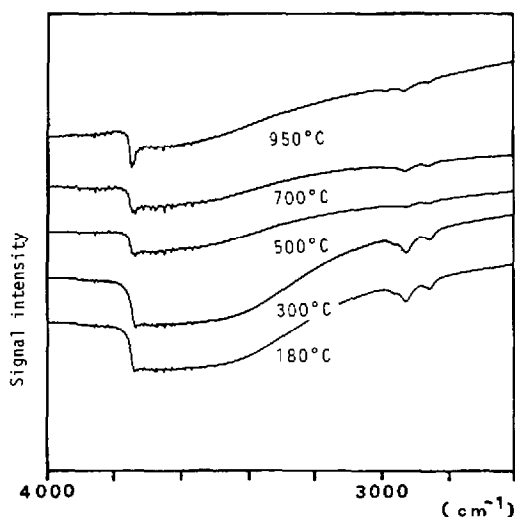


Fig. 1. Infrared spectra of the various heat-treated silicas by calcination.

terminated by elemental analysis using an MT-3 CHN elemental analyser (Yanagimoto, Kyoto, Japan). The specific surface areas, mean pore diameters and pore volumes of the column silicas were determined with an MOD-220 porosimeter (Carlo Erba, Milan, Italy), SA-1000 surface-area pore-volume analyser (Shibata, Tokyo, Japan), FT-IR 1640 infrared spectrophotometer (Perkin-Elmer, CT, USA), and the data are shown in Tables II and III and Fig. 1.

Column preparation

The column silicas were packed into the stainless-steel column (250 × 4.6 mm I.D.) by the slurry technique.

RESULTS AND DISCUSSION

As is well known [9,11], the broad absorption band between 3800 and 3000 cm^{-1} (in Fig. 1) can be assigned generally to the OH bond of silanol groups. By elevating the

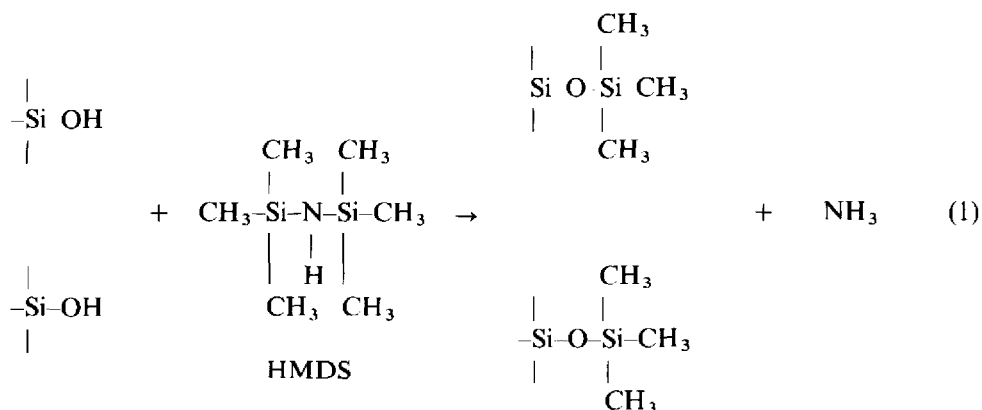
TABLE III

HEXAMETHYLDISILAZANE TREATMENTS AND REACTIVE SILANOL GROUPS PER 100 \AA^2 (1 nm^2)

Column gel	C found (%)	H found (%)	Reactive silanol groups concentration, $\alpha_{\text{OH(s)}}$	
			From C	From H
Silica-180-T	4.09	1.28	2.3	2.9
Silica-300-T	3.62	1.20	2.1	2.8
Silica-500-T	4.07	1.25	2.3	2.8
Silica-700-T	3.50	0.97	1.9	2.1
Silica-950-T	2.47	0.62	1.6	1.6

heat-treatment temperature, this broad band at 180°C becomes narrower, and at 950°C the band shape is sharp as a result of the condensation and dehydration reaction of silanol, which gives rise to a sharp absorption band at 3747 cm^{-1} .

If HMDS is substituted monofunctionally on silica, the change of the surface structure of the saturated silica-180-T to silica-950-T can be described by the following formulae:



The reactive silanol groups per 100 \AA^2 (1 nm^2) of silica is given by

$$[(H/100)/1.0079 \cdot 9] \cdot 6.022 \cdot 10^{23}/S \cdot 10^{18} \quad (2)$$

or

$$[(C/100)/12.011 \cdot 3] \cdot 6.022 \cdot 10^{23}/S \cdot 10^{18} \quad (3)$$

where H = weight percentage of hydrogen, C = weight percentage of carbon, $6.022 \cdot 10^{23}$ = Avogadro's number and S = specific surface area (m^2/g) of treated silica.

Substitution of the values of H and C found by elemental analysis into eqns. 2 and 3 gives the number of reactive silanol groups per 100 \AA^2 (1 nm^2) of silica surface, indicated as "found" in Table III.

Tables II and III and Fig. 2 show the relation between the total and reactive silanol group concentration and the heat-treatment temperature of the silica sorbent. As can be seen from the "found" data in Table III, the reactive silanol group concentration decreases only slightly with respect to the increasing heat-treatment temperature and certainly shows smaller variability compared with the change of total silanol group concentration with temperature (Table II).

As shown in Fig. 2, the total silanol group concentration decreases distinctly by elevating the heat-treatment temperature, while the reactive silanol group concentration is shown to be almost constant, decreasing slightly with increasing temperature of calcination.

Fig. 3 shows the relation of the capacity factors (k') of phthalic acid esters *versus* the various silicas treated by calcination. As can be seen from Fig. 3, the k' of phthalic acid esters increases with elevating heat-treatment temperature.

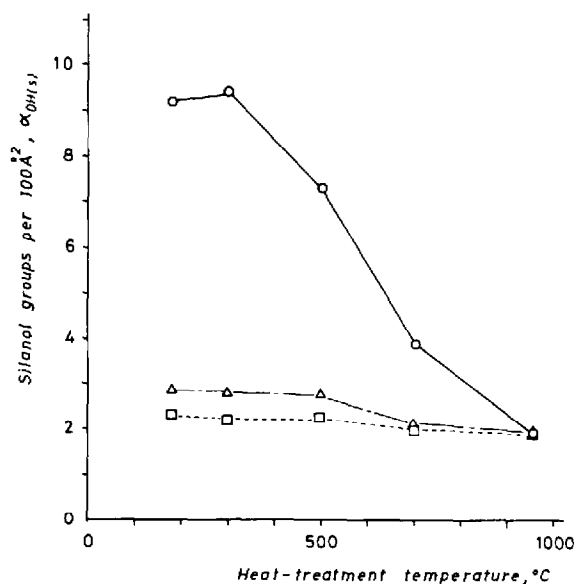


Fig. 2. Relation of the total silanol group concentration versus the reactive silanol group concentration to the various heat-treatment temperatures. ○ = Total silanol groups; Δ = reactive silanol groups (calculated from hydrogen percentages in Table III); □ = reactive silanol groups (calculated from carbon percentages in Table III).

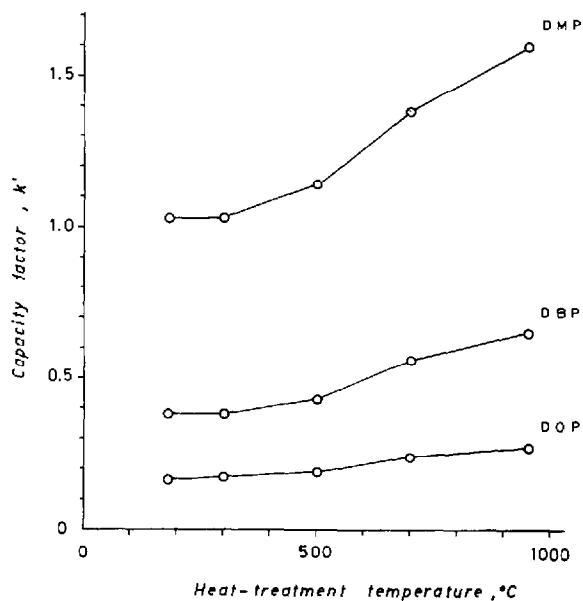


Fig. 3. Relation of the capacity factors (k') of phthalic acid esters versus the various heat-treated silicas by calcination. HPLC conditions: Mobile phase; Methanol-*n*-hexane (1:99, v/v); flow-rate: 1.0 ml/min; detection: 254 nm UV; DOP = dioctylphthalate; DBP = dibutylphthalate; DMP = dimethylphthalate.

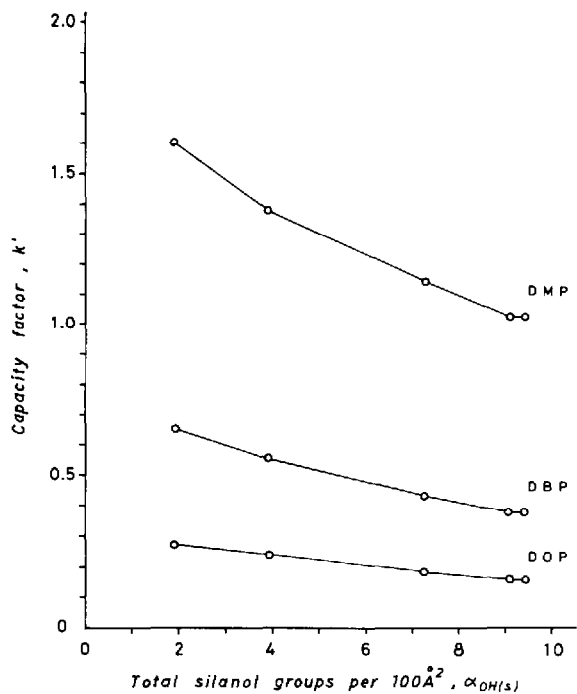


Fig. 4. Relation of the capacity factors (k') of phthalic acid esters *versus* the total silanol groups per 100 \AA^2 ($1 \mu\text{m}^2$). HPLC conditions as in Fig. 3.

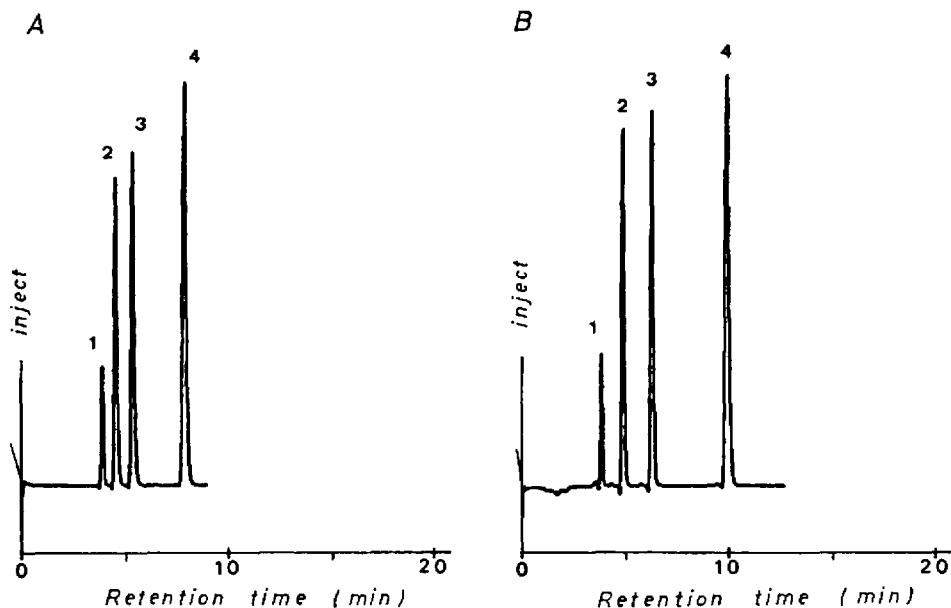


Fig. 5. Comparative typical chromatograms of phthalic acid esters on the 180°C -treated silica (A) *versus* the 950°C -treated silica (B). HPLC conditions as in Fig. 3. Peaks: 1 = benzene (t_0); 2 = dioctylphthalate; 3 = dibutylphthalate; 4 = dimethylphthalate.

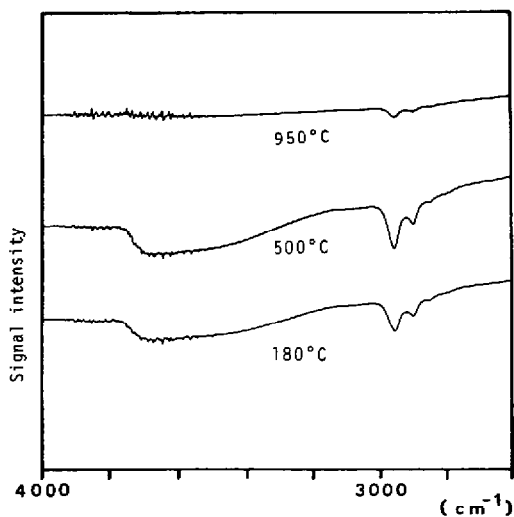


Fig. 6. Infrared spectra showing the effect of hexamethyldisilazane treatment on various heat-treated silica. Samples as in Table III.

From the studies on liquid chromatography with silica as sorbent, it is generally known that the interaction of the silica surface with the solute depends on the silanol groups. The silanol group concentration $\alpha_{\text{OH(s)}}$ decreased by calcination with higher heat-treatment temperature; on the contrary, the k' values of DOP, DBP and DMP were increased under the same HPLC conditions, as is shown in Table II.

Fig. 4 shows the relation of the k' of phthalic acid esters *versus* the total silanol groups per 100 \AA^2 (1 nm^2). As can be seen from Fig. 4, the k' of phthalic acid esters decreases by increasing the total silanol groups per 100 \AA^2 (1 nm^2).

Fig. 5 shows the comparative chromatograms of phthalic acid esters on two types of heat-treated silicas (calcination temperatures at 180 and 950°C).

As can be seen from Figs. 2, 4 and 5, the results indicate that the retention effect was not proportional to the number of silanol groups and the silanol group concentration, $\alpha_{\text{OH(s)}}$, on the silica surface.

It was assumed that the hydrogen-bonded silanol groups on the silica surface have an inhibitory effect on the retention of the solute and that the retention effect was due mainly to free silanol groups on the silica surface. This idea is supported by showing that the broad absorption band between 3800 and 3000 cm^{-1} decreased as a result of elevating heat-treatment temperature (Fig. 6). As can be seen from Figs. 1 and 6, the amount of hydrogen-bonded silanol groups decreases as a result of the condensation and dehydration reactions during calcination. On the other hand, it was proven that free silanol groups exist even after the heat treatment of the sorbent at 950°C . It was also shown that the silanol group concentration, $\alpha_{\text{OH(s)}}$, of the reactive silanol is almost constant (about two groups per $100 \text{ \AA}^2 = 1 \text{ nm}^2$); these are mainly the free silanol groups on the heat-treated silica surface.

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