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THERMAL TREATMENT OF SILICA AND ITS INFLUENCE ON CHROMATOGRAPHIC SELECTIVITY

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SUMMARY

It is generally accepted that the retention of solutes in non-polar eluents with silica as a stationary phase depends on the silanol concentration. By thermal treatment silanols can be removed at temperatures above 200°C. It can be shown by Fourier transform (FT)-IR spectroscopy that the vicinal silanols are removed and that the number of isolated silanols (sharp absorption at 3740 cm^{-1}) increases.

The decrease of vicinal silanols can be detected chromatographically by a corresponding decrease in the retention of hydroxyl group-containing solutes. The retention of solutes with hydrogen-bonding acceptors is not affected by this removal of vicinal silanols. Their retention depends solely on the surface concentration of isolated silanols. At temperatures above 600°C the concentration of isolated silanols also decreases. Consequently, the retention of these solutes decreases only on silicas treated at higher temperatures. Rehydration of the silica surface is completely reversible, if the thermal treatment does not exceed 400°C. It appears that during chemical modification with chlorosilanes only the isolated hydroxyl groups react.

INTRODUCTION

The selectivity of silica gel is determined by the concentration of silanol (hydroxyl) groups on its surface¹. Generally, the presence of two different types of silanol groups is assumed², which can be differentiated by spectroscopic and chemical means. According to Kiselev's group³, one should distinguish between isolated silanol groups and surface silanols which are hydrogen-bonded to adjacent ones. This differentiation is based on the distance of the groups on the silica surface. It is assumed that for the isolated (free) silanol groups the distance between neighbouring oxygen atoms is larger than 0.31 nm, and consequently, hydrogen bonds cannot form. The sharp absorption in the IR spectrum at 3740 cm^{-1} has been assigned to these groups. For the hydrogen-bonded surface silanol groups the distance between the oxygen atoms is less than 0.31 nm and may decrease to 0.24 nm. These "bonded" groups give rise to a broad IR absorption around 3600 cm^{-1} , which may be obscured by the vibrations of absorbed water⁴. Besides these two types of silanol groups, so called geminal silanol groups, in which two silanols are attached to one silica atom, have been discussed. Evidence of their existence is provided by solid state NMR^{5,6}.

Many attempts have been made to differentiate between these two groups of surface silanols. The Russian school^{3,7} concluded that the silanol groups are predominantly free, whereas others⁸ believe that there are mainly paired (vicinal and geminal) surface silanols. Also, some discrepancies exist in the literature concerning the reactivities of the different silanol groups and their influence on chromatographic retention. Bridged silanols have been considered by Snyder and Ward⁹ as the most reactive ones, whereas Hair^{4,10} deduced from vapor-phase silanization and surface IR spectroscopy that only those free silanol groups which give rise to an IR absorption at 3740 cm^{-1} react with chlorosilanes.

By thermal treatment above 200°C the ratio of free to bonded silanol groups can be altered^{2,11}. First, dehydration of vicinal "bonded" silanols takes place, and at temperature above 500°C the vicinal silanol groups are totally removed. Further dehydration by removal of isolated silanol groups is believed to occur at higher temperatures².

By combining FT-IR spectroscopy and chromatography a new attempt was made to evaluate the influence of the different silanols on chromatographic selectivity and retention by comparing chromatographic properties and spectroscopic data of thermally treated silica gels.

EXPERIMENTAL

The chromatographic data were obtained with a modular apparatus, consisting of a HPLC pump, Model 64.00 (Knauer, Berlin, F.R.G.), an additional pulse dampener (Orlita, Giessen, F.R.G.), a $20\text{-}\mu\text{l}$ sampling valve (Model 7125, Rheodyne, Berkley, CA, U.S.A.), and a laboratory-built 254-nm UV detector. Standard $250 \times 4\text{ mm}$ I.D. columns were used. The columns were kept immersed in a thermostated water-bath at 25°C (Ultra thermostat, Model NK.22, Gebr. Haake, Berlin, F.R.G.). Dichloromethane was used exclusively as the eluent. Its water content was kept constant at 160 ppm by a moisture-control system¹².

A silica gel fraction ($d_p = 10\text{ }\mu\text{m}$), obtained from Grace 74 C (Grace, Worms, F.R.G.) was used either as received or after heat treatment (24 h) at 200°C , 400°C , 600°C , 800°C , or 1000°C in a muffle furnace (Model MR 170, Heraeus, Hanau, F.R.G.). Portions of these samples were rehydrated by boiling them in water for 90 min. For chromatographic tests neutral solutes (anisole, nitrobenzene, benzonitrile, benzoic acid methyl and ethyl ester, benzaldehyde, acetophenone) and solutes containing hydroxyl groups (phenol, benzylalcohol, 2-phenylethanol, 3-phenylpropan-1-ol, *o*-, *m*-, *p*-chlorophenols and cresols) were used. Basic solutes did not yield sharp peaks under these conditions. Benzene was used as an inert marker¹³.

The Fourier transform infrared (FT-IR) spectra were obtained with a Digilab FTS 11C spectrometer (Digilab, München, F.R.G.) using a diffuse reflectance technique. Surface area measurements were performed by a "continuous"-flow method¹⁴ or by classical nitrogen adsorption.

RESULTS AND DISCUSSION

Thermal treatment and physical properties

Thermal treatment of silica results in a decrease in the number of surface

silanol groups by a condensation reaction. This affects the physical structure of the silica. As shown in Fig. 1, the specific surface area decreases slightly at temperatures above 200°C and significantly at temperatures above 800°C. In the same figure, the corresponding decrease in the specific pore volume is also shown. The latter has been determined chromatographically from the differences in elution volume between a polystyrene standard with a molecular weight of $2.6 \cdot 10^6$ and benzene and from the packing density. However, the pore diameter distribution, measured by reversed size-exclusion chromatography^{1,5} is not affected by this thermal treatment. This is not surprising, because significant structural changes in silica gel at elevated temperature occur only in the presence of water vapour. Hydrothermal treatment usually results in enlargement of the pore diameter and a consecutive decrease in the specific surface area. On the other hand, thermal treatment in the absence of water has been used to strengthen silica particles. Rehydration of silica gels heated up to temperatures of 800°C by boiling in water yields a silica with structural properties equal to initial one within the error of measurements. Only with the material treated at 1000°C did the rehydration result in an additional decrease of the specific surface area and an increase of pore volume. It is conceivable that strained Si–O–Si bonds are preferentially hydrolysed.

The consecutive weight loss of silica during thermal treatment is shown in the thermogravimetric plot of Fig. 2. As is known from the literature², the main losses occur at temperatures up to 200°C, when the physically adsorbed water is removed completely. The loss of structural water, by condensation of vicinal silanol groups reaches a maximum at 600°C. As described above this dehydration up to temperatures of 600°C is reversible. It should be noted that a pure, almost metal-free silica was used for the thermal treatment. Silica samples containing impurities cannot be exposed to this thermal treatment. In particular, surface sodium oxide acts as a flux material and causes sintering of the silica. Extensive boiling of such samples with

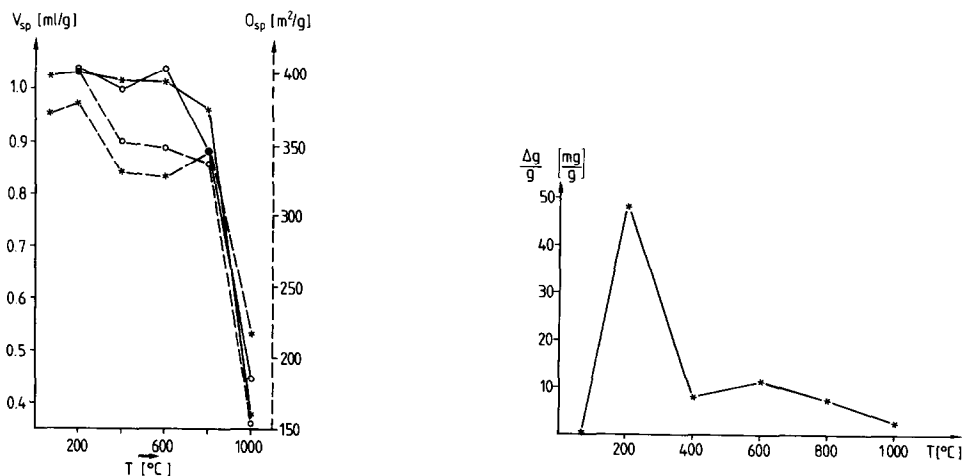
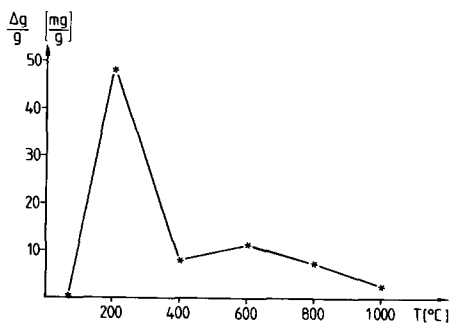


Fig. 1. Changes in specific surface area and pore volume during thermal treatment. Solid lines: pore volume; dashed lines: specific surface area. *, dehydrated; O, rehydrated.

Fig. 2. Specific loss of weight during thermal treatment.



6 *N* hydrochloric acid removes the metal ions, after which thermal treatment will give similar results. However, with spherical silica, especially Hypersil, extensive washing with hydrochloric acid did not prevent sintering. The reason for this may be that with spherical silicas the sodium ions are inside the colloidal micro particles shoot make up the structure.

In Fig. 3 the FT-IR spectra, measured in diffuse reflection in the range between 2500 and 4000 cm^{-1} , are shown. The sharp absorption band at 3740 cm^{-1} , assigned to isolated surface silanol, is present in every spectrum. The broad absorption around 3600 cm^{-1} , assigned to vicinal silanols, decreases with increasing treatment temperature, especially above 400°C. Correspondingly, the height of the isolated silanol band at 3740 cm^{-1} increases with temperature, reaching a maximum for the silica heated at 800°C. This band became smaller after the silica was treated at 1000°C. It is difficult to measure the silanol concentrations quantitatively by diffuse reflectance IR spectroscopy. For comparing the different silicas, the spectra were normalized for a band at 800 cm^{-1} . This band was present in all samples and its intensity was not affected by the thermal treatment. This allows some discussion of the trends in surface silanol changes, at least in qualitative terms. In Fig. 4 the corresponding spectra of thermally treated and rehydrated silica are shown. In every case, surface rehydration with formation of vicinal silanols can be seen. Whereas quantitative statements cannot safely be made, it may be stated that silica heated at temperatures up to 400°C can be completely rehydrated, as described in the literature². Silica treated at a higher temperature exhibits a broad absorption of lesser intensity.

Thermal treatment and chromatographic properties

The surface of the stationary phase in liquid chromatography is covered by adsorbed water and by at least a monomolecular layer of adsorbed eluent mole-

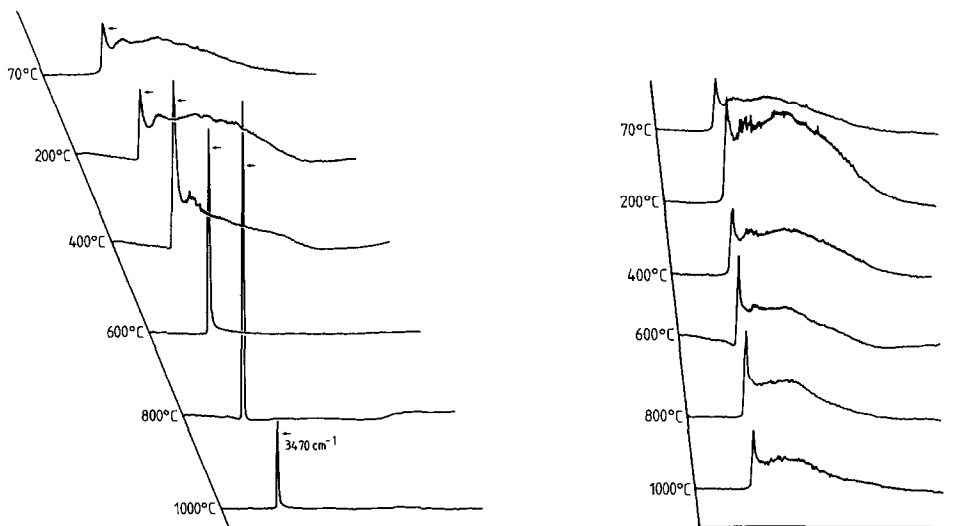


Fig. 3. FT-IR spectra of thermally treated silicas (measured by diffuse reflectance).

Fig. 4. FT-IR spectra of rehydrated thermally treated silica (measured by diffuse reflectance).

cules^{1,11,16,17}. According to the competition model¹, the solutes must be able to displace these eluent molecules from the surface in order to be adsorbed. The selective adsorption of solutes on silica gel has been attributed exclusively to the surface silanols¹.

Thus, it should be possible to correlate the surface silanol concentration to chromatographic retention and selectivity. Fig. 5 shows the k' values of several benzene derivatives on different thermally treated silicas. Samples with basic amino groups were not eluted as well-shaped peaks. It is seen that, the retention of solutes containing hydroxyl groups decreases with increasing treatment temperature of the stationary phase. It can also be seen that the decrease in k' values of solutes with hydroxyl groups is largest in the temperature range between 400 and 600°C. This indicates that these solutes are mainly adsorbed on the vicinal silanol groups by breaking up hydrogen bonds. In contrast, the retention of molecules containing hydrogen-bonding acceptors, like acetophenone and the esters, is hardly influenced by the thermal treatment. Corresponding to the decrease in vicinal surface silanols between 400°C and 600°C, the k' values of benzylalcohol and phenol decrease significantly in this temperature range. As shown in Fig. 1 the physical properties of the silica are also altered during thermal treatment. In order to exclude these effects, the k' values were normalized for the specific surface area of the different silicas per unit column volume. In Fig. 6 these normalized k' values are compared. Here it becomes more evident that the retention of molecules acting as hydrogen-bond acceptors even increases slightly between 400°C and 600°C. This indicates that molecules with "basic" properties are adsorbed preferentially on the acidic isolated silanols, the surface concentration of which increases in this temperature range. The observed retention on dehydrated and rehydrated silicas supports this assumption.

In Fig. 7 the reduction of k' values by thermal treatment is correlated with

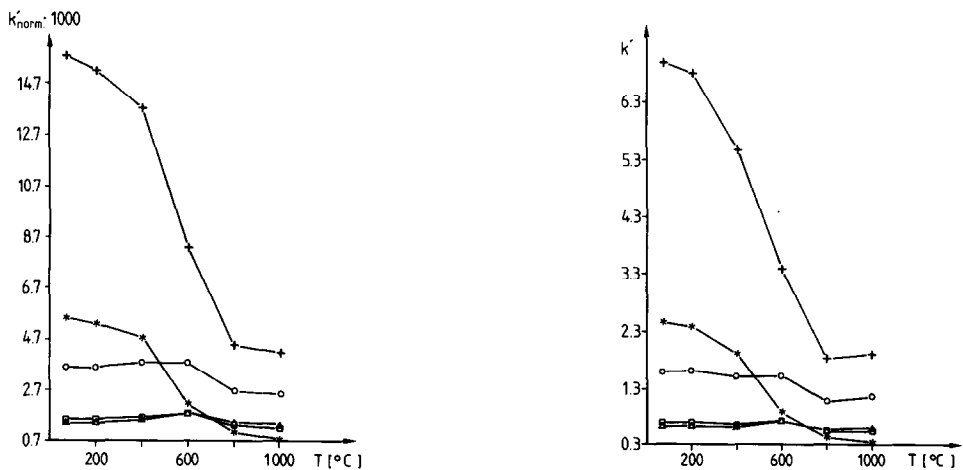


Fig. 5. k' values of benzene derivatives on thermally treated silicas. For experimental conditions, see text. Solutes: (+) benzyl alcohol; (O) acetophenone; (□) benzoic acid methyl ester; (△) benzoic acid ethyl ester; (*) phenol.

Fig. 6. Normalized retention values of benzene derivatives. Conditions and solutes as in Fig. 5.

values determined with a silica heated to only 200°C. As already mentioned, the k' values for hydroxyl-containing solutes decrease significantly in the temperature range 400°C–800°C. Capacity factors are less than 50% of the initial values. The k' values increase again by *ca.* 30% after rehydration. With silica treated at 400°C a 20% decrease in k' is observed, but the initial k' values are approximately restored by rehydration. This is in complete agreement with prior observations on the reversibility of silica surface de- and rehydration. For hydrogen-bond-accepting solutes no significant decrease in k' values can be observed up to temperatures of 600°C. Whereas with silica treated at still higher temperatures the initial k' values have been reduced by 25–30%. Rehydration of materials treated at 400°C and 600°C results in almost the same k' values as those initially observed with the 200°C material.

From these experiments it may be concluded that two different types of surface silanols are predominantly responsible for the retention of hydroxyl-containing solutes and for that of solutes, acting as hydrogen-bond acceptors. Solutes with hydroxyl groups are able to interact with the vicinal hydrogen-bonded silanols and are adsorbed on these sites. Their retention decreases with the removal of these groups. On the other hand, the “basic” hydrogen-bond acceptors are predominantly adsorbed at the “acidic”, free silanols. Because their surface concentration is hardly affected by thermal treatment at 600°C and below, the retention of these solutes does not change significantly with thermal treatment.

Thermal treatment and chemical modification

It is known from vapor-phase chlorosilanization that only the isolated silanols are reactive¹⁸. We allowed the thermally treated silicas to react with dimethyloctylchlorosilane in toluene¹⁹. Fig. 8 shows the FT-IR spectra of the reversed-phase thus

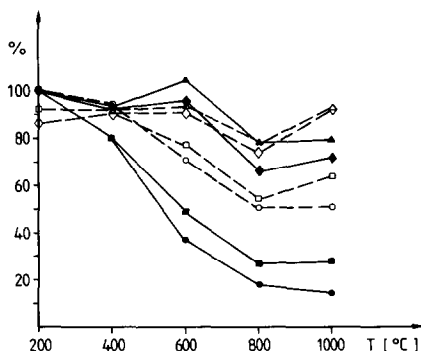


Fig. 7. Relative changes in k' produced by thermal treatment and rehydration. Solutes: (Δ , \blacktriangle) benzoic acid methyl ester; (\blacklozenge , \diamond) acetophenone; (\square , \blacksquare) benzyl alcohol; (\circ , \bullet) phenol. Solid lines: dehydrated silicas; dashed line: rehydrated silicas.

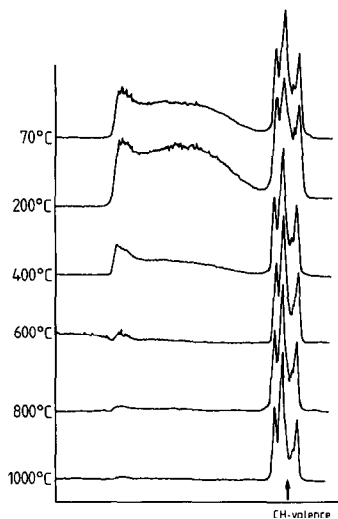


Fig. 8. FT-IR spectra of octyl reversed phase, prepared from thermally treated silicas.

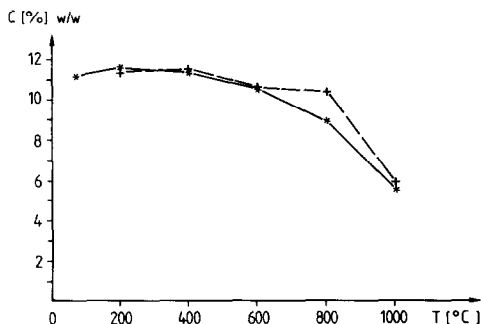


Fig. 9. Carbon content of RP C₈, prepared with dehydrated (*) and rehydrated (+) silicas.

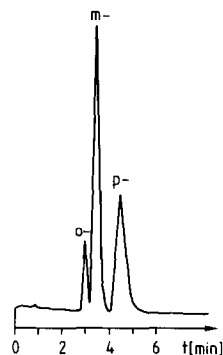


Fig. 10. Separation of toluidines. Stationary phase: RP C₈ on silica treated at 1000°C; eluent: methanol-water (55:45; v/v).

prepared. The spectra are normalized for the CH valence band around 3000 cm^{-1} . When these spectra are compared with those shown in Fig. 3, it is evident that only isolated silanols react with chlorosilanes. Further evidence can be derived from Fig. 9, where the carbon content of these stationary phases is plotted against the pretreatment temperature of the silica. Up to 600°C the carbon content is unchanged within experimental error. Only the phases prepared from silica treated at 800°C show a smaller carbon content, indicating that at this temperature isolated silanols have been removed. However, as indicated by rehydration, these isolated hydroxyl groups can be regenerated.

From the spectroscopic results, it seemed advantageous to test the reversed phases prepared from thermally treated silica where no silanol groups could be detected by IR spectroscopy for their potential to achieve symmetric peaks in the separation of basic solutes with aqueous eluents without additives, such as ion-pairing reagents. Peak asymmetry for basic solutes was less pronounced on these stationary phases than on RP phases prepared from untreated silica, as can be seen in Fig. 10. However, good reversed phases gave better peak symmetry than those prepared here. Reasons for this discrepancy may be caused by the limited sensitivity of FT-IR for silanol groups or by the fast rehydration of the stationary phase during usage. This demonstrates that other techniques than chromatographic methods are of limited value for phase characterization.

CONCLUSION

Chromatographic selectivity with silica stationary phases is not only a function of the specific surface area, pore volume, and packing density, but also of trace impurities of metal ions²⁰. From the discussions here it can be concluded that selectivity also depends on the concentration of surface silanol groups and on the ratio between isolated and vicinal (bridged) silanols. The retention of solutes which are able to interfere directly with hydrogen bonding is more strongly affected by thermal treatment of silica than that of solutes which are preferentially hydrogen-bond acceptors. The reaction of silica with chlorosilanes takes place mainly at the isolated

“acidic” silanols. Thermal treatment of the silica below 600°C does not affect the retention of “basic” hydrogen-bond-accepting solutes nor the chemical reaction with chlorosilanes. A recent paper⁵ describes the influence of the different silanols on selectivity and stability of the stationary phase. Further investigations will be required before taylor-made stationary phases can be prepared for individual applications.

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