Impact of acidic/hydrothermal treatment on pore structural and chromatographic properties of porous silicas

I. The conventional approach

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ABSTRACT

A series of commercial silicas and a laboratory made product were subjected to acidic/hydrothermal treatment with solutions of HCl, HNO$_3$, H$_2$SO$_4$ and HF. The concentration of acid and the temperature and duration of treatment were varied. The specific surface area, content of metal impurities, types and concentration of surface hydroxyl and siloxane groups and crystallinity were determined for native and treated silicas. Only changes in the structural order of the surface could be assessed by means of ^{29}Si cross-polarization magic angle spinning NMR spectrometry and electron diffraction. The native and acid-treated silicas were surface modified to *n*-octyl derivatives and tested under reversed-phase conditions. A notable improvement in the column plate number and the asymmetry of the peaks was observed, whereas the solute capacity factors remained nearly unchanged. The effect of the conditions of acidic treatment (concentration, temperature and duration) was established by factorial experiments. Acidic/hydrothermal treatment caused a more ordered surface structure with quasi-crystalline domains, which improved the chromatographic mass-transfer kinetics and hence the column performance of acid-treated silicas.

INTRODUCTION

Surface treatment of silica adsorbents before use has been a common procedure in classical column liquid chromatography. Simply, the aim was to remove inorganic impurities, mainly metal compounds, to clean and to activate the silica. As silicas in those days were mainly of technical grade and not specifically manufactured for application in column liquid chromatography, such a procedure was certainly required. In a typical procedure the silica was refluxed in a suspension with 2 *M* hydrochloric acid for a given period and then washed to neutrality [1].

Hydrothermal treatment of silicas with water and water vapour at elevated temperatures between 373 and 573 K and atmospheric or higher pressures served as a

suitable means to obtain materials of large pore size from small-pore silicas [2–7]. Depending on the temperature and duration of treatment, the pore diameter of the silica was enlarged at a constant specific pore volume. Correspondingly, the specific surface area decreased. In this way, silicas with average pore diameters larger than 50 nm and a fully hydroxylated surface were prepared. With the advances in high-performance liquid chromatography (HPLC) in pharmaceutical and bioanalysis, stronger requirements were put on silica-based reversed-phase packings, particularly those applied for the analysis of basic compounds. Basic analytes were often strongly retained with tailed peaks in reversed-phase chromatography owing to the residual adsorptivity of the silica base material. To overcome this obstacle, amines such as trimethylamine were added to the mobile phase as modifiers, which were then adsorbed on the surface, blocking the remaining active acidic centres [8,9]. However, the addition of mobile phase modifiers did not prove a satisfactory approach.

In recent years, attempts have been made to subject the silicas to specific procedures prior to the bonding reactions to create a deactivated and stable surface with regard to the chromatography of basic compounds. These procedures included treatment with complexing agents, dehydroxylation and rehydroxylation with acids such as hydrofluoric acid [10], treatment with acids combined with gentle hydrothermal treatment [11] and partial dissolution of the silica by treatment with ammonium hydrogen fluoride $(NH_4)HF_2$ [12]. As a result, a family of base-deactivated reversed-phase silicas were introduced by column manufacturers [13].

Despite the large number of studies in this area, the real effect of surface treatment on the structural properties of silicas remained poorly understood, although a substantial improvement in terms of column performance and column stability was achieved. It was generally assumed that the surface treatment led to a high extent of homogenization of the originally heterogeneous surface. Köhler and Kirkland [10] ascribed the effect to the formation of associated, less adsorptive hydroxyl groups which were monitored by diffuse reflectance Fourier transform infrared spectroscopy. Eisenbeiss [14] suggested a reorganization of the surface in energetic and geometric terms without providing convincing evidence.

The aim of this work was to examine the structural properties of a series of silicas for HPLC before and after treatment with acids such as HCl, HNO_3, H_2SO_4 and HF under mild hydrothermal conditions. After conversion of the acid-treated silicas into their reversed-phase derivatives, the chromatographic properties were assessed in terms of solute retention, column plate number and peak shape.

EXPERIMENTAL

Chemicals

Commercial silicas were LiChrosorb Si 100-7 and LiChrospher Si 100-10 from E. Merck (Darmstadt, Germany), G 250-10 from Grace (Worms, Germany) and Nucleosil 100-7 from Macherey, Nagel & Co. (Düren, Germany). Silica BE-0 was laboratory-made preparation synthesized from tetraethoxysilane according to a procedure described elsewhere [15]. The properties of the silicas are listed in Table I. The same batch of each silica was employed for surface modifications.

All chemicals and reagents were of analytical-reagent grade and a gift from E. Merck. HPLC-grade solvents for chromatographic measurements were also obtained

TABLE I

CHARACTERISTIC DATA FOR NATIVE SILICAS

d_p = Average particle diameter; a_s = specific surface area; v_p = specific pore volume; p_d = average pore diameter.

Silica	d_p (μm)	a_s (m^2/g)	v_p (ml/g)	p_d (nm)
LiChrosorb Si 100-7	7	355	1.1	10
LiChrospher Si 100-10	10	388	–	10
G 250-10	10	250	–	25
Nucleosil 100-7	7	377	–	10
BE-0	10	246	0.97	12

from E. Merck. The synthesis and purification of silanes employed for the modification of silicas were described previously [16].

Treatment of silicas

Hydrochloric, sulphuric, nitric and hydrofluoric acid were used. Three parameters were varied at two levels at acid treatment: the concentration of acid [0.1 and 10 M, except for HF (0.01 and 0.1 M)], the temperature of treatment (273 and 363 K) and the duration of treatment (0.1 and 24 h). The experiments were carried out on the basis of factorial design. The statistical evaluation on the significance of parameters was performed according to the method of Yates [17]; see also Retzlaff et al. [18].

Silica (6 g) suspended in 50 ml of the acid was stirred in a closed 100-ml two-necked flask using a specially designed PTFE stirrer [11] at two temperatures, namely 273 K using an ice-bath and 363 K using a thermostat. The treatment of silicas with HF was performed in a 250-ml polypropylene erlenmeyer flask. After treatment for 0.1 and 24 h, the silicas were washed to neutrality with deionized water. The silicas were then dried at 423 K and 20 Pa for 24 h. A blank experiment with pure water at 363 K for 0.1 and 24 h was carried out under the same conditions.

Characterization of native silicas and reversed-phase derivatives

Specific surface area, a_s. After activation at 423 K and 20 Pa for 24 h, the specific surface area was determined by nitrogen sorption using an Accusorb 2100 E instrument (Micromeritics, Norcross, GA, USA) and by the BET method [19].

Specific pore volume, v_p. The specific pore volume was determined by titration with water according to the method of Fisher and Mottlau [20].

Pore-size distribution and average pore diameter (p_d). The pore-size distribution was measured by mercury intrusion using a laboratory-made porosimeter with a maximum pressure of 400 MPa, and was calculated from the corrected intrusion curve by means of the Washburn equation using a contact angle of mercury of 140°C and a surface tension of mercury of 0.48 mN/m [21]. The average pore diameter was the mean pore diameter at 50% of the cumulative pore volume distribution curve.

Concentration of surface hydroxyl groups. The concentration of surface hydroxyl groups was determined by means of isotopic exchange with deuterated trifluoroacetic acid followed by ^{1}H NMR spectroscopy according to a method of Holik and Matejkova [22]. The procedure is described in detail in ref. 11. The precision of the determination was ±2.5%.

pH of the silica suspension. The apparent pH was measured in a 1% (w/w) suspension of silica in 0.1 M sodium chloride solution using an E50 glass electrode (WTW, Weilheim, Germany) and a Type PH 530 pH meter (WTW).

Content of inorganic impurites. The metal content was determined by X-ray fluorescence spectrometry (XRF) using a instrument PW 100 (Philips, Kassel, Germany) and by atomic absorption spectrometry (AAS) using an ARL 310,000 Quantometer (Philips).

Pellets for XRF were made by employing a mixture of silica and a polyalcohol (Mowviol N 50-98; Hoechst, Frankfurt/M, Germany) in the ratio 30:70 (w/w). For the AAS measurements, about 500 mg of silica were suspended in 5 ml of 40% HF (w/w) (Suprapur; E. Merck) in a platinum crucible. On heating the silica was evaporated as SiF_4. The residue was dissolved in 5 ml of 16% (w/w) HCl (Suprapur; E. Merck).

^{29}Si *cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectrometry.* The measurements were conducted at the Institut für Organische Chemie, Universität Tübingen, using a Bruker (Karlsruhe, Germany) MSL 200 Fourier transform NMR spectrometer with samples of 200–300 mg in double-bearing rotors of Al_2O_3. For further details, see ref. 23.

Electron diffraction measurements. The silica was milled to a fine powder in a ball-mill for 2 h prior to measurement in an Model EN 240 80-kV instrument (Philips) employing thallium chloride as reference material.

Fourier transform infrared (FT-IR) spectrometry. The measurements were conducted at the Haber-Bosch Institut of the Max-Planck Gesellschaft (Berlin, Germany) by Dr. H. Karge. Self-supporting disks of silica were prepared with a thickness between 5 and 13 mg/cm^2. A Model 325 spectrometer (Perkin-Elmer, Überlingen, Germany) fitted with a vacuum cell which could be heated to 700 K was used. IR spectra were run on native silicas after heat treatment at 375, 475, 575 and 673 K. Spectra were also recorded after adsorption of pyridine at 298 K and after desorption of pyridine at 473 K.

Chromatographic measurements. The native silicas were reacted after activation at 423 K and 20 Pa for 24 h with N,N'-dimethylaminodimethyl-*n*-octylsilane according to a procedure described elsewhere [16]. The products were slurry packed in 125 mm × 4.6 mm I.D. stainless-steel columns (Hyperchrom; Bischoff Analysentechnik, Leonberg, Germany). The HPLC system consisted of a pump (Model 2150; LKB, Bromma, Sweden), a Rheodyne Type 2105 injection valve (Latek, Heidelberg, Germany), an oven to thermostat the column (Model 2155; LKB), a variable-wavelength UV detector (Model 2151; LKB) and an integrator (Model CR-3A; Shimadzu Europe, Duisburg, Germany).

The test solutes were mixtures of N-methylaniline and N,N'-diethylaniline (sample mixture I) and of methyl, propyl, *n*-butyl and *n*-pentyl benzoate (sample mixture II). The sample concentration was 0.1 mg/ml, the injection volume 20 μl, the flow-rate 1.0 ml/min, the wavelength of detection 254 nm and the column temperature 301 K. The mobile pase was methanol–water (70:30, v/v). Sodium azide was used as a t_0 marker. Three columns were packed and tested for each silica. Injection of test mixtures was repeated twice.

The chromatographic solute capacity factor (k'), plate number (N) and the peak asymmetry factor (A) were calculated according to the following equations:

$$k' = (t_R - t_o)/t_o$$

where t_R is the retention time of the solute,

$$N = 5.54\ (t_r/w_{1/2})^2$$

where $w_{1/2}$ is the peak width at half-height of the peak and

$$A = b_{0.1}/a_{0.1}$$

where $a_{0.1}$ is the distance from the peak front to the maximum at 10% of the peak height and $b_{0.1}$ the distance from the maximum of the peak to its tail at 10% of the peak height.

RESULTS AND DISCUSSION

Effect of acidic/hydrothermal treatment on the structural properties of silicas
As series of silicas (LiChrosorb Si 100-7, LiChrospher Si 100-10, G 250-10 and a laboratory-made silica Be-0) were treated with solutions of hydrochloric, sulphuric, nitric and hydrofluoric acid under different conditions (see Experimental). The experiments were conducted on the basis of factorial design. The data obtained were subjected to statistical tests to evaluate the statistical significance of the treatment conditions on the structural properties. The structural parameters determined for the native and treated silicas were the specific surface area, a_s, the metal content, the apparent pH of the silica suspension, the total concentration of the surface hydroxyl groups, the types of surface hydroxyl groups and the crystallinity.

Specific surface area, a_s, assessed by means of nitrogen sorption and the BET method. The effect of acid treatment (363 K, 24 h) on a_s was investigated for LiChrosorb Si 100-7 and BE-0 silicas. For LiChrosorb Si 100-7, the a_s values were as follows: native silica, 355 ± 8 m²/g; 0.1 M HF treated, 337 ± 5 m²/g; 0.1 M HCl treated, 358 ± 10 m²/g; 10 M HCl treated, 360 ± 9 m²/g; and 10 M H₂SO₄ treated, 363 ± 4 m²/g. For BE-0, the a_s values were as follows: native silica, 246 ± 6 m²/g; 0.1 M HF treated, 222 ± 8 m²/g; and 10 M H₂SO₄ treated, 252 ± 11 m²/g.

Within the limits of the precision of the method the specific surface area of the treated silicas remained unchanged compared with that of the native product, except for the HF-treated silica, for which a 10% decrease in a_s was observed, caused by the slight dissolution of silica from small pore regions by reaction with HF, forming SiF₄.

Metal content determined by AAS. LiChrosorb Si 100-7 contained the impurities Al 640, Fe 60, Ti 175, Ca 170 and Na 660 ppm. Treatment with 0.1 and 10 M HCl, 10 M H₂SO₄ and 0.1 M HF at 363 K for 24 h reduced the content of metal impurities by about half (for details, see ref. 11). The acidic/hydrothermal treatment of LiChrospher Si 100-10 and BE-0 had only a minor effect on the metal content. The latter was a highly pure silica containing *ca.* 10 ppm of Fe.

Content of surface hydroxyl groups, α_{OH}, by the method of Holik and Matejkova [22]. The treatment conditions were 363 K for 24 h. The precision of the method was $\pm 3\%$ [11]. For LiChrosorb Si 100-7, the α_{OH} values were as follows: native silica, 8.55 μmol/m²; 0.1 M HF treated, 9.03 μmol/m²; 10 M H₂SO₄ treated, 9.18 μmol/m²; and

10 M HCl treated, 8.60 μmol/m^2. For LiChrospher Si 100-10, the α_{OH} values were as follows: native silica, 8.38 μmol/m^2; and 10 M HCl treated, 8.45 μmol/m^2. For BE-0, the α_{OH} values were as follows: native silica, 8.12 μmol/m^2; 0.1 M HF treated, 8.69 μmol/m^2; and 10 M H$_2$SO$_4$ treated, 9.37 μmol/m^2.

The results indicate that the total concentration of surface hydroxyl groups increased by up to 10% compared with the native silica. The most drastic effect was observed for silicas treated with H$_2$SO$_4$.

Apparent pH of the silica suspension. The treatment conditions were 363 K for 24 h. For LiChrosorb Si 100-7, the native silica had pH 7.7, 0.1 M HF treated pH 7.3, 10 M HCl treated pH 7.2 and 10 M H$_2$SO$_4$ treated pH 3.0. For LiChrospher Si 100-10, the native silica had pH 5.8 and 10 M HCl treated 5.7.

Except for the silica treated with H$_2$SO$_4$, the pH remained the same after the acidic/hydrothermal treatment.

Identification of the types of hydroxyl groups and their determination by ^{29}*Si CP-MAS NMR spectroscopy.* ^{29}Si CP-MAS NMR spectroscopy allows the detection of geminal hydroxyl groups, Q$_2$, isolated hydroxyl groups, Q$_3$, and siloxane groups, Q$_4$, from their chemical shifts of -91, -100 and -109 ppm, respectively [24–26]. The absolute amounts of silanol and siloxane groups cannot be determined owing to their different relaxation behaviours [23]. However, it is possible to compare the peak intensities under the same measuring conditions. Fig. 1 shows the spectrum of (a) the native and (b) acid-treated (0.1 M HCl, 363 K, 24 h) LiChrosorb Si 100-7. Compari-
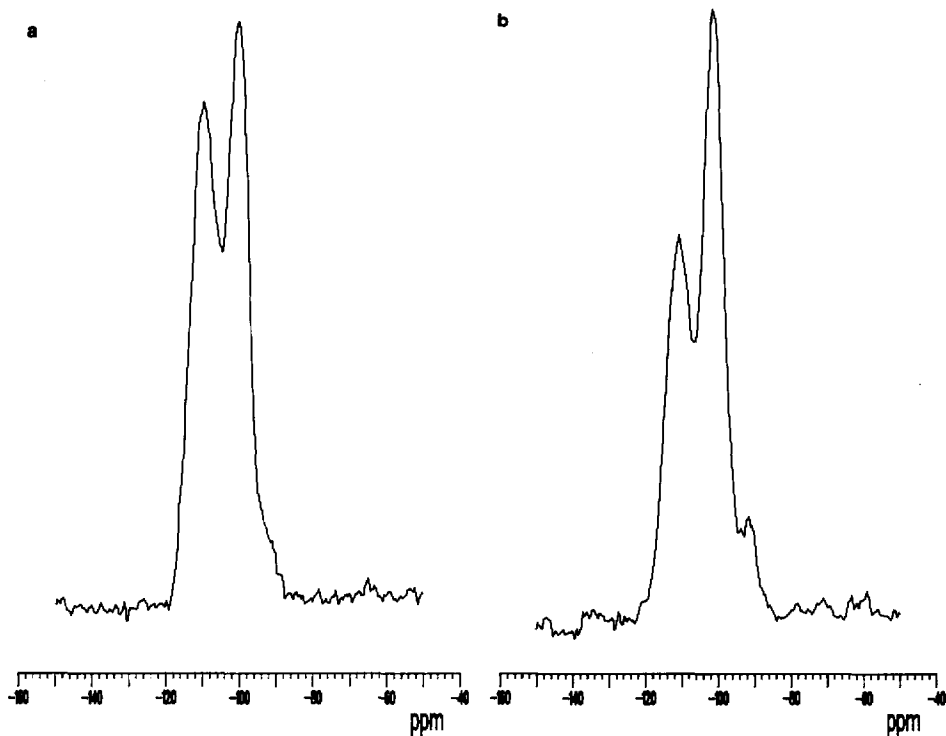

Fig. 1. ^{29}Si CP-MAS NMR spectra of (a) native and (b) acid-treated LiChrosorb Si 100-7. Conditions of treatment: 0.1 M HCl, 363 K, 24 h.

son of the two spectra indicates that the content of geminal and isolated hydroxyl groups increased at the expense of siloxane groups as a result of acid treatment. By peak deconvolution the relative amounts of Q_2, Q_3 and Q_4 were calculated based on peak-area measurements. The results were as follows: for the native silica, Q_2 1.0 ± 0.05%, Q_3 43.9 ± 2.2% and Q_4 54.9 ± 2.7%; and for the acid-treated silica, Q_2 4.6 ± 0.2%, Q_3 50.2 ± 2.5% and 45.1 ± 2.2%. Similar results were found for native and acid-treated (10 M H_2SO_4, 10 M HNO_3, 0.1 M HF; 363 K, 24 h) BE-0.

It should be emphasized, however, that after silanization of the acid-treated silicas with N,N′-dimethylaminodimethyl-n-octylsilane, geminal hydroxyl groups completely disappeared in the ^{29}Si CP-MAS NMR spectrum of the silanized silicas.

By measuring the amplitude of the Q_4 signal as a function of the contact time in milliseconds, a notable shift of the curves of the native BE-0 and the acid-treated derivative (10 M H_2SO_4, 363 K, 24 h) was observed (see Fig. 2). While one broad maximum was obtained at about 15 ms for the native silica, two maxima appeared at 8 and 33 ms for the treated product. The occurrence of the two maxima indicates two types of siloxane groups with different relaxation behaviours [23]. Siloxane groups with the "maximum" in the CP curve at 8 ms show shorter relaxation times than those with the "maximum" at 33 ms. Shorter relaxation times can be ascribed to a more ordered structure with a lower mobility of siloxane groups. There exist at least two different types of domains at the surface of acid-treated silica: regions with poly-crystalline structure interfere with regions with amorphous structure.

Assessment of the crystallinity of silicas by electron diffraction measurements. Electron diffraction measurements on the native LiChrosorb Si 100-7 yielded no detectable reflection pattern whereas on the acid-treated product (10 M HCl, 363 K,
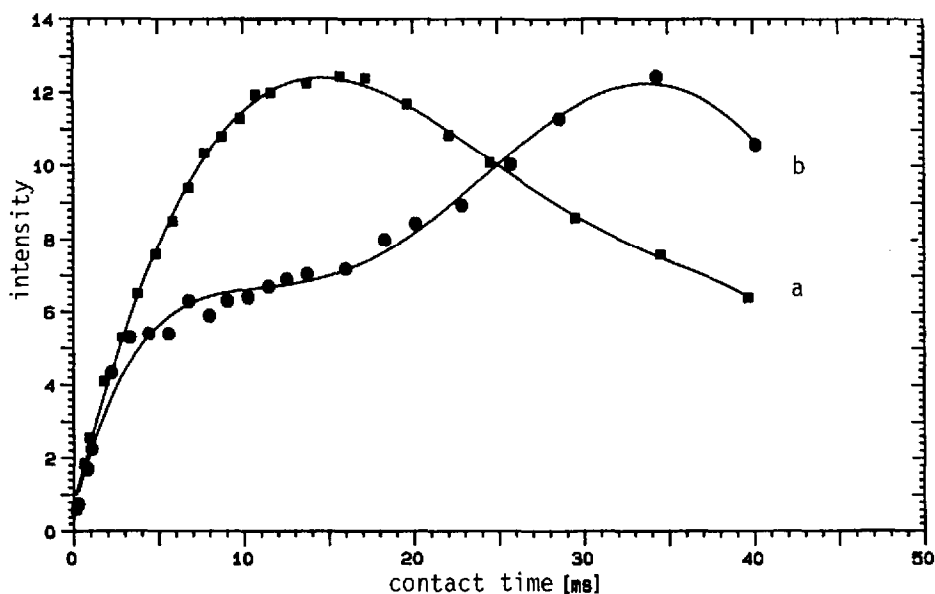

Fig. 2. Amplitude of Q_4 signal as a function of the contact time for (a) native and (b) acid-treated BE-0 silica. Conditions of treatment: 10 M H_2SO_4, 363 K, 24 h.

24 h) a distinct pattern was observed which was identified as a hexagonal structure. Of the possible crystalline polymorphs with a hexagonal structure, β-tridymite seems to be favoured over α-quartz, but a final decision cannot yet be made.

FT-IR spectrometry. FT-IR spectra of native and acid-treated silicas were measured at different activation temperatures. Spectra were also measured after adsorption and desorption of pyridine on the silicas. No differences in the spectra between the native and acid-treated silicas could be observed. Table II summarizes the results of the structural characterization of the native and acid-treated silicas.

Except for the HF-treated silicas, no changes in the specific surface area between the native and treated products were found. Generally, it is questionable whether subtle changes in the microstructure of the surface can be detected by using nitrogen, which has a kinetic diameter of about 0.36 nm [27], as an adsorptive molecule. Smaller adsorptive molecules as sensitive standards for probing geometric changes of the surface structure, such as helium or argon, should preferably be employed.

The decrease in inorganic impurities as a result of acid treatment is trivial and should be seen in the context of an increase in the structural order of the surface. As the impurities are detected as elements, no statements can be made about the chemical composition and structure of surface impurities which have been removed and remained on the surface.

The observed slight increase in the total concentration of surface hydroxyl groups is probably caused by the mild hydrothermal treatment. The result is in agreement with the observation obtained from ^{29}Si CP-MAS NMR spectrometry where the concentration of isolated and geminal groups increased on acidic/hydrothermal treatment.

The pH of a silica suspension is a too crude a measure to detect possible changes in the chemical composition of the silica surface. It appears that the impurities

TABLE II

RESULTS OF STRUCTURAL CHANGES OF SILICAS ON ACIDIC/HYDROTHERMAL TREATMENT

Parameter	Effect of acidic treatment
a_s (BET)	a_s remains constant after treatment with HNO_3, H_2SO_4 and HCl and decreases with HF.
Inorganic impurities	Decrease in metal impurities by about half with LiChrosorb Si 100-7, little effect with the other silicas.
Total concentration of surface hydroxyl groups	OH increases slightly. The effect is most pronounced for H_2SO_4-treated silicas (about 10%).
Geminal hydroxyl, free hydroxyl and siloxane groups	The content of geminal and free hydroxyl groups increased on acidic treatment. Siloxane groups became less mobile and more structured.
Electron diffraction	A reflection pattern arose with acid-treated silicas which could be assigned to a hexagonal structure.
IR spectrometry	No notable changes in the spectra between the native and acid-treated silicas could be observed.

removed from the surface by the treatment did not contribute to the acidic properties of the silica surface to a large extent.

The most notable alteration in the surface structure is the change in the mobility of siloxane groups, which was demonstrated for the first time for a porous silica. Additional methods for detecting changes in the long-range structural order of about 1 nm are needed in other to be able to interpret the NMR data. The occurence of a reflection for the acid-treated silica in the electron diffraction measurements supports the conclusion that a change towards a higher degree of structural ordering had occurred. However, an interpretation in quantitative terms cannot be given.

Tranmission IR spectrometry is too insenstive to diagnose minor changes in the hydroxyl group population as observed by means of isotopic exchange with deuterated trifluoroacetic acid.

In conclusion, it appears that the formation of quasi-crystalline domains at the silica surface occurs as a result of acidic/hydrothermal treatment. The effect is detectable but not very pronounced and requires more intensive examinations by solid-state NMR and diffraction methods.

Effect of acidic/hydrothermal treatment on the chromatographic properties of reversed-phase silicas made from acid-treated base materials

Native and acid-treated silicas (LiChrosorb Si 100-7, LiChrospher Si 100-10, Nucleosil 100-5 and silica BE-0) were reacted with N,N'-dimethylamino-*n*-octylsilane under such conditions that a constant ligand density of $\alpha_{n-octyl} = 3.2 \pm 0.1 \mu mol/m^2$ was obtained. The reversed-phase materials were packed into 125 mm × 4.6 mm I.D. columns. The mobile phase was methanol–water (70:30, v/v). Anilines (sample mixture I) and *n*-alkyl benzoates (sample mixture II) were chromatographed on these columns. From the chromatograms the solute capacity factor, the plate number and the asymmetry factor were calculated. Table III gives typical results for dimethylaniline and *n*-butyl benzoate as test solutes.

Solute capacity factor, k'. The data in Table III show that no consistent changes in k' occurred on al the acid-treated silicas. Hence the results must be considered specifically for each silica. On the silanized BE-0 silica which was treated with HF a decrease in k' of about 20% occurred.The treatment with other acids had only a minor effect on the k' values of the solutes compared with the untreated reversed-phase BE-0 silica. A similar observation can be made on acid-treated and silanized LiChrospher Si 100-10 silicas.

Plate number and asymmetry factor. As the dependences of the plate number (N) and the asymmetry factor (A) on the treatment parameters followed similar trends, but N was determined with a smaller relative standard deviation than A, the discussion of the results will focus on the changes in N as a function of acid treatment. For illustration, Table IV presents the parameters for acid-treated and silanized LiChrosorb Si 100-7 silicas which had a statistically significant impact on N. The results are grouped according to the type of acid employed.

With a given acid, the temperature and the duration of acid treatment affected the plate number significantly, whereas the influence of the concentration of the acid was less pronounced. In some instances the effect of the acid concentration on N was negative, *i.e.*, N decreased with increasing concentration of acid. It can be also seen from Table IV that the sum of the effects of two parameters often exerted a negative influence on N.

TABLE III

EFFECT OF ACIDIC TREATMENT ON THE CHROMATOGRAPHIC PARAMETERS OF REVERSED PHASE SILICAS MADE FROM NATIVE AND ACID-TREATED PRECURSORS

Standard deviations of the parameters: $0.05 < \sigma_{k'} < 0.12$; $250 < \sigma_N < 400$; $0.08 < \sigma_A < 0.27$.

Silica	Type of treatment	Solute					
		Dimethylaniline			n-Butyl benzoate		
		k'	N/m	A	k'	N/m	A
LiChrospher Si 100-10	None	2.78	30 100	2.25	4.72	31 500	1.69
	0.1 M HF, 298 K	2.90	32 300	1.81	4.75	34 300	1.60
	10 M HCl, 298 K	2.92	30 900	1.90	4.70	32 300	1.54
	10 M HCl, 363 K	2.99	31 400	1.75	4.77	33 000	1.58
BE-0	None	1.52	10 200	2.04	2.31	7600	1.83
	0.1 M HF, 363 K	1.21	9900	2.00	1.97	8600	1.55
	10 M H$_2$SO$_4$, 363 K	1.51	11 000	1.82	2.29	7400	1.82
	0.1 M HNO$_3$, 363 K	1.46	10 700	1.81	2.26	7600	1.80
	10 M HNO$_3$, 363 K	1.60	11 800	1.73	2.38	9400	1.19

In detail the results can be summarized as follows. The acid treatment of Li-Chrosorb Si 100-7 with HCl and HNO$_3$ led to similar results: increasing treatment temperature and duration gave an improvement in the plate number. An increase in the concentration of acid had the reverse effect, namely a decrease in N.

With HF-treated LiChrosorb Si 100-7 all three parameters, temperature, duration and concentration of HF, in particular the last parameter, brought about a substantial improvement in the plate number.

LiChrosorb Si 100-7 treated with H$_2$SO$_4$ and silanised showed exceptional behaviour in comparison with the other acids: for the benzoates an improvement in N was obtained on variation of all three parameters, whereas the opposite occurred with

TABLE IV

SURVEY OF STATISTICALLY SIGNIFICANT PARAMETERS OF ACID TREATMENT ON THE PLATE NUMBER OF REVERSED-PHASE SILICA COLUMNS

Silica: LiChrosorb Si 100-7. Parameters: A = temperature, B = duration, C = concentration. Statistical significance $> 97.5\%$ (marked with asterisks), otherwise $> 95\%$.

Acid used for treatment	Solute	Significant parameters
HCl	Dimethylaniline	$A^*, B^*, - (A + B)$
	n-Butyl benzoate	$A, B^* - (A + B)$
HNO$_3$	Dimethylaniline	$A^*, B^*, (A + B)$
	n-Butyl benzoate	$A^*, B^* - C, - (A + B)$
HF	Dimethylaniline	A^*, B^*, C^*
	n-Butyl benzoate	$A^*, B^*, C^*, (A + C)$
H$_2$SO$_4$	Dimethylaniline	$A^*, B, - C, (A + B), - (A + C), - (B + C)$
	n-Butyl benzoate	$A, B^* - (A + C), - B + C)$

anilines as test solutes. The decrease in N for the anilines was most pronounced with 10 M H_2SO_4 and was accompanied by an increase in k' (data not shown). Blank experiments with pure water also showed an improvement in the plate number for LiChrosorb Si 100-7, which increased with increase in treatment temperature.

Similar dependences were obtained on acid-treated and silanized LiChrospher Si 100-10 and BE-0 silicas. However, the effects were less pronounced than those on LiChrosorb Si 100-7.

CONCLUSIONS

Acid treatment of native silicas prior to silanization improved the column performance in terms of plate number and peak symmetry. The extent of improvement increased with increasing temperature and duration of treatment and concentration of the acid, and was partly dependent on the type of native silica.

Considering the changes in the structural properties that result from acidic treatment and combining the results of acid treatment on the column performance, it appears that significant changes in the surface chemistry do not occur on acid treatment and thus the retention of solutes remains unaffected, with some exceptions, and that minor improvements in the structural ordering of the native silica surface on acid treatment exert a statistically significant increase in the column performance of the reversed-phase silicas made from acid-treated precursors. The correlation between these two parameters cannot yet be quantified owing to the lack of precise and reliable structural data for the acid-treated silica surface.

ACKNOWLEDGEMENTS

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