JOURNAL OF Materials CHEMISTRY

Silylation of a crystalline silicic acid: an MAS NMR and porosity study

Peter Heinrich Thiesen,[a] **Klaus Beneke**[b] **and Gerhard Lagaly**[b]

[a]*University of the Federal Armed Forces Hamburg, Department of Mechanical Engineering, Holstenhofweg 85, D-22043 Hamburg, Germany. E-mail: thiesen@unibw-hamburg.de*
[b]*Institute of Inorganic Chemistry, University of Kiel, D-24098 Kiel, Germany. E-mail: h.mittag@email.uni-kiel.de*

Received 3rd May 2002, Accepted 23rd July 2002
First published as an Advance Article on the web 28th August 2002

Tailor-made adsorbents and supports are attracting increasing interest for a wide range of advanced applications in the field of separation techniques and biotechnology. Silica gel silylated with chlorosilanes or alkoxysilanes is a well-established material in chromatography, biotechnology, and affinity separation processes. The surface of the silica gels is disordered, and complete surface coverage with silanes is not always achieved. Crystalline silicic acids from layered potassium silicates, similar to the minerals kenyaite or magadiite, are microcrystalline and their surfaces show a higher degree of regularity. They were modified with different alkyl methoxysilanes to evaluate the possibility of surface silylation. Binding of the silane molecules on surface silanol groups of the crystalline silicic acids was investigated by ^{29}Si MAS NMR spectroscopy. The total surface area was accessible to the silylating agents and almost all surface silanol groups reacted with these molecules. The derivatives contained micropores (between the layers and, possibly, within the layers) and mesopores.

Introduction

Interest in surface modification in the molecular range to obtain tailor-made adsorbents for a wide field of applications is increasing. Silica gel as a matrix material is well known. In the field of biotechnology, modified silica gels are used as supports for affinity adsorbents.[1] One example is the immobilisation of proteins such as lectins[2] and enzymes.[3] To obtain the properties of high affinity and specific adsorption, well-ordered surfaces are required. The degree of crystallinity of the silica gel surface is very low, and the surface shows an irregular structure. Appropriate functionalisation is possible within certain limits. In catalyst and gas adsorption technology, like odour control,[4] defined pore geometry can be helpful to reach a higher degree of specificity. Due to their crystalline structure, layered alkali silicates and crystalline silicic acids should be suitable materials for both fields of application.

Magadiite and kenyaite are examples of natural minerals with a layer structure.[5–8] In 1952, McCulloch[9] first described the synthesis of a layered silicate similar to magadiite. Sodium silicates, like magadiite and kenyaite, but also a lithium potassium silicate, were synthesised from dispersions of silica in aqueous solutions of NaOH, LiOH or KOH.[10–17] Nowadays, many different synthetic layered alkali silicates are known, for example octosilicate,[18] kanemite,[19,20] silinaite,[21] a piperazine silicate (EU19),[22] and a boron-containing layered silicate.[23] The alkali silicates can easily be transformed in the corresponding crystalline silicic acid.[11–13,15,21,24,25–27]Natural magadiite and kenyaite have the compositions $Na_2Si_{14}O_{29}\cdot 11H_2O$ and $Na_2Si_{22}O_{45}\cdot 10H_2O$, respectively. A rosette-like morphology is typical of many layered alkali silicates (Fig. 1). The crystal structure of magadiite and kenyaite is still unknown. Different models based on the structure of makatite have been suggested.[28–30] Almond *et al.*[31] proposed a model that was derived from the structure of the potassium silicate $KHSi_2O_5$ and the piperazine silicate EU19. Garcés *et al.*[32] developed a model of magadiite similar to the silica-rich zeolites epistelbite or dachiadite. This model has been used in the schematic representation of the silylation reactions of the silicic acids shown in Fig. 2.

The grafting of methylvinyldichlorosilane and allyldimethylchlorosilane on mineral surfaces, *e.g.* sepiolite or chrysotile, yielded organomineral derivatives, the surfaces of which are covered with unsaturated organic groups. These derivatives were used as reinforcing components in polymers.[33,34] Organic derivatives of layered polysilicates like magadiite and kenyaite were prepared with chlorotrimethylsilane, allyldimethylchlorosilane, and diphenylmethylchlorosilane.[35–37] Organosilyl groups have been grafted in the interlamellar space of the crystalline silicic acids after intercalation of polar organic substances.[38,39] Interlamellar esterification with aliphatic alcohols was reported by Mitamura *et al.*[40]

^{29}Si MAS NMR spectroscopy is an excellent method for studying silicates,[41–45] silica gels,[46,47] and silylated silica gels.[48,49] ^{29}Si MAS NMR spectra of the trimethylsilyl derivatives of H-magadiite have been reported by Rojo *et al.*[50]

Landis *et al.*[51] reacted the alkylammonium derivatives of

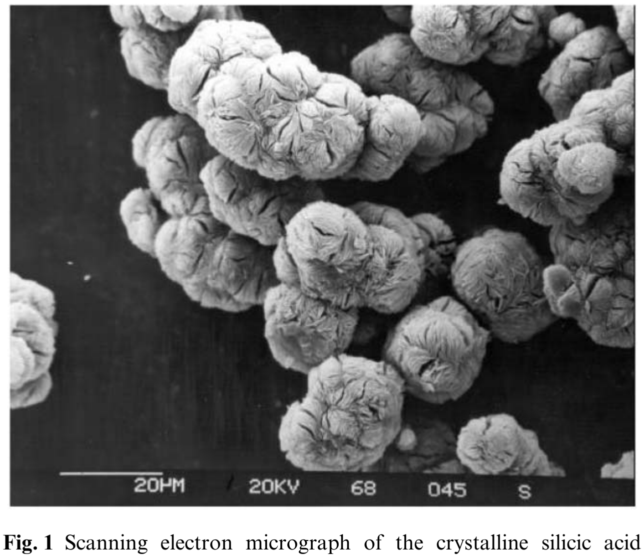

Fig. 1 Scanning electron micrograph of the crystalline silicic acid H 83-O.

DOI: 10.1039/b204314a

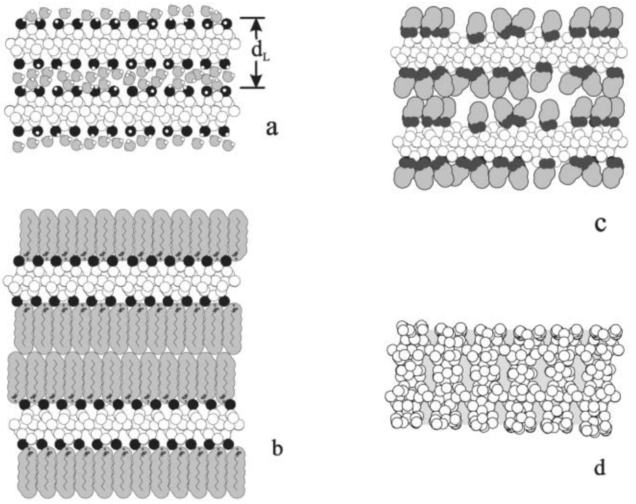

Fig. 2 Schematic representations of (a) the crystalline silicic acid, (b) the octylamine derivative, (c) the silane derivative, and (d) the calcined silane derivative. The layer structure is based on the model of Garcés *et al.*[32]

magadiite, kenyaite, and titanates with tetraethoxysilane (TEOS). Similar derivatives were prepared from the silicic acids of magadiite,[52] octosilicate,[53] and kenyaite.[54] This method can also be used for other inorganic layered compounds such as layered double hydroxides[55] and clay minerals.[56] The specific surface area and pore size distribution of H-magadiite was modified by acid- or base-catalysed reaction with tetraethoxysilane.[57]

An interesting case is the silylation of kanemite. This silicate consists of single layers of [SiO_4] tetrahedra connected to six-membered rings. Due to the flexibility of these layers, the reaction with alkyltrichlorosilanes caused substantial structural changes in them, and new five- and six-membered rings were formed.[58]

For technical uses of modified silicates, the high flexibility of the kanemite layers may be a disadvantage, although it can be advantageous for particular reactions. An alternative is the use of silicates composed of thick silicate layers such as magadiite and, especially, kenyaite. Sodium and potassium silicates identical to the mineral kenyaite can easily be synthesised and consist of 1.77 nm thick, negatively charged silicate layers which are separated by alkali metal ions and one or two layers of water molecules. It is more advantageous to use the potassium form because is more reactive and can also easily be transformed into the corresponding crystalline silicic acid.[12]

Experimental

Potassium silicate

The kenyaite-like hydrous potassium silicate (sample number 83 O) was prepared from a dispersion of silica ("Kieselsäure, gefällt", Merck) in aqueous KOH. The molar ratio $SiO_2 : KOH : H_2O$ was 3 : 4 : 1. The dispersion was allowed to stand for 21 days at 100 °C with occasional shaking. The precipitate was separated by filtration, washed with water, and air-dried.

Crystalline silicic acid

The silicic acid was prepared by dispersing the potassium silicate in a large excess of 0.1 M hydrochloric acid. The samples were left for three days at room temperature with occasional shaking, then filtered off, washed with water, and air-dried.

Silylation

In glass tubes with Teflon plugs, 0.5 g amounts of crystalline silicic acid (about 0.4 mmol) were dispersed in 2 g octylamine with a magnetic stirrer until a gel was formed. Then, different amounts (10, 20, 40, 60, and 100 mmol) of the silylating agent were added. The dispersions were stirred again for 48 h, then separated by centrifugation, washed with ethanol, and dried at 65 °C. The octylamine derivative and the tetraethoxysilane and propyltrimethoxysilane derivatives were also calcined at 450 °C.

We used the following silylating agents: tetraethoxysilane (TEOS); methyl-, ethyl-, and propyltrimethoxysilane (MTMS, ETMS, PTMS); dimethyldimethoxysilane (DMDMS); trimethylmethoxysilane (TMMS) (all from Hüls Troisdorf AG).

^{29}Si MAS NMR spectroscopy

The ^{29}Si MAS NMR spectra of the samples modified with 20 mmol g^{-1} silane (MTMS, ETMS, PTMS) and 80 mmol g^{-1} DMDMS or TMMS were obtained with a Bruker AM 400 instrument at 293 K. The samples were rotated at the magic angle with a frequency of 5 kHz, the frequency of the radiation was 79.796 MHz. The protons were decoupled at high power. The acquisition time was 0.328 s. Pulses were repeated after 60 s, and 700 scans were accumulated. The chemical shifts were related to gaseous tetramethylsilane. Fourier transformation, peak-picking, and deconvolution were performed with the program WIN-NMR (Bruker, Bremen, Germany). Rotational side bands were observed at frequencies about 5000 Hz higher and lower than the resonance frequency of the silicate structure. We could not differentiate between noise and spinning side bands in some cases. Detection and meaningful allocation of the peak area was not possible, but neglecting the area of the rotational side bands did not influence the interpretation of the spectra.

Gas adsorption measurements

Nitrogen gas adsorption measurements were carried out with a home-made volumetric gas adsorption apparatus[27,59] at 77 K. The relative pressure was changed in steps of 0.04 (0.005 for the desorption branches), the time of equilibration was 1 min. The highest relative pressure was 0.965. The data were analysed with the program BET.[60] Micropore volumes were derived from the *t*-plots.[61] The required standard isotherms were calculated after Lecloux and Pirard[62] for C-BET values of 20–30, which yielded *t*-plots with linear sections at lower pressures. A slit-shaped model was used for calculating the mesopore volumes and pore diameter distributions.[63]

Results

^{29}Si MAS NMR spectroscopy

The spectra of the silicic acid, the octylamine derivative, and the various alkylmethoxysilane derivatives showed signals at −92.0 (Q^2) and −101.8 (Q^3), and several signals in the Q^4 range between −109 and −120 ppm (Table 1, Fig. 3). The signal at −110.6 ppm and the shoulder at −114.3 ppm were absent in the spectrum of the octylamine derivative, and the intensity of the signal at −120.4 ppm was reduced. After reaction with propyltrimethoxysilane, new peaks appeared at −49.9, −57.7, −61.7, and –65.4 ppm. The Q^2 signal disappeared and the intensity of the Q^3 signal was strongly reduced. The remaining area of the Q^3 peak was similar to that of the Q^2 peak of the octylamine derivative. The intensity of the central peaks in the Q^4 range increased and the single peaks were no longer resolved. The spectra of the methyl- and ethyltrimethoxysilane derivatives were very similar to that of the propyl trimethoxysilane derivative but the signals at

Table 1 ^{29}Si MAS NMR data (δ/ppm) for the crystalline silicic acid, the octylamine derivative, the alkylmethoxysilane derivatives, and the propyltrimethoxysilane derivative calcined at 450 °C

H 83-O		H 83-O + $C_8H_{17}NH_2$		H 83-O + $C_8H_{17}NH_2$ + MTMS		H 83-O + $C_8H_{17}NH_2$ + ETMS		H 83-O + $C_8H_{17}NH_2$ + PTMS		H 83-O + $C_8H_{17}NH_2$ + DMDMS		H 83-O + $C_8H_{17}NH_2$ + TMMS		H 83-O + $C_8H_{17}NH_2$ + PTMS, calcined	
PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]	PP[a]	DC[b]
												19.8	19.4		
												11.4	11.4		
											−16.0				
										−16.6	−16.3				
						−49.3	−49.3	−49.9	−49.9						
				−57.3	−57.1	−57.6	−57.6	−57.7	−57.9						
								−61.7	−61.9			−62.7	−62.9	−64.1	−63.7
				−64.4	−64.8	−65.4	−65.4	−65.4	−66.1						
−92.0	−92.0	−91.3												−92.6	−93.1
−101.8	−101.8	−101.2	−101.2	−100.3	−100.4	−100.5	−100.5	−100.1	−101.0	−101.7	−101.4	−101.2	−101.2	−101.3	−101.7
−109.1	−109.0	−109.3	−109.2	−108.2	−108.0	−107.8	−107.8	−108.0	−107.9	−109.6	−109.1	−109.0	−109.0		
−110.6	−110.5		−111.0	−111.3	−110.6	−110.6	−110.6	−111.1	−110.7				−110.7		
−111.8	−111.9	−111.5	−111.7							−111.9	−111.8	−111.4	−111.6		
−114.3	−114.1		−112.8											−112.7	−112.4
−115.1	−115.1	−114.5	−114.5	−113.4	−113.1	−113.2	−113.2	−113.4	−113.3	−114.5	−114.6	−114.4	−114.3		
−120.4	−120.4	−119.9	−119.8	−119.2	−119.0	−119.2	−119.2	−119.2	−119.2	−120.6	−120.4	−119.9	−119.9		−120.0

[a] Peak picking (WIN-NMR). [b] Deconvolution (WIN-NMR).

–49 ppm (methyl derivative) and –61.7 ppm were missing (Fig. 4).

The spectrum of the calcined propyltrimethoxysilane derivative showed signals at −64.1 (Q^0), −92.6 (Q^2), and −101.3 ppm (Q^3), a less resolved peak centred at −112.7 ppm, and a shoulder at −120 ppm (Q^4) [Fig. 3(d)].

The shape of the signals of the dimethyldimethoxysilane derivative between −100 and −125 ppm was similar to those of the alkyltrimethoxysilane derivatives (Fig. 5). An asymmetric peak arose at −16.6 ppm. The deconvolution yielding two signals at −16.0 and −16.3 ppm provided an acceptable fit (Table 1).

A different spectrum was obtained for the trimethylmethoxysilane derivative (Fig. 5). Between −100 and −125 ppm, the spectrum was similar to that of the octylamine sample, except that the −101.2 ppm signal lost some intensity and the intensity of the peak at −109 ppm increased. We detected two new peaks at 19.8 and 11.4 ppm.

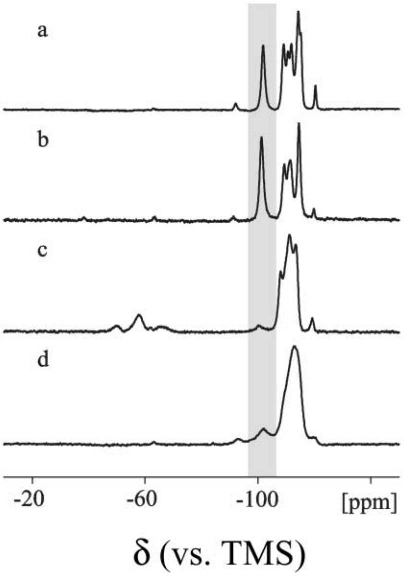

Fig. 3 ^{29}Si MAS NMR spectra of (a) the crystalline silicic acid, (b) the octylamine derivative, (c) the propyltrimethoxysilane derivative, and (d) the propyltrimethoxysilane derivative calcined at 450 °C.

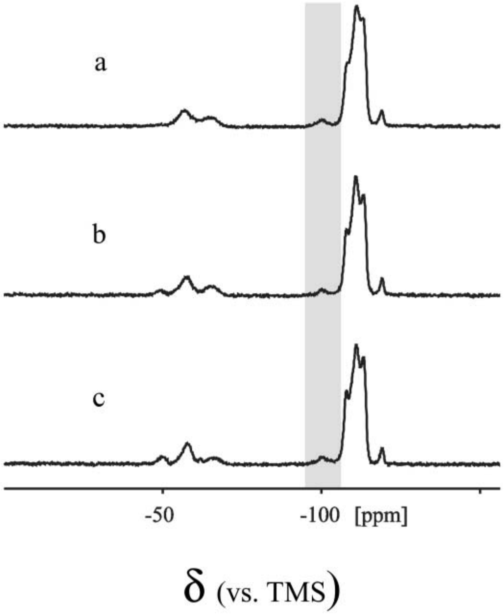

Fig. 4 ^{29}Si MAS NMR spectra of (a) the methyltrimethoxysilane derivative, (b) the ethyltrimethoxysilane derivative, and (c) the propyltrimethoxysilane derivative.

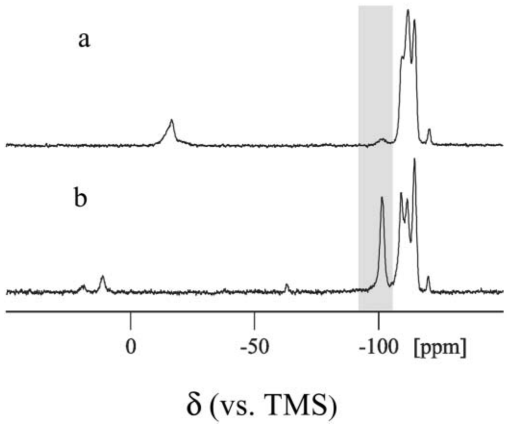

Fig. 5 ^{29}Si MAS NMR spectra of (a) the dimethyldimethoxysilane derivative and (b) the trimethylmethoxysilane derivative.

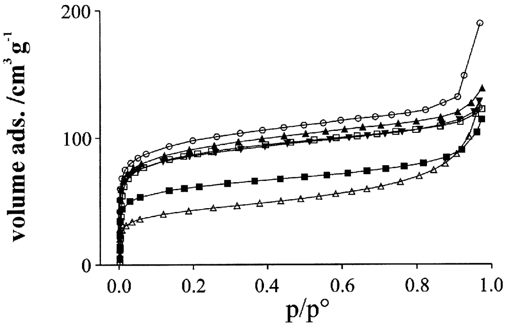

Fig. 6 N_2 adsorption isotherms [ml N_2(STP) g^{-1}] of the propyltrimethoxysilane derivatives of the crystalline silicic acid calcined at 450 °C. Amount of silane in mmol added per g silicic acid: 0 (Δ, octylamine derivative), 20 (■), 40 (□), 80 (▲), 120 (▼), 200 (○).

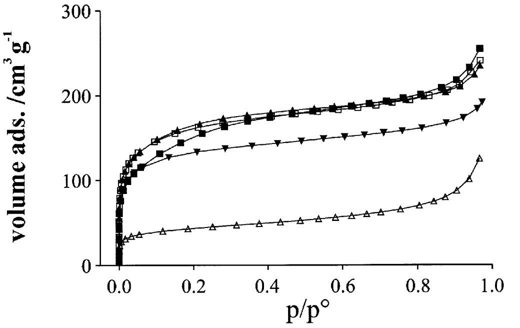

Fig. 7 N_2 adsorption isotherms [ml N_2(STP) g^{-1}] of the tetraethoxysilane derivatives of the crystalline silicic acid calcined at 450 °C. Amount of silane added per g silicic acid: 0 (Δ, octylamine derivative), 20 (■), 40 (□), 80 (▲), 120 (▼).

Gas adsorption

The calcined crystalline silicic acid and the silane derivatives yielded N_2 adsorption isotherms which can be classified as type-I BBDT isotherms[64] or H3 isotherms.[65] The shape of the isotherms for the silylated samples was similar to that for the calcined form of the octylamine derivative of the silicic acid, but the amount of nitrogen adsorbed was significantly higher (Fig. 6). Still higher amounts of nitrogen were adsorbed by the tetraethoxysilane-modified samples (Fig. 7). The micropore volume increased with the amount of silane added for silylation and reached an almost constant value at >40 mmol silane per g silicic acid (Fig. 8). In contrast, the mesopore volume decreased to an almost constant value (Fig. 9). The TEOS derivative showed a distinctly larger specific surface area and larger pore volumes than the propyltrimethoxysilane derivative but the ratio micropore volume/specific surface area was smaller (Table 2).

Discussion

The layer structure of the crystalline silicic acid produces several fingerprint peaks in the Q^4 segment of the ^{29}Si MAS NMR spectra (Fig. 3). The treatment with octylamine slightly changes the layer structure. Morrow and Cody[66–68] described the chemisorption of ammonia on dehydroxylated silica gel. They proposed the adsorption site to be unsymmetrical, strained siloxane bridges. Chuang and Maciel[69] suggested a model of the silica surface in which geminal silanol groups are situated on surface domains similar to the (100) faces of β-cristobalite and single silanol groups on the (111)-type faces. The dehydroxylation process of the silica surfaces could be explained with this model. It was assumed that low strain bicyclo[3.3.0]octosiloxane rings are formed by dehydroxylation between 170 and 450 °C. The mode of dehydroxylation changes between 450 and 650 °C, and highly strained trisiloxane rings form at temperatures above 650 °C.

The signal at −120.4 ppm in the ^{29}Si MAS NMR spectrum of the octylamine derivative [Fig. 3(b)] may be related to strained siloxane bridges in the structure of the crystalline silicic acid. The reaction between such strained siloxane bridges and octylamine reduces the intensity of this peak, but increases the intensity of the Q^3 signal. The disappearance of the two shoulders in the Q^4 segment may also be explained by the reaction of octylamine with the strained siloxane bridges. A shoulder can result from the deformation of a siloxane bridge *within* the layer by the strained siloxane bridges *at the surface* of the layer. This process changes the O–Si–O angles. The relation between the chemical shift and the Si–O–Si angle has been reported in several papers.[70,71] When the strained bridges at the layer surfaces are opened by the reaction with octylamine, the

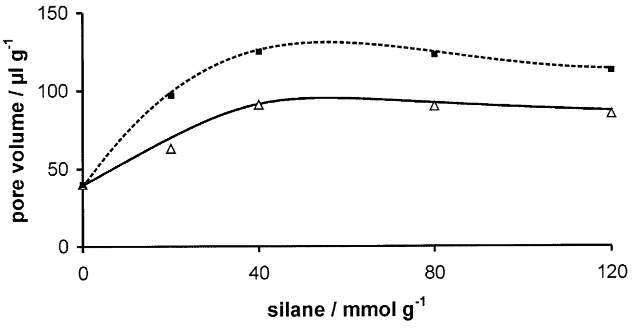

Fig. 8 Micropore volumes of the propyltrimethoxysilane (Δ) and tetraethoxysilane derivatives (■) of the crystalline silicic acid.

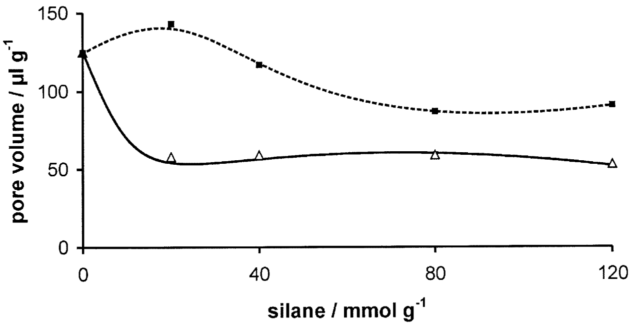

Fig. 9 Mesopore volumes of the propyltrimethoxysilane (Δ) and tetraethoxysilane derivatives (■) of the crystalline silicic acid.

Table 2 Specific surface area and pore volumes of the octylamine derivative and the tetraethoxysilane (TEOS) and propyltrimethoxysilane (PTMS) derivatives of the crystalline silicic acid calcined at 450 °C

Silane added/ mmol g^{-1}	Apparent BET spec. surf. area/$m^2\ g^{-1}$		Spec. surf. area (t-plot)/$m^2\ g^{-1}$		Micropore vol./ µl g^{-1}		Mesopore vol./ µl g^{-1}		Micropore vol./ spec. surf. area/µl m^{-2}	
	TEOS	PTMS	TEOS	PTMS	TEOS	PTMS	TEOS	PTMS	TEOS	PTMS
0	154		75		40		125		0.32	
20	538	215	354	92	97	63	143	58	0.28	0.71
40	570	300	364	128	125	91	117	59	0.34	0.71
80	584	324	374	140	123	90	87	59	0.33	0.63
120	467	305	264	135	113	88	91	53	0.43	0.67

distortion of the intralayer bridges is reduced and the corresponding signals are no longer shifted.

The reaction of the surface silanol groups with alkyltrimethoxysilanes is almost complete because the intensity of the Q^3 signals is strongly reduced in the spectrum of this derivative [Fig. 3(c)]. This indicates that not only the external, but all or most of the interlayer silanol groups have reacted as a consequence of the preceding expansion. The Q^3 signal of the alkyltrimethoxysilane derivatives cannot completely vanish for two reasons. Although the silanol groups in the crystalline silicic acids are more or less regularly arranged, the process of derivatisation probably does not proceed in a regular manner, and, occasionally, some silanol groups cannot find a partner. Then, one of the geminal silanol groups with Q^2 configuration will preferentially react with one silane molecule, forming a Q^3 configuration, whereas the other silanol group will remain unreacted.

The samples did not contain free silane because the signal of pure methyltrimethoxysilane at −40.5 ppm[72] was not observed.

There is a general rule of thumb which states that each additional siloxane bridge on a silicon atom decreases the chemical shift by 10 ppm.[43] Thus, in the spectra of the alkyltrimethoxysilane derivatives, the signal at −49 ppm arises from silicon atoms with one alkyl chain, two silanol groups, and one siloxane bridge, the resonance at −58 ppm is due to silicon atoms with one alkyl chain, one silanol group, and two siloxane bridges, and the peak at −65 ppm indicates one alkyl chain and three siloxane bridges. The ethyl- and propyltrimethoxysilane derivatives show these three types of silicon atoms, but the methyltrimethoxysilane-modified sample did not contain silicon atoms with two silanol groups and one siloxane bridge. The methyl group requires less space than the ethyl or propyl groups and the methyl derivative reaches a higher degree of condensation. The very weak signal at −61 ppm in the spectrum of the propyltrimethoxysilane derivative is due to free silane.

The alkyl groups of the propyltrimethoxysilane derivative are oxidised during calcination at 450 °C. The intensity of the signals from silicon atoms with silicon–carbon bonds and of the Q^2 and Q^3 groups increased. The poor resolution of the signals in the Q^4 range is caused by the loss of crystallinity, but the distribution of the Si–O–Si angles is preserved.

The chemical shift of the silicon atoms in pure dimethyldimethoxysilane is −1.5 ppm.[72] The spectrum of the dimethyldimethoxysilane derivative does not show a signal at this chemical shift. Most of the silane molecules grafted to the surface are resonate at −16.3 ppm. This corresponds to a silicon atom connected to two alkyl groups and two siloxane bridges. Thus, most of the dimethyldimethoxysilane molecules react with two silanol groups, maybe with vicinal silanol groups on the surface or with one surface group and a second silane molecule. As the signal for the Q^2 group is missing and the intensity of the Q^3 signal is negligible, it would appear that almost all surface silanol groups have reacted, as is the case for the alkyltrimethoxysilanes.

Trimethylmethoxysilane shows a ^{29}Si MAS NMR peak at 18 ppm.[72] The very weak signal at 19.8 ppm in the spectrum of the trimethylmethoxysilane derivative is, therefore, due to free silane. The peak at 11.4 ppm is related to the grafted silane molecules and silane dimers. The Q^3 intensity is only slightly reduced and a Q^2 signal is not observed. Thus, only a few surface silanol groups have reacted with the silane molecules. Different explanations are possible. Some silanol groups may be shielded by the methyl groups. The trimethyl groups could retard or impede the diffusion of the silane into the interlayer space. The lack of electronegative side groups, which cause the low field shift, could also be a reason for the low reactivity of the monoalkoxysilanes.

Intercalation of octylamine and subsequent reaction with silanes produces a large expansion of the interlayer space of $\geqslant$1 nm,[52] such that nitrogen molecules can penetrate into the interlayer space. The specific surface area S (m^2 g^{-1}) of the basal planes (without the edge surface area) is estimated from the layer thickness of 1.77 nm and an assumed density of 2.5×10^6 g m^{-3}. Therefore, 1 g silicic acid corresponds to $(S/2) \times (1.77 \times 10^{-9}) \times (2.5 \times 10^6)$ g, and we obtain $S = 452$ m^2 g^{-1}.

The specific surface area after the reaction with TEOS is 350–370 m^2 g^{-1}, which indicates that a large part of the surface is available to nitrogen adsorption. As this value is derived from the *t*-plot, it does not include the micropore surfaces, but does include the surfaces of the mesopores. Almost all silanol groups are esterified when 20 mmol g^{-1} silane are added. At larger silane additions, the surface area remains constant but the micropore volume increases still further. The micropores (diameter < 1 nm) are very likely located in the interlayer spaces within the network of the condensed tetraethoxysilane. Reaction with larger amounts of silane (between 20 and 120 mmol g) does not yield a more densely packed siloxane network in the interlayer space, but increases the layer separation,[52] so that a higher number of micropores or larger micropores are created. Only the largest amounts of silane led to clogging of some micro- and mesopores.

We also mention another hypothesis. If the layer has a structure analogous to a zeolite with microporous channels, the structure could contain micropores, even if all surface silanol groups have reacted with the silane. This hypothesis could also explain why the unmodified but calcined crystalline silicic acid shows a noticeable pore volume.[27,73]

Reaction with the larger propyltrimethoxysilane strongly reduces the specific surface area and, to a lesser extent, the pore volume of the silylated product as compared to the starting materaial. This indicates that the structure of the interlamellar network of condensed propyltrimethoxysilane molecules is denser (containing smaller or less numerous pores). It also implies that the arrangement of the silane molecules at the silicate surface is different from that of the condensed tetramethoxysilane molecules. Because of the distinctly smaller specific surface area, the micropore volume/specific surface area ratio is larger, which could be an advantage for adsorption and separation processes.

Conclusion

The silanol groups of the crystalline silicic acid react almost quantitatively with alkyltrimethoxysilanes and dialkyldimethoxysilanes. This offers a wide area of applications. Calcination of the silylated samples yields microporous and mesoporous materials, but the functional groups are removed by the calcination. This offers the possibility of "scaleable zeolites". The creation of mesoporous and macroporous derivatives with preservation of active surface groups is still unresolved and is our aim for coming investigations.

Acknowledgements

We acknowledge the assistance of Dr G. Peters, Institute of Inorganic Chemistry, University of Kiel, during the MAS NMR measurements and thank him for his co-operation. We are grateful to the Fonds der Chemischen Industrie for financial support.

References

1 G. T. Hermanson, A. K. Mallia and P. K. Smith, *Immobilized Affinity Ligand Techniques*, Academic Press, San Diego, 1992, p. 11.

2 S. Cartellieri, O. Braaß, H. Helmholz, P. Thiesen and B. Niemeyer, in *Biotechnology 2000, Berlin, Book of Abstracts*, DECHEMA, Frankfurt, 2000, vol. 4, pp. 79–81.

3 P. Thiesen, U. Fritz, O. Braaß and B. Niemeyer, in *Adsorption and*

Nanostructures – from Theory to Application, Third International Conference of the Kolloid-Gesellschaft, Budapest, Book of Abstracts, ed. I. Dékány, Szeged, Hungary, 2000, p. 71.

4 P. Thiesen, I. T. Mahlke and B. Niemeyer, *Prog. Colloid Polym. Sci.*, in press.

5 H. P. Eugster, *Science*, 1967, **157**, 1177.

6 J. L. McAtee, R. House and H. P. Eugster, *Am. Mineral.*, 1968, **53**, 2061.

7 T. P. Rooney, B. F. Jones and J. T. Neal, *Am. Mineral.*, 1969, **54**, 1034.

8 P. O. Bricker, *Am. Mineral.*, 1969, **54**, 1026.

9 L. McCulloch, *J. Am. Chem. Soc.*, 1952, **74**, 2453.

10 G. Lagaly, K. Beneke and A. Weiss, *Proc. Int. Clay Conf., 1972*, 1973, 663–673.

11 G. Lagaly, K. Beneke and A. Weiss, *Am. Mineral.*, 1975, **60**, 642.

12 K. Beneke and G. Lagaly, *Am. Mineral.*, 1983, **68**, 818.

13 K. Beneke, H. H. Kruse and G. Lagaly, *Z. Anorg. Allg. Chem.*, 1984, **518**, 65.

14 W. Schwieger, W. Heyer, F. Wolf and K.-H. Bergk, *Z. Anorg. Allg. Chem.*, 1987, **548**, 204.

15 K. Beneke and G. Lagaly, *Am. Mineral.*, 1989, **74**, 224.

16 W. Schwieger, K.-H. Bergk, D. Heidemann, G. Lagaly and K. Beneke, *Z. Kristallogr.*, 1991, **197**, 1.

17 K.-H. Bergk, P. Grabner and W. Schwieger, *Z. Anorg. Allg. Chem.*, 1991, **600**, 134.

18 R. K. Iler, *J. Colloid Sci.*, 1964, **19**, 648.

19 K. Beneke and G. Lagaly, *Am. Mineral.*, 1977, **62**, 763.

20 I. A. Crone, K. R. Franklin and P. Graham, *J. Mater. Chem.*, 1995, **5**, 2007.

21 K. Beneke, P. Thiesen and G. Lagaly, *Inorg. Chem.*, 1995, **34**, 900.

22 A. J. Blake, K. R. Franlin and B. M. Lowe, *J. Chem. Soc., Dalton Trans.*, 1988, 2513.

23 W. Schwieger and E. Brunner, *Colloid Polym. Sci.*, 1992, **270**, 935.

24 G. Lagaly, K. Beneke and A. Weiss, *Am. Mineral.*, 1975, **60**, 650.

25 G. Lagaly, *Adv. Colloid Interface Sci.*, 1979, **11**, 105.

26 G. Lagaly, H.-M. Riekert and H. H. Kruse, in *Chemical Reactions in Organic and Inorganic Constrained Systems*, ed. R. Setton, D. Reidel, Dordrecht, 1986, pp 361–379.

27 H. H. Kruse, K. Beneke and G. Lagaly, *Colloid Polym. Sci.*, 1989, **267**, 844.

28 W. Schwieger, D. Heidemann and K.-H. Bergk, *Rev. Chim. Miner.*, 1985, **22**, 639.

29 T. J. Pinnavaia, I. D. Johnson and M. Lipsicas, *J. Solid State Chem.*, 1986, **63**, 118.

30 A. Brandt, W. Schwieger and K.-H. Berg, *Rev. Chim. Miner.*, 1987, **24**, 564.

31 G. G. Almond, R. K. Harris and K. R. Franklin, *J. Mater. Chem.*, 1997, **7**, 681.

32 J. M. Garcés, S. C. Rocke, C. E. Crowder and D. L. Hasha, *Clays Clay Miner.*, 1988, **36**, 409.

33 E. Ruiz-Hitzky and A. Van Meerbeck, *Colloid Polym. Sci.*, 1978, **256**, 135.

34 Van Meerbeck and E. Ruiz-Hitzky, *Colloid Polym. Sci.*, 1979, **257**, 178.

35 T. Yanagisawa, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3743.

36 T. Yanagisawa, K. Kuroda and C. Kato, *React. Solids*, 1988, **5**, 167.

37 T. Yanagisawa, M. Harayama, K. Kuroda and C. Kato, *Solid State Ionics*, 1990, **42**, 15.

38 E. Ruiz-Hitzky and J. M. Rojo, *Nature*, 1980, **287**, 28.

39 E. Ruiz-Hitzky, J. M. Rojo and G. Lagaly, *Colloid Polym. Sci.*, 1985, **263**, 1025.

40 Y. Mitamura, Y. Komori, S. Hayashi, Y. Sugahara and K. Kuroda, *Chem. Mater.*, 2001, **13**, 3747.

41 W. Schwieger, D. Heidemann and K.-H. Bergk, *Rev. Chim. Miner.*, 1985, **22**, 639.

42 D. Heidemann, A.-R. Grimmer, C. Hübert, P. Starke and M. Mägi, *Z. Anorg. Allg. Chem.*, 1985, **528**, 22.

43 G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley & Sons, New York/Chichester/Brisbane/Toronto/Singapore, 1987.

44 G. Scholzen, K. Beneke and G. Lagaly, *Z. Anorg. Allg. Chem.*, 1991, **597**, 183.

45 G. G. Almond, R. K. Harris, K. R. Franklin and P. Graham, *J. Mater. Chem.*, 1996, **6**, 843.

46 A. Tuel, H. Hommel, A. P. Legrand, Y. Chevallier and J. C. Morawski, *Colloids Surf.*, 1990, **45**, 413.

47 B. A. Morrow and I. D. Gay, *J. Phys. Chem.*, 1988, **92**, 5569.

48 E. J. R. Sudhölter, R. Huis, G. R. Hays and N. C. M. Alma, *J. Colloid Interface Sci.*, 1985, **103**, 554.

49 J. M. J. Vankan, J. J. Ponjeé, J. W. De Haan and L. J. M. van de Van, *J. Colloid Interface Sci.*, **126**, 604.

50 J. M. Rojo, J. Sanz, E. Ruiz-Hitzky and J. M. Serratosa, *Z. Anorg. Allg. Chem.*, 1996, **540–541**, 227.

51 M. E. Landis, B. A. Aufdembrink, P. Chu, I. D. Johnson, G. W. Kirker and M. K. Rubin, *J. Am. Chem. Soc.*, 1991, **113**, 3189.

52 J. S. Dailey and T. J. Pinnavaia, *Chem. Mater.*, 1992, **4**, 855.

53 K. Kosuge and A. Tsunashima, *J. Chem. Soc., Chem. Commun.*, 1995, 2427.

54 O.-Y. Kwon and S. W. Choi, *Bull. Korean Chem. Soc.*, 1999, **20**, 69.

55 S. K. Yun, V. R. L Constantino and T. J. Pinnavaia, *Clays Clay Miner.*, 1995, **43**, 503.

56 T. J. Pinnavaia, A. H. Galarneau and A. F. Barodawalla, *US Pat.*, 5834391, 1998.

57 S.-Y. Jeong, O.-Y. Kwon, J.-K. Suh, H. Jin and J. M. Lee, *J. Colloid Interface Sci.*, 1995, **175**, 253.

58 A. Shimojima, D. Mochizuki and K. Kuroda, *Chem. Mater.*, 2001, **13**, 3603.

59 H. H. Kruse and G. Lagaly, *GIT Fachz. Lab.*, 1988, **32**, 1096.

60 W. Ewald, Doctoral Thesis, University of Kiel, Germany, 1995.

61 B. C. Lippens and J. H. de Boer, *J. Catal.*, 1965, **4**, 319.

62 A. Lecloux and J. P. Pirard, *J. Colloid Interface Sci.*, 1979, **70**, 265.

63 W. B. Innes, *Chem. Ind.*, 1957, 757.

64 S. Brunauer, L. S. Demming, W. E. Demming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

65 C. H. Gilles, T. H. MacEwen, S. N. Nahkwa and D. Smith, *J. Chem. Soc.*, 1960, 3973.

66 B. A. Morrow and I. A. Cody, *J. Phys. Chem.*, 1976, **80**, 1998.

67 B. A. Morrow and I. A. Cody, *J. Phys. Chem.*, 1976, **80**, 1995.

68 B. A. Morrow, I. A. Cody and L. S. M. Lee, *J. Phys. Chem.*, 1976, **80**, 2761.

69 I.-S. Chuang and G. E. Maciel, *J. Phys. Chem. B*, 1997, **101**, 3052.

70 J. V. Smith and C. S. Blackwell, *Nature*, 1983, **303**, 223.

71 G. Engelhardt and R. Radeglia, *Chem. Phys. Lett.*, 1984, **108**, 271.

72 N. Janes and E. Oldfield, *J. Am. Chem. Soc.*, 1985, **107**, 6769.

73 H. H. Kruse, Doctoral Thesis, University of Kiel, Germany, 1987.