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Chemistry and Properties of Porous, Organically Modified Silica

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Sol–gel techniques were used to prepare porous, organically modified silica materials. The introduction of organic groupings was carried out with alkoxysilanes as precursors; methyl and propyl amino groups were used. The results show that high-porosity materials can be synthesized; the microstructure strongly depends on reaction conditions such as composition, solvent, catalyst type, and concentration. Microstructure tailoring affects mechanical as well as adsorption properties, and custom-made materials such as abrasives and adsorbents with special properties were synthesized.

SILICA IS AN OXIDE with innumerable variations. On the basis of this structural variability, a variety of different types of materials have been prepared, such as compact fused silica, in the form of plates, fibers, or finely dispersed pellets, and porous materials. Because compact silica is mostly used for optical components or applications for which high chemical durability is required, porous and finely dispersed materials have completely different applications, for example, as fillers, adsorptive materials, or strengtheners in composites. Various aspects of the chemistry, physics, and applications of silica are described in detail in the book by Iler (*1*), with special consideration given to finely dispersed and porous materials.

The main preparation method for fused silica still involves melting technology, but a few other methods are used that involve sol–gel or

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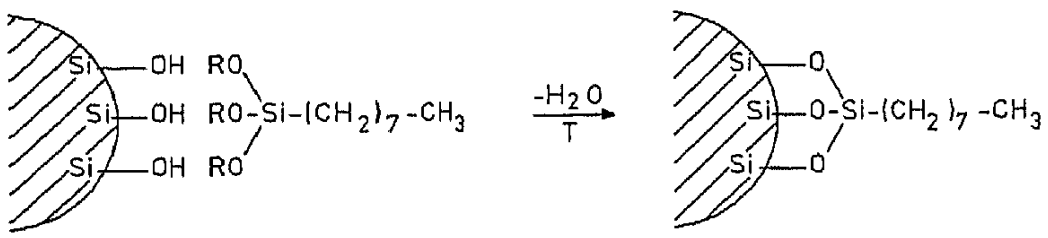
related routes (2). For fibers and coatings, sol–gel technology has become more and more important (3–5). For dispersed materials, pyrolytic and precipitation processes are the dominating technologies for large-scale production (6–7). To adapt these types of silica to a variety of special applications, various types of chemical surface modifications have been performed. A survey is given in reference 1. By surface modification (e.g., by organosilicon compounds) the hydrophobicity or hydrophilicity can be varied. For example, chromatographic materials (for reverse-phase chromatographic columns, for example) are prepared by reacting alkylsilanes that have well-defined alkyl chain-lengths (e.g., C_8) with the silica surface (Scheme I):



Scheme I.

This type of surface modification, if adequate functional groups are used, can be useful in incorporating silica particles into polymeric matrices (e.g., into rubber for tires) or in increasing the hydrolytic stability of high-surface-area silica (e.g., that used for membranes). Surface modification of silica is a very important principle and is widely commercialized.

General Considerations

Another principle of modification, the modification of the network by organic groups, is not as important now compared to the surface modification principle. The exchange of an –O– group of a $[SiO_4]^{4-}$ tetrahedron by a CH_3 group drastically changes the properties of the modified "glass" compared to fused silica. The density drops from about 2.2 (fused silica) to about 1.3 g/cm^3, and the thermal coefficient of expansion increases from 0.5×10^{-6} to 100×10^{-6} K^{-1}. Bulk materials modified by CH_3 are used as spin-on glasses for coating purposes in microelectronics. They can be oxidized to SiO_2 glassy films if desirable (8). The partial substitution of ≡Si–O– bonds by ≡Si–CH_3 groups leads to densification temperatures far below the densification of inorganic SiO_2 sol–gel films. The examples indicate an interesting effect of organic

modification of silica on properties as well as on structure. This chapter focuses on porous silica materials that have been bulk-modified by ≡Si–C– bonds and derived by sol–gel methods.

High porosity or high surface areas can be obtained by various preparation or special processing techniques, for example, by leaching of phase-separated sodium borosilicate glasses. Small dimensions of building units are required; small particles or small pores between units must be created (Figure 1). In materials with small pores between units, a high rigidity of material is required to avoid the collapse of the pores during the network synthesis.

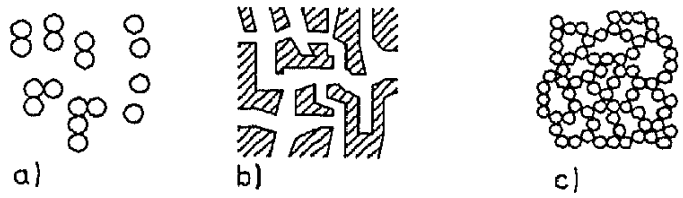
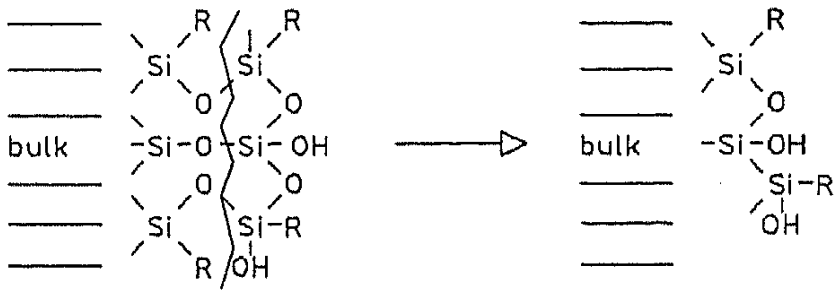


Figure 1. Model of high-surface-area materials: a, small particles; b, "reverse" system, small pores; and c, porosity generated by aggregation of small particles (a).

The required network rigidity results from the three-dimensional cross-linking of the $[SiO_4]^{4-}$ tetrahedrons. Bulk modification by introduction of organic units through ≡Si–C– bonds leads to a change of network connectivity and should also affect porosity or surface area. On the other hand, in this case the modification becomes an intrinsic property that should not be affected by surface corrosion (Scheme II), because after removal of the surface layer by hydrolytic processes, the following layer exhibits the corresponding structure and properties. The properties to be developed determine whether a surface or a bulk modification is more appropriate.



Scheme II. Model of corrosion of organic modification of silica ("bulk" denotes the $-CH_3$-modified structure).

Preparation of Porous Materials

Reactivity of Precursors in Sol–Gel Processes. If multicomponent systems are prepared by hydrolysis and condensation of alkoxide precursors in methanol, the reaction rates of hydrolysis and condensation (including aggregation) of the different components become very important for the distribution of the different components. The simple question of how CH_3 groups might be distributed within a porous two-component system with $Si(OR)_4$ and $CH_3Si(OR)_3$ or $(CH_3)_2Si(OR)_2$ as precursors leads to serious mechanistic problems. A comparison of the hydrolysis rates with acid catalysis indicates an increase with increasing number of organic ligands (*9–11*) and the opposite with bases. The effect on specific surface areas of the resulting materials is shown in Figure 2. Similar results with $(CH_3)_2SiO$-containing systems for membrane formation were obtained with ethanol.

The surface areas were measured by multipoint Brunauer–Emmett–Teller (BET) techniques. In NH_3-catalyzed materials, the fraction of micropores is extremely low (<1 vol %). In acid catalysis, the micropore content increased with decreasing surface area. The CH_3 content was determined by IR spectroscopic analysis of CH_3 groups only in NH_3-catalyzed composites could a loss of CH_3-containing units be observed.

The experimental process for synthesizing the porous materials was standardized as follows. The silanes were mixed in the ratios as indicated in MeOH (Me, methyl) as solvent, and then at room temperature 1 mol of water per ≡SiOR group was added. The water contained the indicated concentration of catalysts. The reaction mixture was stirred for 5 min and then stored in a closed flask. The two different catalysts show opposite tendencies with respect to increasing concentrations of CH_3 groups in the system. With NH_3, the surface areas decrease with increasing CH_3 group content in both systems (SiO_2–$CH_3SiO_{3/2}$ and SiO_2–$(CH_3)_2SiO$), but there is no significant difference between both systems.

In the acid-catalyzed systems, very high surface areas are observed in CH_3-containing composites. The effect of the HCl concentration is significant. In basic catalysis, the reaction conditions do not seem to influence structure and porosity to the same extent as in the acid case. In acid catalysis, the total surface area increases with decreasing gelling times and increases with increasing CH_3 concentrations. The gelling times are given in Table I.

The increase of surface area with increasing CH_3 concentration (decreasing network connectivity) can be explained by the interaction of CH_3-covered pore walls with water; this interaction leads to reduced interfacial tensions. Synthesis yields are a function of catalyst and composition (Figure 3). This fact can be explained by a reaction rate consideration. As shown in reference 9, the hydrolysis rate of the CH_3-

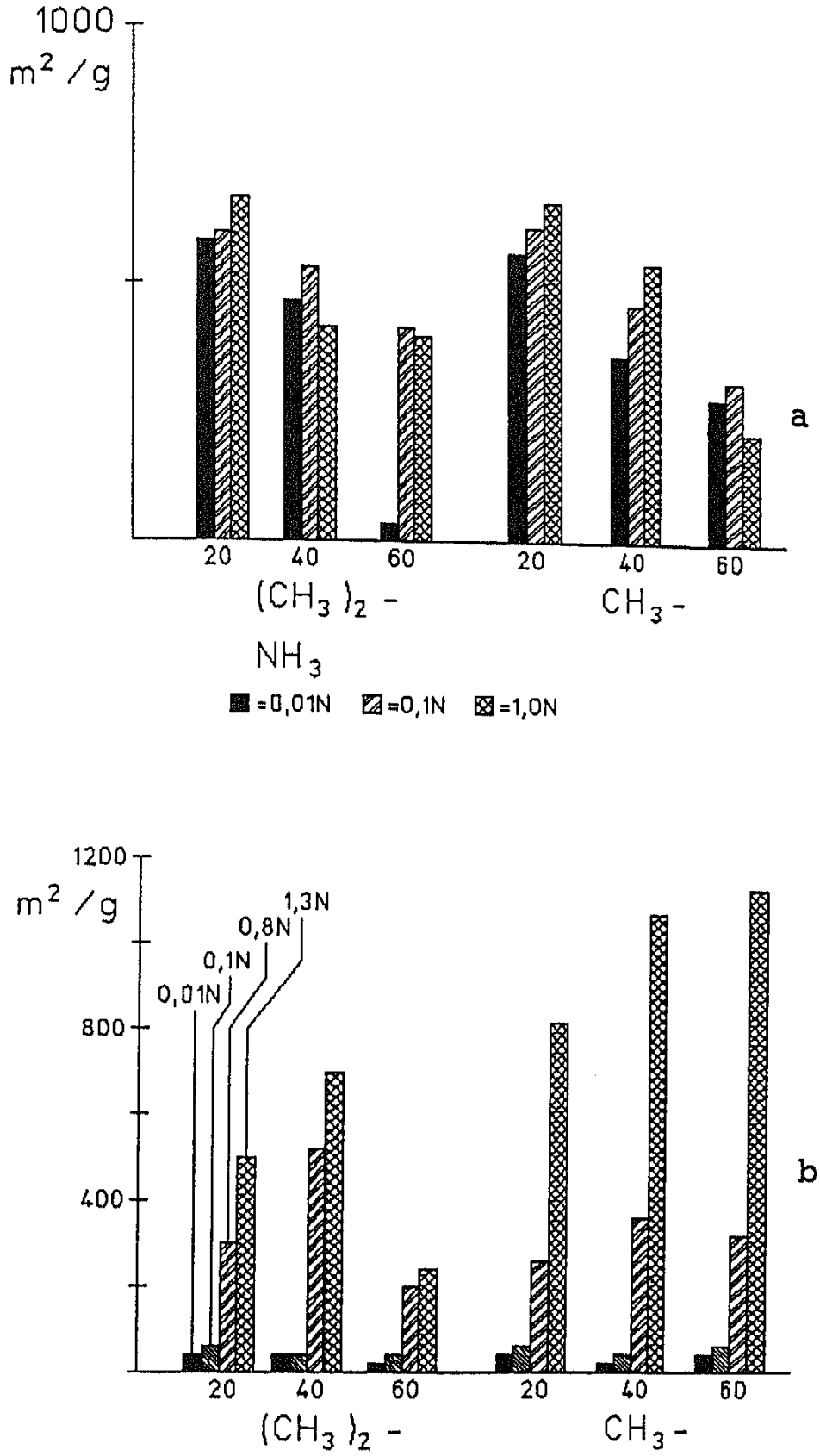


Figure 2. Effect of reaction conditions and composition on the specific surface area of $-CH_3$-modified silica [tetramethoxysilane (TMOS) as shown]. Part a: catalyst, NH_3; abscissa numbers, weight percent of $CH_3SiO_{3/2}$ or $(CH_3)_2SiO$. Part b: catalyst, HCl; abscissa numbers, same as in part a.

Table I. Gelling Times of Various Composites

Catalyst Type and Concentration	*80:20*	*60:40*	*40:60*
1 N NH_3 (2 N HCl)	~1 (~3 × 10^5)	~1 (~3 × 10^5)	~1 (~3 × 10^5)
0.1 N NH_3 (0.1 N HCl)	300 (~23 × 10^5)	~840 (~11 × 10^5)	~2700 (~13 × 10^5)
0.01 N NH_3 (0.01 N HCl)	1200 (~47 × 10^5)	~10^5 (~80 × 10^5)	~3 × 10^5 (~60 × 10^5)

NOTE: Times are reported in seconds. In the composite ratios, first number is the weight percent of SiO_2 in SiO_2–$CH_3SiO_{3/2}$.

substituted silanes in NH_3 catalysis drops rapidly. This decrease does not necessarily lead to longer gelation times because the gel formation could be caused by the tetraorthosilicate network only. As shown in reference 11, the condensation rate increases with higher pH values, leading to shorter gelling times in the composite sol compared to the acid-catalyzed case. Because of the low hydrolysis rates in the basic case, the gelling occurs mainly from the $Si(OR)_4$ hydrolysis and condensation, and the unhydrolyzed CH_3-containing precursors can evaporate if the gels are dried shortly after gelling. IR spectra in the base-catalyzed case show a corresponding decrease of the CH_3 signal in basic gels, too. If the composites are stored in a closed system for several weeks without drying after gelation to allow further reaction, higher yields can be obtained from basic catalysis, too. This process was carried out for surface area and H_2O adsorption measurements.

To support the hypothesis of weaker pore wall interaction in the CH_3-modified case, H_2O adsorption experiments were carried out on several

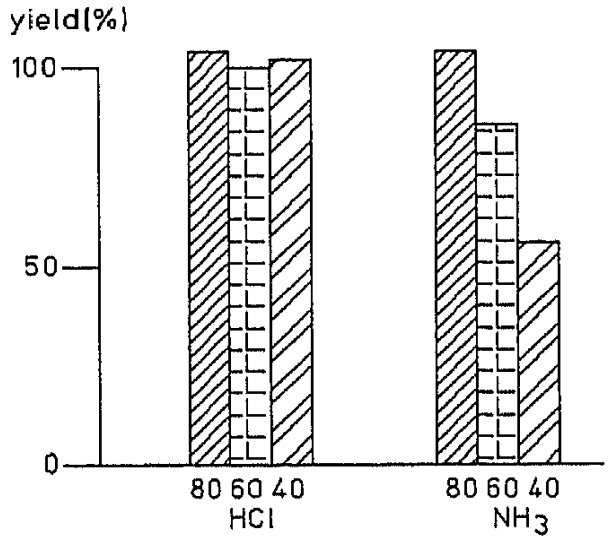


Figure 3. Percentage of product yield depending on catalyst and composition. The samples were dried after gelling to a constant weight at 110 °C; yields above 100% are due to residual water. Catalyst concentrations were 1.0 N NH_3 and 1 N HCl; abscissa numbers denote wt % SiO_2 in SiO_2–$CH_3SiO_{3/2}$ composites.

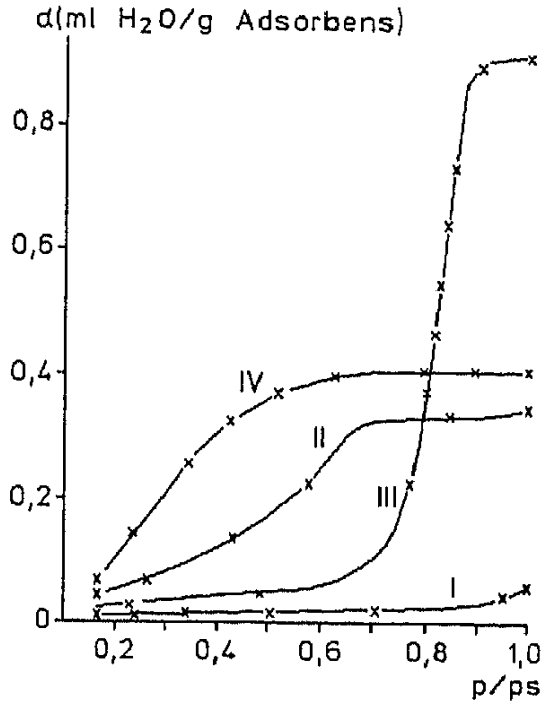
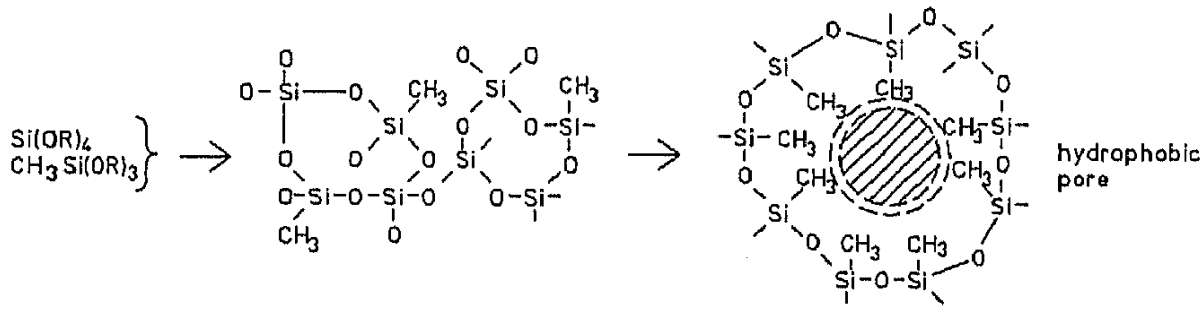


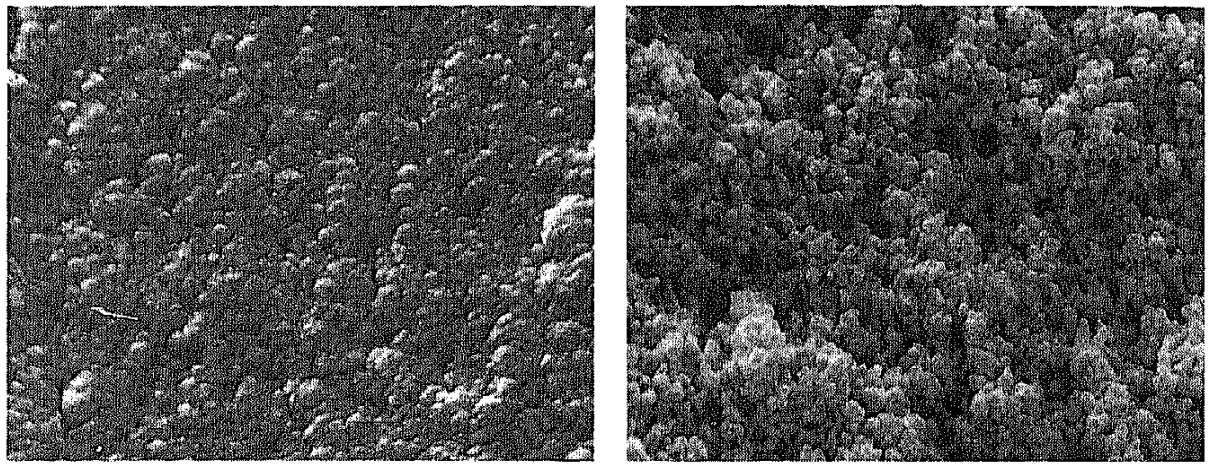
Figure 4. H_2O adsorption isotherms (partial pressure over saturation pressure) on four different silicas: I, CH_3-modified 300 m^2/g; II, $-CH_2-CH_2COOH-$, 800 m^2/g; III, $(CH_2)_3NH_2-$, 310 m^2/g; and IV, unmodified, 450 m^2/g.



Scheme III. Self-arrangement of CH_3-modified systems.

porous silica gels with different compositions (Figure 4). The CH_3-modified system shows almost no H_2O adsorption, a result indicating extremely hydrophobic pores. Increasing hydrophilicity (II → IV) changes the adsorption behavior gradually. During the condensation step of the CH_3-containing gels, a self-adjustment of the system seems to take place, and the CH_3 groups "turn" to the inner pore walls (Scheme III).

In summary, high-surface-area systems can be prepared from $CH_3-Si\equiv/SiO_2$ and $(CH_3)_2SI=/SiO_2$ composites even if the network stiffness is expected to be decreased substantially, perhaps because of the decrease of interaction between hydrophobic (self-arranged) pore walls and H_2O and the reduction of interfacial forces.



a b

Figure 5. Images of gel surfaces: a, 0.1 N NH_3, 450 m^2; b, 6 N HCl, 270 m^2 g. The bar is 4 μm.

The influence of the catalyst does not only affect the physical properties; the morphology can be influenced, too. Figure 5 shows two gels with 60 wt % $(CH_3)_2SiO$ in a $(CH_3)_2SiO/SiO_2$ composite. Whereas the NH_3-catalyzed material is transparent, the HCl-catalyzed material is cloudy. Pore analysis shows a maximum at radius r of 4.2 and 500 nm. The larger radii can be of interest as "transport pores" for kinetics in liquid adsorption processes. This example shows how processing conditions can be used for the generation of special microstructure properties.

Preparation of Materials with Special Functions. The porosity not only defines the adsorption parameters of a material, but also its mechanical stability. On the basis of this idea and the hydrolysis and condensation kinetics and its effect on microstructure, an abrasive powder was developed (*12–13*) with an abrasion-controlling mechanism for human skin. The investigation of the synthesis parameter shows a direct connection between the composition and the mechanical properties of the granular material (Figure 6). As expected from the previous experiments, HCl had to be used to provide reproducible CH_3 concentrations and well-defined, reproducible material properties.

The increase of the abrasion number (not representing higher abrasion) at higher $(CH_3)_2SiO$ contents is misleading and due to the increasing elasticity of the grains, which is not covered by the test. For the hydrolysis and condensation step, HCl had to be used because NH_3 did not lead to satisfying products for reasons pointed out in the section "Reactivity of Precursors in Sol–Gel Processes". The abrasive material was incorporated into a soap matrix and is used for the medical treatment of acne papulo pustulosa very successfully. It has been on the market for several years as a commercial product (*14*).

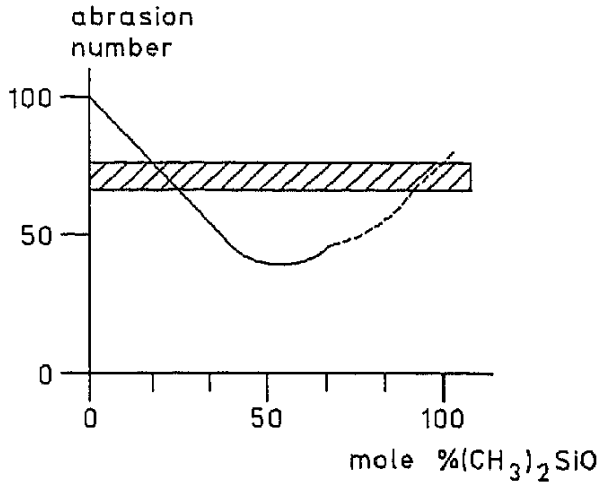


Figure 6. Abrasion numbers of a $(CH_3)_2SiO-SiO_2$ composite. The number represents the fraction of unaffected grains of an average diameter of 0.3 mm (in percentage) after a special abrasion test (15). The hatched area represents abrasive behavior recognized to be satisfying by test persons. The dashed line represents data that were not useful because of elasticity.

To customize the adsorption of functional molecules, the incorporation of organic groupings increasing the interaction between the adsorbent and the molecule to be adsorbed should be an adequate method. Several mechanisms can be taken into consideration, for example, an acid–base or a hydrophobic interaction mechanism. If larger molecules such as enzymes are considered, the pore size plays an important role, and the area of the accessible surface is an important parameter, too. To create basic sites, various types of silica with amino groups were synthesized by cohydrolyzing $(CH_3O)_3Si(CH_2)_3NH_2$, $Si(OC_2H_5)_4$, and optionally $(CH_3)_2Si(OC_2H_5)_2$ at room temperature with 50 vol % methanol as solvent.

Because amino groups act autocatalytically (*15–17*) in the presence of water, for acid catalysis an excess of HCl was used to overcompensate the formation of $-NH_3^+Cl^-$. In these cases, the gels were washed with methanol and water until no Cl^- could be detected in the filtrate. How far the incorporation of amino groups into silica could affect the adsorption of acid components was of interest. Lactic acid and a sulfonic acid (a commercially available dye named Telon Light Yellow) were chosen as test components (*18*). In Figure 7 the adsorption isotherm of lactic acid is shown. Unmodified SiO_2 does not have remarkable adsorption in aqueous solution under these circumstances. The result shows the effect of the amino modification quite clearly, because the lactic acid load of the adsorbent is remarkable, and it is difficult to adsorb small water-soluble molecules in an aqueous environment.

The kinetics of the adsorption are shown in Figure 8, which demonstrates an almost ideal breakthrough curve that indicates fast kinetics. The

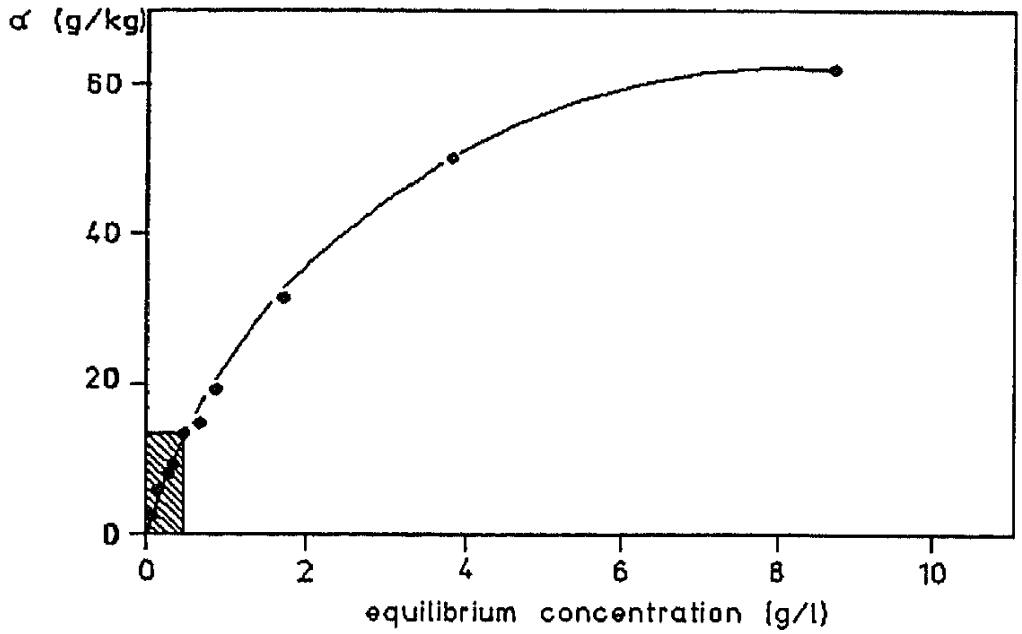


Figure 7. Adsorption isotherm of lactic acid on an amino-modified adsorbent. The composition was 5/95 (weight percent) in $NH_2(CH_2)_3SiO_{3/2}/SiO_2$. The mole surface was found to be 9.8×10^{-5} $-NH_2/g$; the method was that of reference 17. The BET surface area was 350 m^2/g; the hatched area indicates high loads even at low equilibrium concentrations.

breakthrough level represents almost the equilibrium value and does not depend on the flow rates used in the experiment. A glass tube 0.5 cm in diameter was used. Chemical analysis was carried out in steps of 5 mL to monitor the lactic acid concentration during the absorption experiment.

The sulfonic acid did not have remarkable adsorption under these circumstances. If, in addition to amino groups, a $(CH_3)_2Si=$ unit is incorporated, the adsorption rates increase remarkably. The best results were obtained with the composition SiO_2:$(CH_3)_2SiO$:amino = 40:60:2.5 with 9 N HCl as catalyst. The high concentration was found to lead to a maximum of load in a series of experiments with varying catalyst concentrations. The aromatic sulfonic acid could be loaded to 120 g per kilogram of adsorbent with an equilibrium concentration of 1.6 g/L and to 26 g/kg with 0.2 g/L (Figure 9). This fact can be attributed to a "double function" adsorption mechanism of a hydrophobic interaction of $-CH_3$ groups with the phenyl group of the sulfonic acid and the acid-based interaction. The kinetics of the flow experiments could be improved by microstructure tailoring (Figure 9) by variation of the catalyst concentration. Figure 9b shows the optimized microstructure with "transport pores" and a surface area about three times that of the adsorbent in Figure 9a.

Another interesting case is the adsorption of CO_2, which does not show dipole moment but is able to dissociate with water to an ionic compound

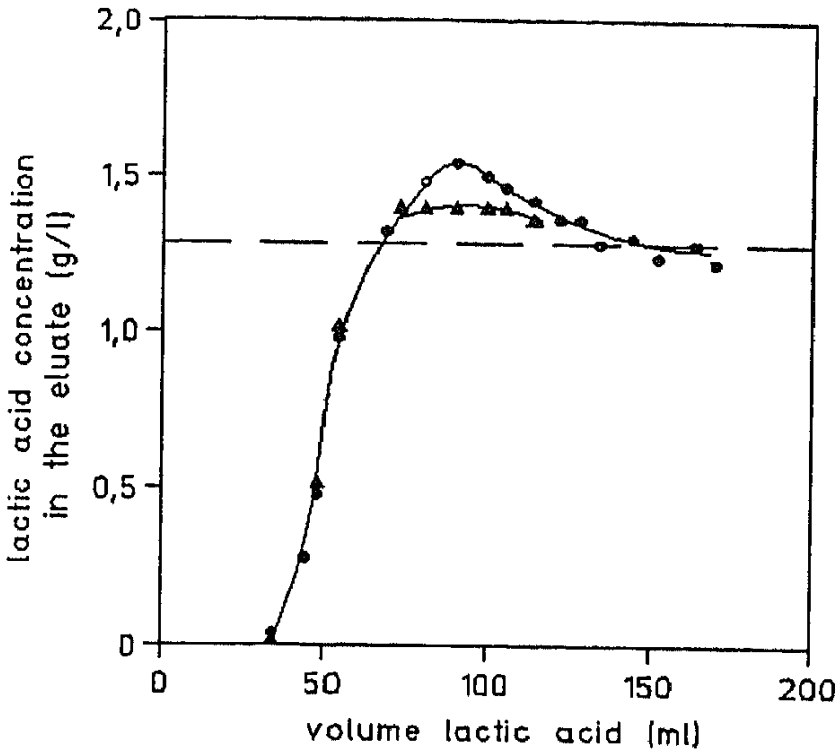


Figure 8. Breakthrough curves of a column-flow experiment. Flow rates were 2.0 (▲) and 0.83 (●) mL/min; 3 g of adsorbent was used. The dashed line indicates input lactic acid concentration.

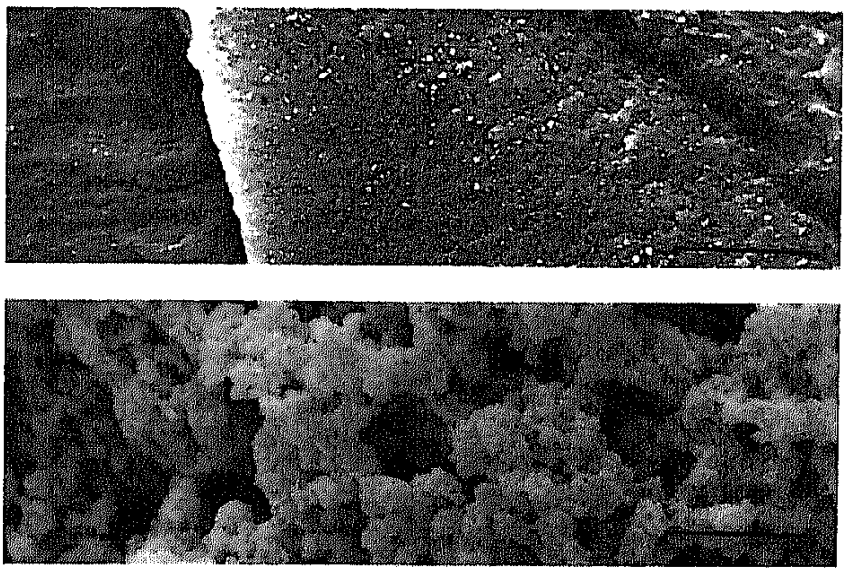
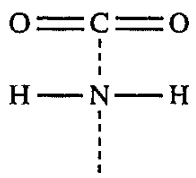


Figure 9. Amino- and CH_3-modified silica: a, 9 N HCl, 67 m^2/g; b, 12 N HCl, 188 m^2/g. The bars are 20 μm.

according to $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. The question arises whether amino groups in combination with water adsorbed to the pore walls are able to act in a dissociative way for the adsorption of CO_2 according to $H^+CO_3^- + H_2N- \rightarrow HCO_3^- + H_3N^+-$. Therefore, a series of adsorbents with varying $-NH_2$ concentrations were prepared, and the adsorption isotherms were determined. The influence of H_2O on the adsorption isotherms was determined by thermogravimetric analysis (TGA) with a N_2 gas flow loaded with water vapor. The adsorbents loaded with CO_2 were flushed with the H_2O-containing N_2, and the H_2O content of the gels was determined after the experiment. The evaluation of the mass balance and the amount of residual water led to the conclusion that the H_2O completely replaces the adsorbed CO_2. On the other hand, as a function of the NH_2 content, remarkable amounts of CO_2 were able to be adsorbed on adsorbents dried at 150 °C. These adsorbents show far lower OH peaks in the IR spectra than pure silica. This observation indicates that the ionic mechanism does not play any role, and a weak dipole interaction is postulated instead:



IR spectra, however, did not show a significant shift of the =C=O vibration. Figure 10 shows some of the most important results.

The NH_2 groups affect the amount of adsorbed CO_2 as well as the thermal behavior and illustrate the change of thermodynamics with composition. At higher pressures (not displayed in Figure 10), the amino-modified adsorbents show a saturation plateau around 5 bar CO_2 and a load of about 5–10 wt % CO_2, depending weakly on the surface area, whereas the CH_3-modified material (880 m^2/g) shows no significant plateau up to 15 bars (the end of the test) and a load of about 36 wt % at room temperature, which is an extremely high load. This observation leads to the question of whether these materials can be used for CO_2 storage or as propellants with CO_2. In reference 19, a heat pump is proposed; it uses two types of tailored adsorbents for CO_2 in a closed-system process.

The determination of the heat of adsorption shows higher values on adsorbents with amino contents above 10 mol % (e.g., SiO_2, 45 kJ/mol; 10 $-NH_2$, 43 kJ; 20 $-NH_2$, 58 kJ; 30 $-NH_2$, 65 kJ; experimental error, ±7%) and a decay as a function of the CO_2 surface coverage (e.g., in an adsorbent with 20 mol % $-NH_2$ from 58 kJ/mol ≡ 2 mL CO_2 per gram to 17 kJ/mol ≡ 10 mL CO_2 per gram). Thus, the amino-modified materials interact rather strongly in the first step with the CO_2, and the interaction decreases

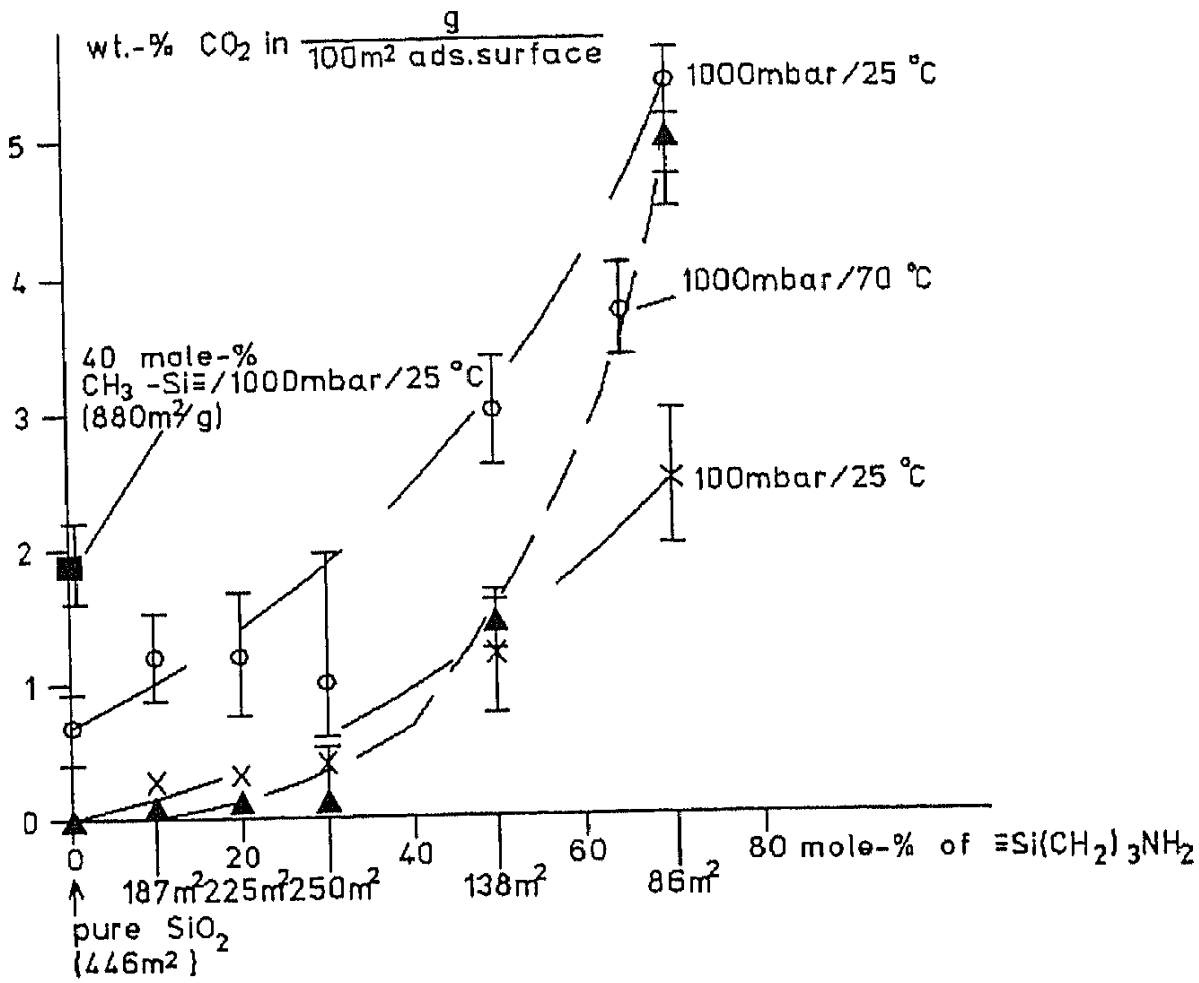


Figure 10. NH_2-containing silica with CO_2 at 100 and 1000 mbar and two different temperatures. The load is normalized on 100-m²/g surface area. Data of pure silica and a $-CH_3$-modified silica are given for comparison; the numbers with m² as units at the abscissa display the surface areas of the investigated adsorbents.

with increasing load; this observation suggests a population of various adsorption sites.

Conclusions

The organic bulk modification of silica can be used for tailoring specific surface properties. One advantage of this reaction route is the possibility to use a one-step process, but the reaction must be controlled very carefully. Multifunctional materials can be synthesized, too.

Acknowledgments

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