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COMPLEXING AND CHELATING AGENTS IMMOBILIZED ON SILICA GEL AND RELATED MATERIALS AND THEIR APPLICATION FOR SORPTION OF INORGANIC SPECIES

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ABSTRACT

Solid materials bearing bonded organic functional groups are reviewed. The properties of the oxide supporting materials, silica gel in particular, their chemical and physical properties and the nature of the surface residues are part of this review. Processes leading to modification of the silica gel surface with mono- and polylayers of other oxides resulting in materials with modified properties as well as their susceptibility to chemical modification are also presented.

Data on silanization procedures to bond supporting materials with commercial or synthesized organosilicon compounds have been carefully collected and discussed. Special emphasis has been paid to reactions which change the chemical nature of the bonded organic residues leading to valuable materials for

partition, ion, ion-exchange, and affinity chromatography as well as for specific separation methods. Data on the collection, separation and preconcentration of inorganic species using these materials are an important part of this review.

The bonded organic residues usually include typical ligating groups which are able to form complexes with inorganic species. Although most of these ligating materials have been seldom used, they have been included in this review.

Current and prospective trends in usage of chemically modified supports, primarily for large scale procedures, are discussed. Important progress in the technology of inorganic supporting materials in the form of fibers or aggregates of high specific surface, which can be chemically modified, and which should stimulate future research in solid packings, has been outlined.

CONTENTS

1. INTRODUCTION, SCOPE AND LIMITATIONS

Many of the materials used today in technology and analyses possess specific surfaces and their usefulness is a result of physical and chemical interactions on the surface. Charcoal, talcum, Fuller's earth, precipitated calcium carbonate, cellulose, clays and silica gels are common examples. Ion exchange and chelating ion exchange resins are examples of organic matter that fit into this category. The major drawbacks of resins are derived from the organic backbone which carries the functional groups.

Inorganic supports with immobilized organic residues behave differently when compared to either organic resins or materials that have been adsorbed onto a surface. The first difference lies in the higher stability, both chemical and thermal, of the bonded materials.[1,2] When comparing ion-exchange resins and inorganic supports with immobilized materials,[3,4] it is necessary to consider that in polymers the active groups are uniformly distributed throughout the particles. This means that the reaction rates are controlled by diffusion which tends to be slow.[5] Ion-exchange resins require extended equilibration periods. Many authors have compared silica gel supported ion-exchange materials with the corresponding polymeric materials.[3,6,7] Da Mota and coworkers[8] found that columns packed with a resin ion-exchanger and 8-

hydroxyquinoline immobilized on controlled pore glass beads had about the same efficiency, but the latter took less time and labor. This limits the utility of organic packing in modern high pressure liquid chromatography (HPLC) columns.[9-11] Macroporous styrene-divinylbenzene copolymers such as XAD-2 or PRP-1, although much better, still are not free of the undesirable properties of the organic polymers.

Another problem with organic resins is that they shrink and swell, thus affecting mass transfer[12] and causing slow changes in the composition of the mobile phase. Moreover, solvation of the functional groups in the polymer results in changes in the volume of the resins. This may increase bead volume, and consequently, cause unacceptably high back pressures. A decrease in volume leads to the formation of large solvent filled pockets (dead volumes).[6] A consequence of repeated shrinking and swelling is cracking of the beads. Since equilibrium is attained slowly, the necessary ratio of a resin to a treated (liquid or gaseous) solution increases as well. This increases the dimension of the industrial or analytical device and increases overall costs.

Despite their drawbacks, polymeric ion-exchange and chelating resins do have substantial advantages in at least two areas; much higher capacity and higher chemical stability at low temperatures. Also, due to a longer history, the chemistry of organic resins serves as a starting point for the synthesis and study of chemically modified inorganic supports. Hence it is worthwhile to list reviews dealing with ligands attached to organic resins.[13,14] Many materials having improved properties have been introduced first of all, as packing for gas (GC) or liquid chromatography (LC).

In 1967, Horvath and Lipsky[15] recognized the limitations of conventional ion-exchange resins and developed a pellicular or solid-core packing to improve the speed of ion-exchange separations. The pellicular ion-exchange chromatographic column packing consists of a thin coating of the resin on a nonporous core. Kirkland in 1970[16] introduced a packing for high speed ion-exchange chromatography that consisted of glass beads coated uniformly with ion-exchange material. Later,

Kirkland and DiStefano[17] described how superficially porous particles could be modified with chemically bonded stationary phases to create new packing that are both durable and chromatographically efficient. Such packings, however, are susceptible to similar mass transfer problems (slow diffusion through the polymer) as has been observed with similar bonded-phase partition materials.[6] With respect to chemical stability, some silica packing materials coated with polymer layers have become available,[18] which have a longer life at high pH values than conventional reversed-phase packing, but not as long as the organic polymer gels.[19] A new procedure for surface modification which involves the absorption of allyl or vinyl compounds onto the surface of porous supports followed by copolymerization of the monomers has been developed. The polymer network covering the silica gel can subsequently be functionalized with various kinds of chelating reagents[20] (see Section 3.4.).

Many of the disadvantages of organic resins can be excluded by introducing chemically modified inorganic supports. Inorganic matricies have been well studied, which helps in predicting the properties of the modified support. With the wide variety of groups available for attachment to the surface, it is fairly easy to choose one that will have the type of interaction most favorable for the task at hand.[21] The interactions of these surface-bonded groups may be estimated by analogy to liquid phase chemistry.

Chemically modified inorganic supports behave similarly to the starting inorganic phase; they have high mechanical strength, and do not shrink or swell. These type of carriers have a rigid framework, providing consistent properties throughout their lifetime. Inorganic carriers for chemical modification are relatively inexpensive and readily available in a variety of grades suitable for almost any purpose.

Modified silica gels show fast metal ion-exchange kinetics.[22,23] Knox and Pryde[24] showed that ion-exchange modified inorganic supports have efficiencies comparable to those of underivatized silica and alumina. The property which is

changed during chemical modification is the pore diameter, which is smaller than in the starting support by the thickness of the immobilized layer.[25,26] Swelling problems and cracking of the particles due to osmotic shock are less likely than in the case of resin beads. Inorganic matricies, unlike resins, cellulose, agarose, and sepharose, do not support microbial growth,[27] and therefore sterile conditions may be more easily maintained than with resins.[28]

Silica based materials are not free of problems. Free silanol groups and metal ions are present in the inorganic matrix. These cause tailing of polar species such as protonated amines or carboxylic acids.[19] The stability of silica gel-based supports decreases in solutions of high or low pH. The capacity of chemically modified supports is low. In this respect, ion exchange resins have a great advantage. Many efforts have been made to improve the capacities of inorganic supports.

This review deals with inorganic materials bearing functional groups bonded to their surface. The beginnings of this science can be found in the surface chemistry of reinforced plastics. It was the need to increase the chemical compatibility of mineral ionic fiber surfaces with the surrounding organic material, preferably by covalent modification, which pushed the development of the materials discussed in this review. Silanization of reinforcing fibers, which consists of chemical modifications to the polar (fiber) surface by organic residues, improves many of the properties of these materials.[29-37] Extension of this general concept to the modification of inorganic supports, which may, in general, play the role of ion-exchanger or ion chelator for inorganic substances, is the subject of this review.

The chemistry of complexing and/or chelating agents covalently bonded to inorganic supports has been growing in diverse directions. Often, little effort has been made to correlate the results of many different research groups. Moreover, as most of the published papers deal with chromatography, the principal problems studied are selectivity, efficiency, detection methods and the mechanism of separation. Scientists discovering new "heterogenized" homogeneous catalysts are interested in finding effective catalysts to induce desired chemical conversions. From

an analytical chemistry point of view, it is most important to preconcentrate the species of interest whose concentration may be much lower than the detection limit. This is a primary problem in environmental analyses.

The organic residue may be bonded to the silicon atom on the surface via an ester bond (Si-O-C), an amide bond (aminosilane Si-NR-C), or a siloxane bond (SiO-Si-R). The first two types of bonds are hydrolytically unstable and the respective materials may be used only in GC or with nonaqueous solvents. This review will refer only to the last type of chemical modification of silica gel and other inorganic oxide supports. Polystyrene like materials will be discussed only briefly, for comparison. The main emphasis of this review is two-fold: 1, synthesis of bonded ligands and/or ion-exchange materials and 2, interactions of inorganic species with chemically modified surfaces.

This review contains information on the interactions of inorganic molecules, ions, or their complexes with various modified supports. Alkylsilylated supports are mentioned when studies of sorption have been performed or when they are a subject of chemical modifications. Since alkylsilylation is frequently used and a large number of theoretical studies have been performed, the reader is referred to papers having more specific information than the general aspects mentioned in this review. Additional information is available in the specific reviews listed in this paper. Other ligands (aromatics, alkenes, alcohols, amino-acids and amides, for example) bonded to different supports are listed in the Tables whether or not they were used for sorption of inorganic species. These materials may adsorb inorganic species or their complexes or they can be converted into ion-exchange or chelating ligands. All materials used in Merrifield's solid phase peptide synthesis[5,38] were excluded from this review unless they were used for chromatographic separations. Also, cyclodextrins were excluded as they preferentially form complexes with organic compounds.[39] The literature referred to in this review has been collected from Chemical Abstracts, up to the end of 1992.

2. THE SURFACE OF SILICA GEL AND OTHER INORGANIC SUPPORTS

The ideal support for many chromatographic and other purposes should possess the following properties:

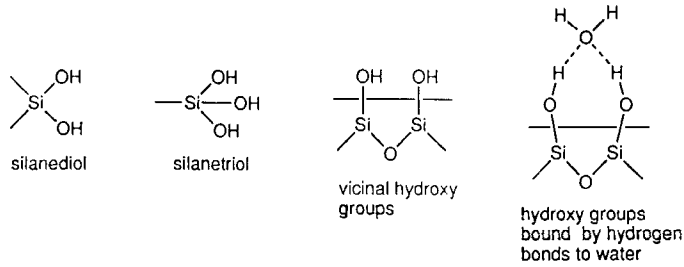
1. The particles should be of uniform and/or spherical shape with a narrow size distribution.
2. Equally distributed reactive sites of high specific surface area should be present.
3. The particles should be porous to allow free passage of molecules, thus allowing rapid diffusion and rapid equilibration.
4. The particles should be mechanically stable.

Nearly all of the mentioned properties are typical for different kinds of silica. Silica can be classified on the basis of four main features: crystal structure, dispersity, surface composition and porosity.[11,40-44] Naturally occurring quartz or cristobalite are examples of crystalline silica, whereas opal and diatomaceus earth are amorphous.

The main categories of silicas that have good dispersity are:

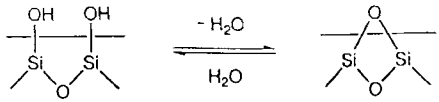
1. silica hydrogels (commonly called silica gels),
2. xerogels, obtained by thermal treatment of silica hydrogel and
3. aerogels obtained by high temperature hydrolysis, e.g. Aerosil and Cab-o-sil.

Non porous silica (Aerosil and Cab-o-sil), glass beads, and porous silica are generally amorphous. The surface silanol groups (Si-OH) which are common to all of these materials provide the reactive sites for surface modification. Depending on the pretreatment of the surface, the following types of silanol groups can be distinguished:



1

Vicinal hydroxyl groups may condense to form water and a siloxane anhydride:



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The last reaction is reversible. Up to 200° only the hydrogen bonded and absorbed water molecules are removed. At about 500° the vicinal silanol groups are completely condensed. Only half of the original hydroxyl groups on this surface are available for silylation.[40,45] The concentration of isolated Si-OH groups decreases at temperatures above 600°.[46] It has been suggested[47] that fully dehydrated silica surface obtained by thermal treatment at 600 - 1000° is completely rehydroxylated by boiling in water at 100°, however, Meuss and Engelhardt[46] claim that rehydration is reversible only if the thermal treatment does not exceed 400°.

The overall concentration of hydroxy groups among amorphous silica (silica gels, aerogels, and porous glasses, which differ in production conditions, surface area and pore size distribution) is constant. This means that the density of SiOH groups (silanol number) is a physicochemical constant for a fully hydroxylated surface (about 8 μmole/m^2)[48] and the density of silanols as a function of temperature of vacuum treatment does not depend in a significant way on the type of silica.[49] This consistency does not imply, however, that all silanol groups are available for chemical reaction. For example,[48] LiChrosorb SI-100 has a total of 4.6 silanol groups per nm^2, but only 2.95 active Si-OH sites per nm^2.

The structure of the silica gel surface may be examined by many techniques such as cross polarization and magic angle ^{29}Si-NMR spectroscopy.[53] A simple procedure leading to the determination of the SiOH group population consists of deuterium exchange coupled with IR spectroscopy[51,52] or reaction with diborane[53] or with alkylaluminium compounds.[54] Interactions of the silica gel surface with solvents and solutes in liquid chromatography (LC) are discussed by Scott.[11]

It is generally observed that the density of these reactive groups decreases as the specific surface area increases. Similarly, higher specific surface area silicas have lower average pore diameters. Very small pores exclude large molecules leading to incomplete surface coverage.[11,25,44] It is worth noting that in addition to the BET method of specific surface area determination, simple procedures including titration or dye adsorption have been reported.[55,56]

Silanol groups possess significant acidic properties. The determined pK_a value is 7.1. For comparison, pK_a values of OH groups of magnesia, boria and silica-alumina are 15.5, 8.8 and 7.1, respectively,[57] whereas the acidity of aluminum modified borosilicate glass[58] resembles that of the zeolites. Acidities have also been determined by spectrophotometric, TG-DSC and back titration methods for silica gel, alumina and activated carbon.[59] The intrinsic acidity constant (K_{intr}) of surface silanol groups has been determined by calorimetric titration of silica gel at 25° in solutions of ionic strength = 0.1 to be log K_{intr} = -6.8.[60]

Since silica gel is a glass product of rigid structure, shrinkage and swelling are practically non-existent.[28] One may select a specific type of silica gel according to the desired properties. Several methods leading to silica gels of specific properties have been developed. The porosity and specific surface area may be controlled as well as other factors affecting the utility of the gel (mesoporous silica is available[61]). The shape of the beads may also be controlled. Spherical beads of porous silica described by DeVries and coworkers[62] are available in different particle sizes, and the pore size distribution may be chosen from a wide range, depending on the desired

application. Recently, a process for making uniform size porous silica spheres was patented.[63]

The mechanical behavior of wet silica gels formed by various sol-gel processes have been characterized by their breaking strength. The mechanical properties of gels are dependent upon gel composition, gel age, and other manufacturing parameters such as pH, temperature and pressure. Models for the structures of various gels which explain variations in mechanical behavior have been proposed.[64] Silica gel may be modified by using water glass.[65]

The siliceous materials frequently used for chromatographic purposes are:[66]

1. Superficially porous silica supports

   Corasils I and II are spherical particles consisting of a solid glass core coated with a single or double layer, respectively, of fine silica particles. Vydac is an example of a spherical core porous silica surface material of carefully controlled particle size in the 30-44 μm range.

2. Porous silica materials

   Porasils are a series of spherical silica beads with controlled pore sizes in the range 100-1500 Å. LiChrosorb - Si 60 possesses very small diameter particles with a uniform pore diameter of 60 Å and a surface area of over 200 m^2/g. LiChrosorb SI-100 has average diameter 100 Å. Less known is Silochrom S-80 (USSR) which is a silica gel with pores of 400-600 Å and specific surface area of 100 m^2/g.

More information concerning these materials may be found in several reviews.[66-69]

Among silica gels, porous glass has found wide application.[70] Controlled porosity glass beads possess many valuable properties and are frequently used as supports for different kinds of liquid chromatography. Large particles, like sand may also be suitable for attaching molecules to the surface via the silanol sites.[71]

Many other silicate-like materials have Si-OH groups on their surface such as olivine, hemimorfite, sodalite, natrolite and laumonite[72] and chrysotile asbestos[73]

and the zeolites.[74] Moreover, surfaces of amorphous oxides of titanium, zirconium, hafnium, and thorium are hydrated oxides, M-OH, as shown by thermal analysis and IR spectroscopy.[75] This means that the M-OH groups on the surface are possible sites for binding. It has been shown, that the oxides of aluminum, titanium and zirconium produce chromatographic matrices capable of adsorption.[76,77] Similar properties may be expected on NiO, Cr_2O_3, SnO_2, MgO, talc, carbon and other materials. For these materials, surface phenomena (dehydration, rehydration, etc.) are similar to those observed for silica surfaces. Other inorganic materials possessing surface OH groups function as ion-exchangers.[78] Materials like $Al_2O_3.nH_2O$., $TiO_2.nH_2O$; $MnO_2.nH_2O$, $Sb_2O_3.nH_2O$, $Ti(HPO_4)_2.nH_2O$; $Zr(HPO_4)_2.nH_2O$ and others possessing porous structure are the subject of a recent review.[79] Surface analysis[80] by ^{13}C cross polarization magic angle spinning NMR spectroscopy of n-butylamine adsorbed on γ-Al_2O_3 characterized the acid sites on the surface. Dehydration of silica-aluminas was monitored by high-resolution solid-state ^1H NMR spectroscopy[81].

The properties of silica undergo significant changes when part of the $(SiO_2)_n$ lattice is replaced by other oxide species. Gels containing other metal oxides may be obtained, for example, by coprecipitation. Zirconia-silica gels containing 10 to 90% of ZrO_2 were prepared by coprecipitation from aqueous solutions of the respective salts at pH = 9.[82] The synthesis of varying porosity materials based on silica gel - ZrO_2 as a support for catalysts has been described.[83] Titanium ions as admixtures in silica gel increase its specific surface.[84] In principle, these materials may be used for the immobilization of organic ligands.

A major problem is that these mixed oxides are difficult to obtain commercially in a wide-pore form and in the desired particle size range. Hence, coated silica seems to be a good alternative choice.[76] The silica gel surface (as well as other materials possessing surface OH groups) may be easily modified by covering the surface with other metal oxides. A method to coat silica consists of the reaction of volatile metal derivatives in the form of a gas or vapor with the silica surface. The monomolecular layer formed by this process may be transformed into its oxide.

Aerosil and porous glass have been modified with BCl_3, $TiCl_4$ and $SnCl_4$ followed by hydrolysis with steam.[85] Various monomolecular layers can be deposited in a desired sequence.[86,87] By repeated treatment with $TiCl_4$ and steam, 1, 2 or 3 deposited layers were obtained.[88] This latter process changed the acid-base properties of the surface.[89] Less reactive alkyl titanates were also capable of modifying these types of surfaces.[90] The alkyl titanates also possess unique properties as coupling agents between inorganic and organic compounds.[91]

An improved silica-gel support was obtained by treatment with aqueous aluminium salts. After drying, the product had increased stability in alkaline media.[92] TiO_2 was also grafted onto a high surface silica gel.[77] Analogously, zirconyl chloride and hafnyl chloride[87,93,94] were used for pretreatment of Silochrom SI 120. Procedures leading to surfaces covered with vanadium or molybdenum residues using $VOCl_3$[95] or $MoCl_5$,[96] respectively, have also been described. Chromia layers bonded to Silica gel grade 62 or LiChrosorb SI-100 were obtained by treatment with chromyl chloride.[97-99] Boria layers were obtained using BBr_3.[100,101] Silica gel surfaces treated with alkyl borates or boric acid formed Si-O-B-OH bonds.[102,103] Inorganic layers of Fe_2O_3, Al_2O_3 and SnO_2 on silica gel for liquid chromatography were obtained by reacting $FeCl_3$, $AlCl_3$ and $SnCl_4$ with silica gel.[104] Silica gel may also be modified with montmorylonite.[105] Tin(IV) oxide[106] and Nb(V) oxide[107] can be grafted on the silica gel surface. A special kind of glassy material was obtained by heating to partial melting, silica gel-bonded organometallic compounds of titanium, zirconium, boron and aluminium.[108] Sometimes chromatographic supports are carbonized by pyrolysis of organic compounds adsorbed on the silica surface.[109-111] Phosphoric acid treated silica gel contains phosphate groups on the surface.[112] In each case the coverage not only changes the properties of silica gel surface, but also decreases the size of the pores. This must be considered when altering the surface of silica gels.[25,26,88] When selecting a support for large scale separation, it is necessary to consider its capacity, ease of regeneration, chemical and mechanical stability, availability, and ease and speed of equilibration. Due to availability, relatively low

cost and many other desirable properties, silica gel is a good choice for a solid support. Silica gels layered with inorganic materials and also CrO_3 particles layered with SiO_2 all behave similarly.[113]

Unlike many other supporting materials (particularly organic ones such as cellulose) inorganic materials do not support microbial growth, they are relatively cheap (unlike controlled porosity glasses), they possess excellent mechanical durability, thermal stability and good kinetic characteristics. Silica gel and carriers based on it have a rigid framework which controls the specific surface area and pore dimensions. They have been well characterized and thoroughly studied. Silica gels do not need soaking before use because they do not swell which prevents stress fracture and crumbling during use. The basic properties that make silica gel useful for cyclic operation are its negligible solubility in water, except at high and low pH, and in organic solvents, and the possibility of modifying the surface via the SiOH groups to obtain particles with the desired functional groups. These functional groups may be varied according to the type of interaction desired. Large specific surface areas make all functional groups accessible to solutes so that diffusion may be reduced to a negligible level.[12,22,27]

3. CHEMICAL MODIFICATION OF THE SURFACE

3.1. General

A solid matrix should be chosen based on the conditions and application in which the modified form will be used. Therefore, everything from controlled pore glass,[114-116], glass fibers, Aerosil, crushed Vycor[28] and silica gel, to silica gel coated with zirconia, alumina, etc. may be used depending upon the desired performance. The reaction between the above materials and silanizing agents depends on the accessibility of the porous silica surface to different reagents.[117]

The best silanizing reagents possess chlorosilyl or alkoxysilyl groups, which are reactive under most circumstances. These materials are readily available[118] and

many of them are produced in commercial quantities. Chlorosilanes may be easily transformed into alkoxyderivatives by anhydrous alcohols. A method which bypasses HCl formation involves the use of alkylorthoformates. The products are the alkoxysilane, an alkyl chloride and the alkyl formate. The hydrosilylation of alkenes is the main reaction leading to silyl derivatives used in the synthesis of bondable ligands (see Section 3.2.2.).

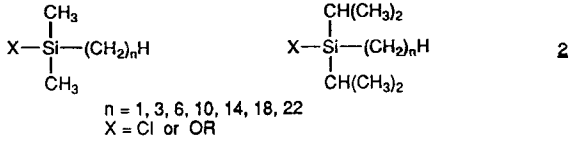
Chlorosilanes are often used for silanization and are extremely reactive towards hydroxy groups and water. The silanizing chloro- or alkoxysilanes substitute on the surface Si-OH groups to form Si-O-SiR residues. The introduced R residues cause lipophilization of the surface. When the R groups represent long alkyl chains, the so called "reverse" chromatographic phases are obtained. A detailed description of lipophilization of silica gel and related materials is not in the scope of this review. There are many commercially available lipophilic stationary phases and reagents applicable for this purpose and the procedures used are mostly standardized.[119] In this review, a theoretical treatment and some new generalizations concerning the silanizing process are given.

The siloxane bond is rather stable (see Section 4.2). A new approach has been used by Kirkland and coworkers[120] who applied bifunctional, "bidentate" α,ω-polymethylenedisilanes to form stable bonded layers.[121] The attachment of organic residues on hydroxy-containing solid surfaces is a point for detailed discussion. It has been shown, that only when the silanizing agent is monofunctional (containing one reactive group such as SiOR or SiCl), attachment is unambiguous.[122] When the support undergoes immobilization under anhydrous conditions, "monomeric" coverage, sometimes called a brush structure, is obtained. When the silicon atom of the silanizing reagent has three reactive substituents it reacts under dry conditions to form brush like coverage. When the support is wet, oligo- or polycondensation of the silanizing agent occurs in solution or on the surface and the bonded layer has a polymeric nature. The direct one-place attachment between organosilane and silica without intentional polymerization was found to be the most reproducible bonding technique.[123] Polyfunctional chlorosilanes tend to "condense" to siloxanes when

water is present. If the polymerization is carefully controlled, uniform coverage is obtained[1,124] and this makes them an excellent complement to monomeric type phases.

A major objective in preparing reverse phase silica gel is the modification of as many surface hydroxy groups as possible to diminish the chromatographic retention they cause, even in the case of long chain bonded phases. For this reason, di- and trichloro- and di- and trialkoxysilanes have been favored over monochloro- and monoalkoxysilanes because of their greater reactivity and the potential to react with two or three surface hydroxy groups. However, this latter point is debatable, because unreacted chloro or alkoxy groups will be quickly converted to silanol groups in the presence of water from the mobile phase.[125]

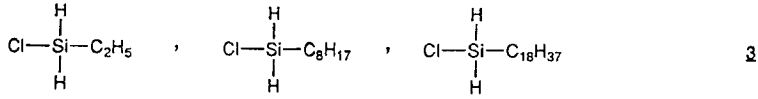
Usually, with the use of trichlorosilanes, the surface coverage decreases with increasing alkyl chain length.[126] Nearly equal coverages, independent of chain length, may be reached using chloro- or alkoxy-substituted alkyldimethylsilyl[126] or alkyldiisopropylsilyl derivatives[120] shown in Stucture 2.



2

The bulky Si-methyl or Si-isopropyl groups are the deciding factor in determining the surface coverage and the chain length has a negligible effect[52,122] (see, for example, difunctional silylating agents).[127]

In order to increase the coverage the following silanes have been used:



3

They react with the silanol surface groups to a greater extent than the analogous alkyldimethylchlorosilanes. This results in chromatographic stationary phases with

reduced silanol activity.[128,129] Further discussions of steric effects on the silica surface have been published.[130-132]

In the preparation of chelating groups immobilized on a solid support, the choice between mono-, di- or trichloro- and mono-, di- and trialkoxysilanes is regulated first of all by their availability, and secondly by their stability. The second condition requires compatibility of the silicon atom substituents versus the active precursor group for the introduction of a chelating or complexing residue in subsequent stages.

Lipophilization and end-capping are in principle the same. They consist in reacting residual silanol groups in a chemically modified support with small alkyl, preferably methyl, groups bearing chloro- or alkoxysilanes. [Removal of the remaining silanol groups after immobilization is important for good chromatographic performance, since they influence the peak shape. Complete blocking of these groups is not always necessary, particularly when the silanol groups are sterically hindered from interaction with the solute or when there is negligible affinity between the silanol and the solute.] To complete the discussion of procedures leading to chemically modified supports, methods of blocking residual silanol groups will also be presented.

Reaction between silanizing or end-capping reagents and the silica surface results in approximately 1/2 of the available sites being reacted. This is due to steric hindrance created on the surface. Even in the case of the small trimethylsilyl group, its size is such that not all of the surface silanol sites will react. Even with the wide variety of reagents available today, surface coverage will end before all the silanol sites can react. Accessibility of porous silica surfaces toward different reagents have been investigated.[117]

Probably the most important feature governing the chromatographic properties (selectivity and efficiency) of bonded phases is the uniform distribution of monomeric or polymeric organic groups over the entire surface. Monomeric coverage can be determined analytically. Leyden and coworkers[133] stated, "One of

the concerns related to bonding functional groups to surfaces is the distribution of these groups on the surface. This involves such factors as the degree of coverage, whether there is a two-dimensional polymer and other concerns. The topography of the functional groups can influence the stoichiometry and structure of the complex formed between the immobilized ligands and metal ions".

Sander and Wise[131] synthesized monomeric, oligomeric, and polymeric stationary phases on Zorbax 300, Hypersil WP 300, Vydac TP, LiChrospher 300 and Protosil 300 for LC and tested their properties using a mixture of aromatic hydrocarbons. Selectivity was related to the total coverage.

Although in past work, intentional polymerization has usually been avoided in the preparation of alkyl-bonded phases, the unique selectivity of polymeric phases may outweigh the potential problems. A more detailed discussion of structural possibilities between brush and polymeric phases, and their influence on selectivity has been reported by Pesek and Graham[1] and later by Engelhardt and Ahr[137] and Lochmüller and coworkers.[138,139] One obvious drawback of polymeric stationary phases is slow mass transfer due to the thickness of the film[5,13-14,40,45,140] (see Section 4.4).

Some general aspects of silanization in organic solvents has been described by Weetal.[141] Again, the material most used in these experiments was silica gel. A number of reviews concerning this subject have been published.[67,141-151]

3.2. Chemical Procedures Involving Silanizing Chloro- and Alkoxysilanes

3.2.1. Lipophilizing and End-Capping

End-capping is a procedure to remove residual SiOH groups from the inorganic matrix after immobilization of desired residues on the surface. It is done with a mild reagent possibly containing small alkyl groups bonded to silicon. Mild means a silylating agent which preserves the previously bonded functional groups.

End-capping the remaining silanol groups is necessary when a solute interacts strongly with a silanol.

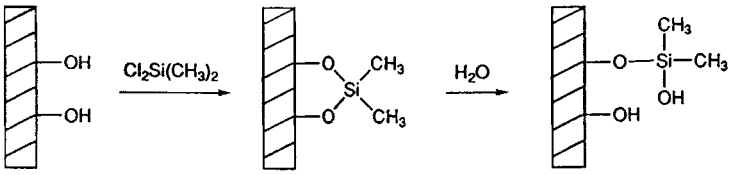
It is important to make all OH groups accessible to the silylating reagent by removing air from the pores. This is especially important for those procedures wherein the reaction between the solid support and the silane occur at room temperature. Sonication of the reaction mixture is often used to enhance the release of air.

It has been shown, that even very low concentrations of silanol groups could be responsible for a considerable amount of chromatographic retention.[19,152,153] Unreacted silanols also prevented a clean elution of U, Zr and Th compounds from an N-acetyl-N-methylaminopropylsilylated chromatographic support. An attempted deactivation of the silanols by end-capping improved the situation only slightly.[153]

End-capping may be performed in the gas phase as well as in solution. The first example given here is rarely used for making chromatographic supports. Aerosil silicas were treated with gaseous methyltrichlorosilane above 250° but only the external SiOH groups were silylated. Trimethylchlorosilane and dimethyldichlorosilane reacted similarly.[154] Generally, a 1:1 reaction was observed, although 1:2 bridging occured on preheating the solid to temperatures of about 500°.[155,156] Kinetic analysis of the curves obtained spectroscopically for the reaction of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3 and $SiCl_4$ with the free hydroxy groups on silica showed that the monofunctional silicon follows 1st order kinetics with respect to the number of surface bonding sites. The multifunctional silanes all followed 1.5 $\pm$ 0.2 order kinetics with respect to the number of surface bonding sites. The 1.5 overall reaction order was attributed to the presence of about 50% geminal $Si(OH)_2$ groups. The four chlorosilanes listed above have an experimental activation energy of 22 $\pm$ 2 kcal/mole. A fast initial reaction, to the extent of 10-15%, takes place and it is believed to be due in part to direct replacement of OH by Cl.[45,157]

End-capping with trimethylchlorosilane (TMS) seems to be the generally preferred method by many authors. This reagent is able to form only one bond to the

surface. The silanol sites that do not react with this reagent may be blocked because of the steric hindrance caused by the introduced trimethylsilyl groups. Dichlorodimethylsilane is sterically smaller and is capable of blocking two closely located silanol groups. Unfortunately, only 50-60% of the silanol sites are capable of reacting with both chlorine atoms. The new Si-O-Si units can also be hydrolyzed. Thus, after hydrolysis, only a small decrease in the number of silanol sites was observed.



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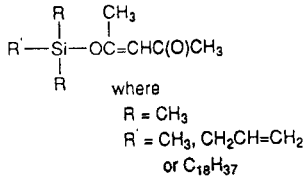
Analogously, trichloromethylsilane, if used for endcapping, increases the number of silanol groups. These are the major reasons that the TMS group is preferred.

Evans and coworkers[158] recommend a 2 h reaction of the bonded phase with an excess of trimethylchlorosilane in toluene at room temperature.

To perform end-capping of chromatographic supports, the following silane derivatives are usually used: trimethylchlorosilane, hexamethyldisilazane,[159] and dimethyldichlorosilane.[157,160,161] Hexamethyldisilazane reacts only with OH groups available on the Aerosil surface.[157] The following reagent:



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reacts with silanol groups in vacuum, as a vapor. 2,4-Pentanedione is released. The reaction proceeds at 25-80° for 3-4 hours at 2 x 10^{-6} mbar.[18] In liquid systems, trimethylchlorosilane, hexamethyldisilazane and other reagents such as bis-trimethylsilylacetamide, bis-trimethylsilyltrifluoroacetamide, trimethylsilyl-

imidazole[162] or bis(trimethylsilyl)carbodiimide[163] are effective. The last reagent does not affect groups bonded on silica gel at an earlier stage. A comparison of the end-capping ability of bis-N,O-trimethylsilylacetamide, bis-N,O-trimethylsilyltrifluoroacetamide, hexamethyldisilane, trimethylchloro-silane with and without pyridine, 2-trimethylsiloxypenta-2-en-4-one, trimethylsilyldimethylamine and trimethylsilylimidazole indicated that trimethylsilylimidazole has the highest reactivity.[164]

Typically, end-capping is performed with trimethylchlorosilane in boiling toluene, or with trimethylsilylimidazole in dry dimethylformamide.[162] Hexamethyldisilazane was used in a suspension of modified silica gel in benzene at 75° for 8 hours[165] as well as with trimethylchlorosilane in methylene chloride and pyridine (45 hours at reflux).[166] A comparison of end-capping and surface modification methods has been made.[167] An analysis of these methods based on methyl red adsorption to determine the residual silanol groups has been done.[168] Only phases with negative methyl red tests are suitable for comparisons of the chromatographic behavior of the bonded groups. A discussion on trimethylsilylation of silica gel for HPLC was presented by El Rassi and Gonnet.[169] Recently, Lindoy and coworkers[170] end-capped the unreacted silanol groups of chloropropylsilylated silica gel by reacting it in four times its weight of chlorotrimethylsilane and refluxing the suspension for 2 hours under an inert atmosphere. The excess reactant was removed by evaporation under vacuum and the modified silica gel was washed with water to remove traces of hydrogen chloride. The final product was dried in high vacuum and showed no presence of silanol groups in the ^{29}Si NMR spectrum.

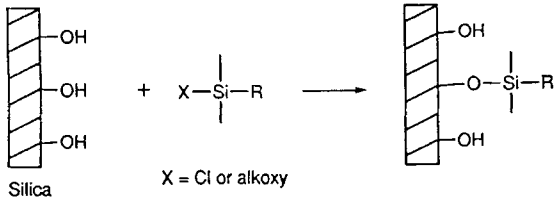
The availability of silanol groups for end-capping also depends on the length of the alkyl or arylalkyl groups attached to the silica gel surface in earlier stages. In the case of materials with long chains bonded to the surface, the trimethylchlorosilane was not as effective as other trimethylsilylating agents.[171] Silanization is accompanied by the formation of other species including silanetriol and cyclic tetramers. The reaction is strongly dependent on the conditions, especially the medium, in which the reaction occurs.[172]

Lastly, a novel method for the preparation of bonded stationary phases was described in which a hydrocarbonaceous moiety was bound to silica surfaces through a direct Si-C linkage. The process involved chlorination of SiOH residues followed by reduction to form intermediate materials containing fairly stable SiH groups.[173] Due to the small size of the hydrogen atom, the surface coverage with SiH groups is large.[129] Alternatively, the surface may be modified with SiH- containing silylating agents.[174]

Silicate minerals[72] and silica surfaces covered with metal oxides also react with end-capping reagents. In toluene or carbon tetrachloride, trimethylethoxysilane reacted with SiO_2, TiO_2 or α-Al_2O_3 at room temperature. At higher temperatures, the reaction also occured on SiC.[175] According to Belyakova, and coworkers,[176] the reaction of alumina with 3-aminopropyltriethoxysilane was incomplete at room temperature, but it was driven toward completion at 300°. Surface modifications of zeolites and asbestos minerals by silanes have also been studied.[74]

3.2.1.1. Silanizing Under Anhydrous Conditions

Chloro- and alkoxysilanes react with silanol groups under essentially anhydrous conditions to form new siloxane bonds:



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The most obvious and simple case is to use a monofunctional silane R_3SiX for this purpose.[124] After reaction with an SiOH group, the silane molecule is linked via a single siloxane bond to the surface. Disiloxane, R_3Si-O-SiR_3, is formed as a by-product during the reaction. This material may react with the remaining free SiOH

groups or may be adsorbed on the surface. By choosing an appropriate solvent, the unreacted species can be completely removed by washing.[124] A more complicated situation takes place when trifunctional silanes, $RSiX_3$, are employed as silanizing reagents. With dry silica and under anhydrous conditions, the silanes reacts with the surface hydroxys in a 1:1 or 1:2 stoichiometry, yielding a monomerically bonded layer. However, in the presence of water which would react with the third X group, these materials may form a complex three dimensional layer. The thickness of this layer is dependent upon the amount of $RSiX_3$ used. Formations of 1:3 reaction products with the surface silanol groups are unlikely.[159-161]

Reactions between SiOH and silanes of the R_2SiX_2 type may be treated as intermediary between those just discussed. Attachment to the silica gel surface proceeds by two siloxane bonds with an approximate probability of 50%. Batch to batch variations influence the reaction between silica gel, or OH groups on different supports. Proper pretreatment can greatly reduce the variability between different batches or materials for the reasons described in Section 2.

3.2.1.2. Silanizing With Gaseous Silanes

Hertl[177] studied the reaction of silica gel with gaseous methyltrimethoxysilane at 90-220°. About 40% of the silane reacted monofunctionally and 60% of the molecules reacted difunctionally. Similar studies using ^{29}Si CP/MAS NMR were performed on silica gel with vapors of chlorotrimethylsilane, dichlorodimethylsilane and trichloromethyl silane.[178]

Disilazanes are less reactive and have been reacted with LiChrosorb SI-100 at temperatures up to 400°. It was shown that up to 350°, triorganosilyloxy groups prevailed as the dominant species on the surface.[179] Comparing reactivities of gaseous trimethylethoxysilane, trimethylchlorosilane and trimethylacetoxysilane with Aerosil, the first two reagents gave a high degree of surface coverage at room temperature whereas the last reacted at about 300°.[180,181]

Besides some applications involved in modifying glass fibers, silanization by gaseous silanes is rarely used to prepare chromatographic supports, since reactions in the liquid phase between the solid support and the corresponding silane are possible, and they are easier to control.[182]

3.2.1.3. Syntheses in the Anhydrous Liquid Phase

3.2.1.3.1. Pretreating Silica Gel

The conditions and factors discussed so far concern the properties of covalently bonded supports. Unfortunately, there is a lack of comparative studies of this subject because it is hard to have the same reaction conditions and supports every time. In many publications dealing with a particular silanization step, the support used changed from different kinds of silica gel (mesh, porosity, supplier), fumed silica and glass beads, to controlled pore glass beads and so on. Similarly, the reaction conditions differed (temp., reaction time, etc.).

Octadecyl-containing silanes, used to prepare "reverse" phase packings, are the sole system where some comparative studies have been done.[137] The quality of the packings was determined by the quality of the chromatographic separation using standard mixtures. The most detailed and complete treatment is given in a paper by Evans and coworkers.[158] Those authors compared the properties of phases obtained by octadecylsilylation of Partisil-5, (1) air-dried (wet), (2) fresh as purchased and (3) predried for 2 h at 800°. In chromatographic experiments, supports (1) and (2) exhibited no significant differences in efficiency and resolution. The pre-dried support gave inferior resolution and a progressive deterioration of peak symmetry. This was probably due to formation of silanol groups as some of the strained Si-O-Si bonds were hydrolyzed by water molecules present in the solvent. It was concluded that reliable bonded phases can be produced from commercial adsorbents without any type of pretreatment. Equally good results can be obtained using Hypersil, LiChrosorb and Spherisorb.[48,183,184]

3.2.1.3.2. Selection of Reactive Silane Reagents

Chlorosilanes are used more frequently then alkoxysilanes for the synthesis of chemically bonded phases due to their higher reactivity. Chlorosilanes react at room temperature, nevertheless, many authors recommend reaction at reflux temperatures for extended periods. Evans and coworkers[158] established that the reaction of trichlorooctadecylsilane in carbon tetrachloride is virtually complete after 10-15 minutes at room temperature. They found that elongation of the reaction time or increasing the temperature caused a drop in flow rate and/or a decrease of resolving power of the chromatographic column. Thus, prolonged heating at reflux temperature with chlorosilanes is not only unnecessary, but inadvisable.

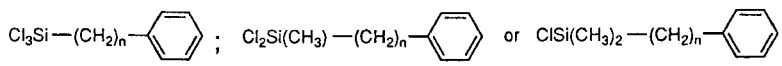
In the case of alkoxysilanes, the reaction is much slower and many hours of heating are required for the reaction to be completed. Because of the difference in the reactivity of chloro- and alkoxysilanes, the products obtained under similar conditions may not be identical.[185]

Studies have been done on the mechanism of the silylation reaction,[149,151,186] as well as the kinetics of immobilization.[149,187]

3.2.1.3.3. Catalytic Procedures

The catalytic influence of amines was observed in the reactions of both chloro- and alkoxysilanes.[188-191] Amines increased the immobilization rate and are used as catalysts[192] or as solvents.[193] Pyridine[190,194] and di-*n*-butylamine at reflux[195] play a catalytic role. Imidazole was the best catalyst when chlorosilanes were used for silylation.[196] Catalysts not only increase the reaction speed but also increase the coverage[126,197] and reproducibility.[190,198]

In order to increase surface coverage, the following silanes have been used:



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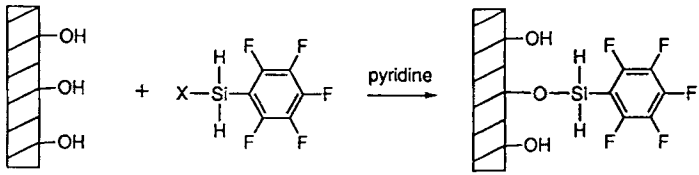
These phenyl-substituted silanes react with the surface silanol groups to a greater extent than the analogous alkyldimethylchlorosilanes. This results in chromatographic stationary phases with reduced silanol activity.[128,129] The steric effects of these substituents on the surface has been discussed.[130-132]

3.2.1.3.4. Influence of Solvent Used in Syntheses

In many publications, the solvent used in immobilization has received only cursory attention. The range of solvents used for this purpose includes hexane,[199] benzene,[200] tetrahydrofuran[201] and pyridine.[202] Evans and coworkers[158] found marked changes in chromatographic behavior depending on the nature of the solvent used for the synthesis of an octadecylsilyl-silica gel phase. The polarity of the solvent used for the reaction was found to have no significant effect upon the extent of the bonding reaction. However, the physical properties of the chromatographic support were markedly different. The supports obtained in acetonitrile, nitromethane, and pyridine were flocculant and the resulting chromatographic columns had significantly higher back pressures. These columns also gave low capacity ratios and practically no resolution of the test mixtures. This may be attributed to the formation of a polymeric film on the surface of the silica. Hydrocarbons and halogenated hydrocarbons, when used as solvents, produced materials with high chromatographic efficiency coupled with excellent resolving power. Of the chlorinated hydrocarbon solvents, carbon tetrachloride appeared to be the best. Other good solvents were: dichloromethane, chloroform (free of alcohol), hexane and toluene in the order of decreasing usefulness. In many papers, toluene was used as a solvent at room temperature[203] which is a good choice.

Another systematic study by Kinkiel and Unger[196] on the influence of different solvents revealed that the solvent order in which the reactivity of silanizing agent increases is: THF < benzene < ethyl ether < acetonitrile < methylene chloride < DMF. Imidazole is the best catalyst when chlorosilanes were used for silylation. These findings were based on silylation density as the criterion for reactivity.

Many authors have claimed that they obtained good chromatographic supports using pyridine, acetone, dioxane or tetrahydrofuran as solvents. Some of them use boiling toluene (4-5 hours) in the presence of a catalytic amount of pyridine to immobilize the phases as shown below:[190]



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Others used dry di-n-butylamine at reflux.[195]

The course of the reaction between the silanes and the solid support has also been studied by using spectroscopy (IR, NMR, etc.),[204,205] and ^{29}Si and ^{13}C CP/MAS NMR.[206,207] This subject has been reviewed.[208] Other examples of stationary phase syntheses have been reported.[141-151]

3.2.2. Use of Chloro- and Alkoxysilanes Bearing Organic Functional Groups

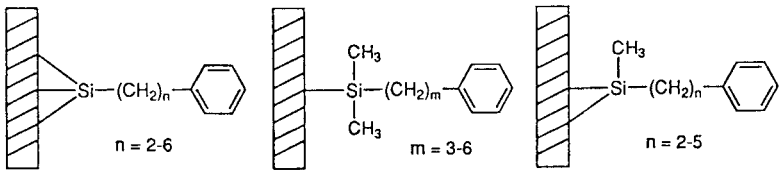
There are many immobilized materials with groups capable of further modification to form chelating, basic or acidic species.

3.2.2.1. Anhydrous Conditions

3.2.2.1.1. Alkenyl, Alkylaryl and Chloroalkyl Derivatives

The best substrates capable of forming chelating (acidic or basic) groups upon mild chemical modification are phenyl, vinyl and allyl groups bonded to the surface. Many chlorosilanes as well as the corresponding alkoxysilanes bearing these substituents are available. Diphenylsilyl residues were attached onto silica gel and Aerosil[209] and then converted into sulfonic acids. Phenyl-, diphenyl- and

triphenylsilylated silica gel as well as the corresponding benzyl derivatives have been described.[210] Chlorosilanes possessing terminal phenyl groups were used for the modification of silica gel[6,194] leading to the following products:



Mercosorb
LiChrosorb
Spherisorb

LiChrosorb

LiChrosorb

6

The capacity of these products was 0.9 meq/g. Some typical examples are as follows.

Spherisorb S5W[6] was heated at reflux with 2 M HCl for 4 h, filtered and washed with water and acetone. The silica (5 g), dried over night at 200°, was heated at reflux with 2 mL of (2-phenylethyl)trichlorosilane in 100 mL of dry dioxane for 4 h. The product was collected, washed thoroughly with dioxane and acetone and dried.

At this point it is necessary to comment about stirring the reaction mixture. Stirring is necessary when refluxing the reaction mixture to avoid overheating. Magnetic stirring should to be avoided as it crushes the silica gel particles, thus changing the mesh size. Silica fines may be eliminated by repeatedly slurring and decanting the gel in a suitable solvent.[211]

LiChrosorb Si-100 (10 μm, surface area 282 m^2/g) (3.5 g) was dried for 8 h at 180° under vacuum (0.1 mm Hg) to remove the surface water. Then it was transferred into a round-bottomed flask containing 100 mL of dry toluene and 5 mL of pyridine. To this solution, 0.01 mole of a chlorophenylsilane (see Eq. 8) was added. The mixture was refluxed for 5 h while being purged with nitrogen. After reaction, the silylated silica gel was carefully washed with toluene, methanol, methanol-water, water and acetone and was dried for 8 h at 70° (0.1 m Hg).

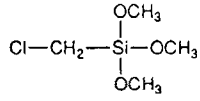
Chmielowiec[212] also prepared phenylsilylated silica gels using phenyltrichlorosilane in pyridine as a solvent whereas Den and Kettrup[194] used pyridine as a catalyst. Another example is also reported.[213]

Alkylene derivatives, such as vinylsilylated silicas, may be obtained in a similar way.[214] The reaction of vinylmethylchlorosilane with the silanol groups is fast. During the first minute of the reaction, 70-80% of the substrate is consumed[215] as shown by IR studies. A comparison of vinyltrichlorosilane and vinyltriethoxysilane was done.[185] E-glass fibers have also been modified with vinyltrichlorosilane vapors.[216]

3.2.2.1.2. Halogen and Pseudohalogen Derivatives

A reagent that is frequently used for further modifications is (3-chloropropyl)silylated silica gel. The starting materials (commercially available) are 3-chloropropyltrichlorosilane, 3-chloropropyltrialkoxysilane or the corresponding 3-bromo- or 3-iodo- analogues. The immobilization procedure is essentially the same as for the previously described phenyl and vinyl derivatives. Pretreated LiChrosorb Si-60 (10 g) was suspended in 200 mL of dry dioxane and 4 mL 3-chloropropylsilane was added. The reaction mixture was refluxed for 4 h, the product was collected, washed with dioxane, water and acetone and dried under vacuum.[217]

More reactive than the 3-chloropropyltrichlorosilane are the chloromethylsilyl residues and the (chloromethyl)phenylsilanes. These substrates are valuable in derivatizing silica gels. Thus, 10 g of LiChrosorb SI-60 was heated for 24 h in a refluxing solution of 8 g of (chloromethyl)trimethoxysilane in 300 mL of n-octane.[218]



(chloromethyl)trimethoxysilane

After removal of the excess silane and washing, the product was dried.

According to Waddell and Leyden[219], to 100 mL of a 5% solution of Cl_3Si-$C_6H_4CH_2Cl$ in dry toluene was added 25 g of Silica gel G (E.M. Reagents). After 1 h at room temp, the reaction mixture was filtered and the solid washed thoroughly with benzene. After being cured at 85° for 2 h and vacuum dried, the sample contained 2.87% of immobilized carbon.

Cyano derivatives may be similarly synthesized.[52,220] The isothiocyano derivatives may be obtained by thermal decomposition of the respective dithiocarbamates.[221]

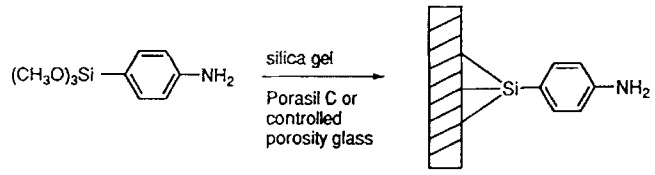
3.2.2.1.3. Aminoalkyl and Aminoaryl Derivatives

Aminopropyltrialkoxysilanes are readily available and have been widely used to modify solid supports. Aerosil treated with aminopropyltriethoxysilane[222] gave an aminopropylsilylated surface. Similar reactions were performed on porous glass, alumina, hydroxyapatite,[223] fiber glass,[224] and different kinds of silica gel.[12,27,124,225,226] The reaction of aminopropyltriethoxysilane with alumina at 300° has been described by Belyakova and coworkers.[176] Aminopropyl-modified silica gel with a very high capacity (1.18 mmol/g) was obtained by Porsch.[227] According to Robinson and coworkers,[228] the reaction of 3-aminopropyltrialkoxysilanes with porous glass beads proceeds better in acetone, and the capacity of the obtained product reached 80-90 μm/g. Reactions with [N-(2-aminoethyl)-3-aminopropyl]triethoxysilane and higher members of the ethyleneimine derivatives proceeded in a similar fashion. For example, aminopropyltrimethoxysilane or [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane was applied as a 5% solution in dry toluene using 25 mL of the solution and 5 g of silica gel. The mixture was kept at room temperature for 2 h with occasional stirring. The silica was separated, washed with toluene, methanol and dried at 80° in an vacuum oven.[229] Fumed silica (Cab-o-sil) was silylated in a similar manner.

Upon a carefully controlled reaction of an aminopropyltrialkoxysilane with silica gel in dry toluene, the silane becomes attached by one or two siloxane bonds. Subsequent heating at 200° changes the structure by forming more covalent links with the surface, in essence crosslinking the layer on the surface. Water treatment causes a complete loss of the monodentate structures to form crosslinked structures, while bidentate linkages are not necessarily affected. Curing at 200° again results in

the formation of more tridentate linkages, since extra linkages to surface silanols are possible.[230] Northcott and Leyden[231] applied a 1% toluene solution of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane onto a controlled pore glass for 30 minutes at room temperature. Capacity of this material, determined by column breakthrough, was 0.35 mmole UO_2^{2+}/g. Supports containing more than two amine groups have also been prepared.[124,226]

Attachment of aminophenylsilanes to silica gel, Porasil C and controlled pore glass, required 4 h. in boiling toluene.[232]



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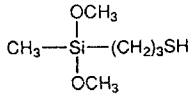
The capacities of the products were 0.216, 0.104 and 0.058 meq/g, respectively.

3.2.2.1.4. Mercaptans

The synthesis of supports containing mercaptan functions is generally similar to that for the corresponding amines. LiChrosorb SI-100 (1g) in 9.5 mL of toluene was placed in an ultrasonic bath at 50° and 0.5 mL of freshly distilled mercaptopropyltrimethoxysilane was added to the mixture which was kept under these conditions for 1 h. The silica was washed, dried at 40°, and used immediately for further synthesis.[233] A SnO_2 electrode was mercaptopropylsilylated in the same way.[234]

The reaction of mercaptopropylmethyldimethoxysilane with silica followed by end-capping was described as follows:[235] Silica (10 μm, Whatman Chemical Co.) (10 g) was placed in a microwave oven set on full power for 25 minutes. Freshly distilled toluene (200 mL) and 10 mL of 3-mercaptopropylmethyldimethoxysilane was added.



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The reaction mixture was maintained for 24 h at 80°, then 10 mL of trimethylchlorosilane and 10 mL of pyridine were added to "endcap" the phase. This endcapping procedure was allowed to continue for another 6 h. The bonded silica was washed several times with methanol and acetone, and dried in a vacuum oven overnight at 90°.

A detailed synthesis of mercapto group-containing starting materials has been reported.[236] Mercaptan-containing solid supports have been prepared by a thermal decomposition of the respective surface bonded dithiocarbamates.[237]

3.2.2.1.5. Phosphines

Phosphine derivatized silica gels are useful to prepare "heterogenized" homogenous catalysts. A typical synthesis is presented here for the preparation of a chiral menthylderivative:[238] Kieselgel 100 (Merck) (0.063-0.2 mm particle size, 100 Å mean pore diameter, surface area of 365 m^2/g) was dried at 180° at 5 mm Hg for 5 h. A mixture of 50 g of this silica and 17 mmoles of (1-dimenthylphosphinomethyl)triethoxysilane dissolved in dry toluene was refluxed for 5 h. Then, about 200 mL of the solvent was distilled for the azeotropic removal of ethanol formed during the reaction. The support was filtered, extracted three times with 100 mL of toluene and dried in vacuum.

3.2.2.1.6. Glycidoxypropylsilylated Surfaces

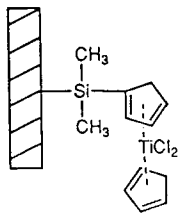
Glycidoxypropylsilane[239] and aminopropylsilane modified supports are very important for the immobilization of enzymes.[240] In the case of glycidoxypropylsilylation, predrying the support is fully justified, since it reduces the

possible hydrolysis of the oxirane moiety. In a typical example, 10 g of LiChrosorb SI-100 (10 μm, Merck) was dried for 2 h at 150° and suspended in 50 mL of benzene. After addition of 5 mL of 3-glycidoxypropyltrimethoxysilane, the suspension was refluxed for 6 h. The reflux condenser was kept at 65° in order to remove methanol from the mixture as it was formed.[241]

Amines increase the immobilization rate and are used as catalysts[192] or as solvents.[193] Porous silica (15 g) and all equipment were dried at 220° overnight. Sodium dried toluene (300 mL), dried triethylamine (KOH, 450 mL) and 3-glycidoxypropyltrimethoxysilane (12 mL) were slurried together with the silica under nitrogen in a flask provided with a glass rod stirrer. When the mixture had been refluxed for 5 h, an additional 10 mL (and after another 15 h an additional 5 mL) of 3-glycidoxypropyltrimethoxysilane were added to the reaction mixture. The total reaction time was 24 h. The epoxy derivatized silica was collected and washed in succession with toluene, acetone, diethyl ether, and sucked dry under vacuum. Both "monomeric" and "polymeric" versions of glycidoxypropyl modified silica gel were prepared for thin layer chromatography (TLC).[242,243]

3.2.2.1.7. Other Organic Functional Derivatives

Often, the starting silanes have been chemically modified as monomers prior to immobilization on a solid support. Thus, for example, Lauth and Gramain[48] reacted 3-aminopropyltriethoxysilane with 4-(chloromethyl)benzoyl chloride and further reacted the intermediate with LiChrosorb SI-100. Jackson and coworkers[244] produced a Grace-Davison 952 support containing titanocene on the surface:



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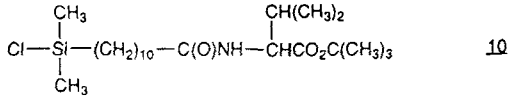
For binding more complex derivatives[245] onto silica gel, 10 mmoles of the following chorosilane



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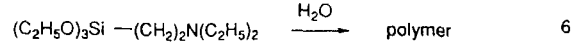
was dissolved in 20 mL of dry pyridine (a basic solvent is necessary to prevent loss of the *tert.*-butyl ester). The solution was filtered through a 0.45 μm filter onto 3 g of dried silica. The mixture was slowly rotated at room temperature for at least 5 h. The silica was then collected, thoroughly washed with dichloromethane and methanol, and dried at 60°. It was endcapped with hexamethyldisiloxane in pyridine, filtered and washed as above. The *tert.*-butyl ester protecting group was removed using trifluoroacetic acid at room temperature. The carboxy group is then available for further reaction.

3.2.2.2. Aqueous or Wet Conditions

In this method, the silanizing agent is applied onto a support in the form of an aqueous solution.[137,150] Oligomeric or polymeric entities are formed by polycondensation prior to deposition and binding to the silica surface.[124] There is no evidence to indicate whether monomeric bonded phases are more stable than the polymeric. The polymeric products are usually more than a monolayer so loadings can be higher with respect to the amount of bonded organic material. However, the capacities of such materials are lower than the loading would indicate. This is due to poor accessibility of the solute of interest to groups located under the surface of the polymeric layer. This resistance to mass transfer is the source of the kinetic problems with polymeric coatings. One of the first amino-modified silica gels was prepared in this way.[246] The trialkoxysilane was mixed with water



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which produced a polymer as shown. Heating the polymer on silica gel gave the silica immobilized material. Similarly, polymeric silicones chemically bonded to silica were obtained by partial hydrolysis of di- and trifunctional silanes.[247] Many of these reactions have been discussed by Weetall and Harewala.[248]

3-Chloropropylsilylated silica was prepared under wet conditions as follows.[170] Porous silica gel (Nucleosil 100-5, pore size of 100 Å, 10 g) was suspended in 80 mL of xylene containing 2 mL of distilled water and the mixture was gently stirred for 4 h with a mechanical stirrer. 3-Chloropropyl-trimethoxysilane (11 mL) was then added and the stirred suspension was heated at 80° for 6 h under nitrogen. The solvent was removed by vacuum distillation and the product was dried under high vacuum.

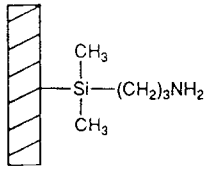
The reaction of mercaptopropylsilanes with silica gel under wet conditions was described by Wheels.[249] Micro-particulate silica was shaken with hexane, water and 3-mercaptopropyltrimethoxysilane and refluxed for 1 h. A detailed description of mercaptopropylsilanization of silica gel was also given by Howard and coworkers.[250]

Hydrolysis and condensation of neat γ-glycidoxypropyltrimethoxysilane resulted in the formation of the cyclic tetramer, which has a high affinity for the silica gel surface.[243] The glycidoxypropylsilylated support is also a convenient starting material for many chemical modifications as shown below.[239]

Sometimes it is necessary to perform silanizations in aqueous solutions. Use of water may be justified when the substrates are insoluble in other solvents. Also, some silylating reagents form monomolecular layers in the presence of water. Kvitek and coworkers[134] examined the reaction of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane with the surface of a controlled pore glass. The reaction appeared to involve the rapid (about 1 minute) formation of a covalently bound monolayer at room temperature. Multiple layers of bound material were formed by reaction at elevated temperatures, though at a slower rate. Similar observations have been made on binding of [N-(2-aminoethyl)-3-

aminopropyl]trialkoxysilane (and also glycidoxypropyltrialkoxysilane) to Fractosil 500 (Merck).[251] The coverage after 1 minute is much higher in case of the amine, which is attributed to physical adsorption of the amino group on the silica gel surface.

Henry and Sweet[136] prepared a "monomeric" coating of γ-amine (Structure 11) using a monoalkoxysilane.



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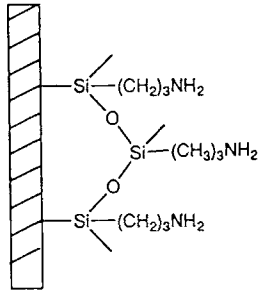
They also prepared a "polymeric" γ-amine using wet silica gel and the trialkoxysilane. This process produced a three-dimensional network as a result of the hydrolysis of unreacted alkoxy groups on the silane.



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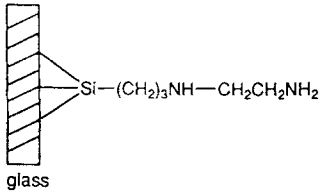
The authors reported, that the efficiency of the polymer packing was very poor. Tailing was observed for many cations, some were carried with the solvent front, and others were not separated. The reproducibility was also low. In 1982, Kvitek, and coworkers[134] stated that amino bonded phases on controlled pore glass



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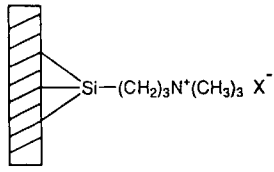
deposited from aqueous solution gave a monolayer or "monomeric" coverage. Verzele and Musche[135] presented arguments showing that the distinction between so-called "monomeric" and "polymeric" phases is not simple. Their conclusion was that most polymeric phases are in fact monomeric.

Comparison of "monomeric" and "polymeric" N-aminoethylaminopropylsilane bound to mesoporous silica gel was done by comparing NMR spectra and scanning electron micrographs.[29,252] The results indicated that aminopropylsilylation performed in water produces material, from which the amino group is lost during washing. It was also found that the extent of leaching depended on the kind of support used.[252] Later, it was reported that the aminopropylsilyl, (N-aminoethyl)aminopropylsilyl and similar residues undergo rapid leaching.[191,211] Reaction of 3-aminopropyltrialkoxysilane with silica in water gave a product without monofunctional attachments and with considerable difunctional bidentate and trifunctional tridentate covalent linkages to the surface. This resulted in the formation of crosslinked structures (which become more pronounced on heating at 200°).

In procedures using water as the solvent, the reaction is rapid, and consequently, a short reaction time produces better results. Coupling agents (methacryloxy-, glycidoxy- and aminopropyltrimethoxysilane) were hydrolyzed in deionized distilled water (pH = 3, acetic acid) for varying lengths of time from 30 minutes to 4 h. The hydrolysate was added to silica gel and after 5 minutes the product was centrifuged.[253]

Water was also used as a solvent for silica gel immobilization of carboxymethylated aminopropylsilane, N(aminoethyl)aminopropylsilane,[124] and quaternary ammonium salts.[254]



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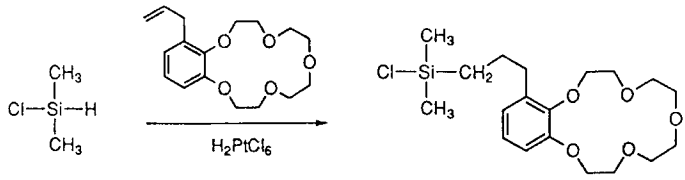
Water as a solvent for silylation reactions is of special interest for industrial processes. Many siloxane couplings were performed in water for a variety of reasons.[32]

3.2.3. Synthesis and Use of Some Complex Silanizing Agents

The synthesis of silylating agents usually involves reactions in the presence of catalyst of unsaturated organic compounds with chloro- or alkoxysilanes bearing a SiH residue. Platinum compounds or triruthenium dodecacarbonyl cluster[255] are often used for this purpose. As an illustration of the applicability of this reaction to different, even sensitive substrates, the following examples of the preparation of benzo-15-crown-5-containing chlorosilane is given below.[256]



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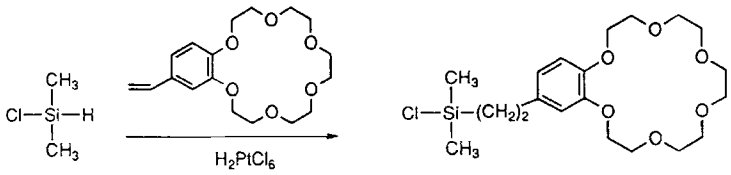
A similar reaction with benzo-18-crown-6 was performed by Blasius and coworkers.[257]



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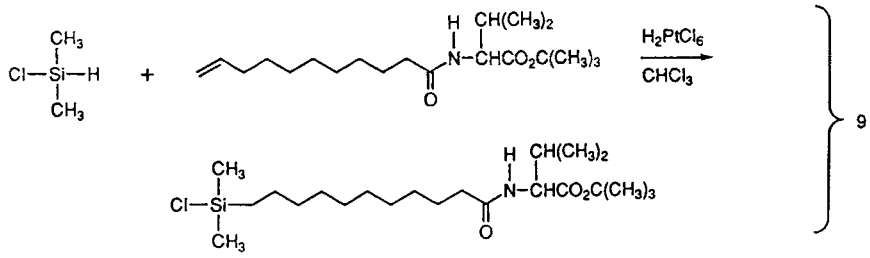
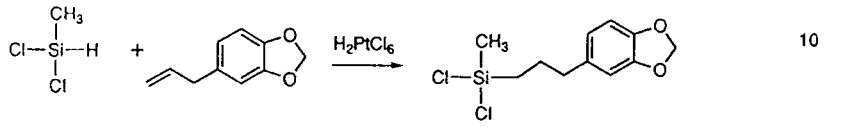
The hydrosilylation of dimethylchlorosilane with N-(-)-10-undecenoyl-L-valine *tert*-butyl ester in chloroform by Feibush and coworkers[245] illustrates the mild conditions under which this reaction takes place, since the chiral center was not racemized and the sensitive ester group was unaffected.



An 11 mmole sample of N-(-)-10-undecenoyl-L-valine *tert*-butyl ester was dissolved in 5 mL of ethanol-free chloroform. To this solution was added 45 mmole dimethylchlorosilane. The solution was heated and then a small amount of hexachloroplatinic acid was added. Reflux was maintained for 1 h, then the volatiles were removed under vacuum (below 0.2 Torr) at room temp. The oily material showed the expected NMR spectrum and was used for immobilization.

Hydrosilylation of saphrol[190] was described as follows.



In a 100 mL three-necked flask was placed 16 g (0.1 mole) of saphrol and 0.5 mL of $H_2PtCl_6 \cdot 2H_2O$ solution in 2-propanol (0.025 g). Dichloromethylsilane, CH_3SiHCl_2 (15g, 0.13 mole), was added at 5° and the mixture turned brown. The mixture was refluxed until it turned dark brown, and it was distilled under vacuum. 3-(3′-4′-Methylenedioxyphenyl)propylmethyldichlorosilane (11g, 40%) was obtained (Eq. 10).

The hydrosilylation reaction may be performed directly on the silica gel surface if it contains SiH groups.[173,174,255]

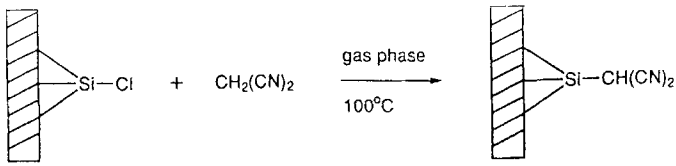
3.3. Use of Organometallic Compounds to Bind Organic Residues onto Silica Gel

Si-C bonds may also be formed by two consecutive reactions on the surface. Reactive Si-Cl bonds are formed by the reaction of silanol groups with thionyl

chloride or silicon tetrachloride. The chlorinated silica gel is then reacted with lithium or magnesium organometallic compounds. An example is the synthesis of benzylsilica.[258] To a carefully pre-dried (200°) Davison grade 62 silica (129.4 g), thionyl chloride (585 g) was added and the mixture was refluxed for 24 h. The solid was washed with dry benzene under nitrogen and the excess $SOCl_2$ was removed under vacuum. Benzyllithium (60 mmole) in THF-ethyl ether was added to a portion of the silica (25 g) at -20° in an argon atmosphere. The chocolate-brown mixture was allowed to warm to room temperature, stirred slowly for 16 h and finally heated to reflux (6 h). The reaction mixture was cooled to - 30° and 25 mL conc. HCl was added to decompose the excess benzyllithium. The solid was collected and washed with successive portions of acetone, methanol and water. Finally it was washed with ethanol and vacuum dried at 100° to give 24.7g.

Similar reactions have been performed with phenyllithium,[259,260] naphthyllithium, triphenylmethyllithium,[259] and allylmagnesium chloride.[220,261,262] Chlorinated Silochrom SI-120 was treated with octylmagnesium bromide to give an octylsilylated surface.[263] Chlorinated LiChrosorb was reacted with alkyllithium reagents (C_4, C_6, C_{10}, C_{16})[264] or with allylmagnesium bromide.[265] Chlorinated Corasil and Merckosorb were ω-hydroxyalkylated using Grignard reagents.[266]

It is of interest that chlorinated silica reacts with malodinitrile at 100° to form dicyanomethylsilylated silica as shown.[220,261]



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Porasil,[267] when reacted with $TiCl_4$ forms an active derivative similar to those formed when it was treated with $SiCl_4$ or $SOCl_2$. [Activation with $TiCl_4$ should produce a surface capable to further reaction with metallorganic reagents.] Alkylation of other inorganic supports activated by chlorination was also studied.[268] Generally,

using organometallic reagents does not prevent occlusion by salts and makes this approach much less realistic than silylation.[269]

3.4. Grafting of Reactive Groups onto Silica Gel or Similar Supports

Irradiation[270-271] or cold plasma treatment of vinyl or allyl monomers adsorbed on silica gel caused polymerization and grafting onto surfaces containing OH groups. Homopolymers were removed from silica gel beads by extraction while the grafted fraction remained on the surface.[272] Kageyama and coworkers[273] reported the γ-irradiation of predried silica gel (specific surface of 480 m^2/g) saturated with styrene vapor at room temperature. This material was extracted with benzene and dried. After sulfonation, this product had a high capacity (1.9 mmole/g) and a high exchange rate. Grafting of acrylonitrile and other vinyl- and allyl- monomers has been performed on other inorganic matrixes such as bentonite, glauconite and kaolinite.[274-280] Cold plasma grafting was used by Zhao and Qiu[281] and by Shi and coworkers[282] for the preparation of bonded chromatographic stationary phases. Semi-industrial plants performing graft polymerization of acrylonitrile, styrene, and acrylic acid onto silica gel use monomers in the gas phase.[283]

3.5. Xerogels

Xerogels, prepared by the hydrolysis of organosilanes, contain organic residues not only at the surface, as in the case of modified silica gels, but distributed throughout the bulk of the material. Such materials are used as packings for gas chromatography. They are prepared by the co-hydrolysis of vinyl-, octadecyl-, or phenyltrichlorosilane, or methyl 10-trichlorosilylundecanoate with silicon tetrachloride.[284] Xerogels of various specific areas and large pore volumes were obtained from chloromethyltriethoxysilane.[285] Co-hydrolysis of glycidoxypropyltrialkoxysilane and aminopropyltrialkoxysilane followed by

condensation with polyethoxysiloxanes also produces xerogels.[286] These materials are capable of forming reactive, chelating or complexing groups such as alkenes, esters, chloromethyl groups, diols and amines. Trialkoxysilyl-terminated N-acetyleneimines co-hydrolyzed with tetraethoxysilane produced hydrophilic or amphiphilic polyoxazoline xerogels.[287] Xerogels with phenylphosphonic acid residues have also been reported.[288]

3.6. Chemical Modification of Immobilized Residues Leading to Bound Acidic, Basic and Chelating Ligands

Modification of organic macromolecules is a well known method to give organic ion-exchangers or chelators (chloromethylation or sulfonation of copolymerized styrene with divinylbenzene, sulfonation of coal, etc.). Ligands anchored to inorganic supports may be analogously modified. Chemical modification of immobilized organic residues on silica and other inorganic supports requires short reaction times because of rapid diffusion, short times for washing, and mild reaction conditions to supress possible release of organic groups from the inorganic matrix.

Many reactions to modify covalently immobilized groups have been developed. For convenience, the reactions have been divided into the following groups based on the nature of the starting materials:

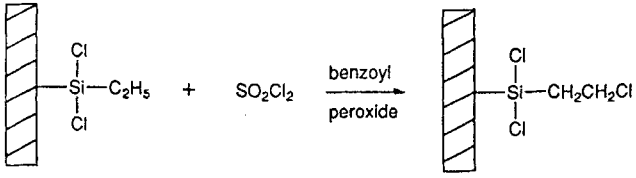
1. Functionalization of alkyl derivatives;
2. Functionalization of aryl residues;
3. Functionalization of alkenyl derivatives;
4. Reactions of halogen derivatives;
5. Modification of aminoderivatives;
6. Reactions of thiol derivatives;
7. Reactions of epoxides;
8. Synthesis of more complex materials;

9. Immobilization of crown ethers;

10. Miscellaneous immobilized groups.

3.6.1. Functionalization of Alkyl Derivatives

There are few examples of the functionalization of immobilized alkyl derivatives described so far in the literature. An example is the free radical chlorination of ethyldichlorosilylated silica gel with sulfuryl chloride.[246]



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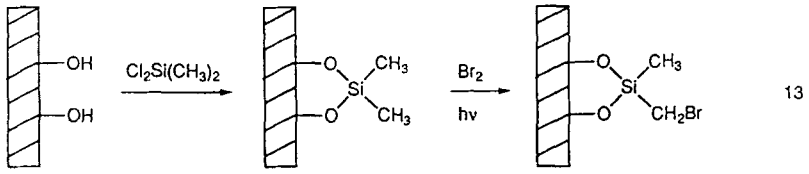
Sebestian and Halasz[2,289] treated silica gel and glass beads with dichlorodimethylsilane. The product, suspended in carbon tetrachloride, was brominated using bromine under UV radiation.



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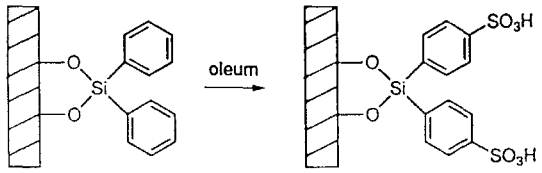
A similar procedure leading to halogenated alkyl silicas was described.[290] Halogenated materials serve as substrates for further reactions with nucleophiles.

Weigand and coworkers[291] performed sulfochlorination of butyl-silylated Kieselgel in the gas phase using a mixture of SO_2 and Cl_2. Conditions were established under which removal of the immobilized butyl residue was low. The product, possessing $Si(CH_2)_4SO_3H$ residues had a capacity of 0.25 mmole/g.

3.6.2. Functionalization of Aryl Residues

The first sulfonation of diphenylsilyl-modified surfaces was described in 1952[292] and later by Neimark and Chertow.[293]



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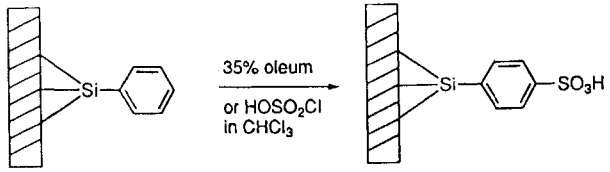
The capacities were 0.51 meq/g and 0.26 meq/g for diphenyl-substituted silica gel and aerosil, respectively. Phenyl-substituted silica gel sulfonated with 35% oleum has a capacity of 0.46 meq/g.[294,295] Sulfonation may also be performed in chloroform with chlorosulfonic acid.[6] Both reactions are accompanied by partial removal of functional groups from the surface.[262,294]



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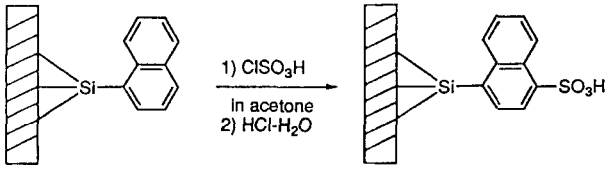
A similar observation was reported by Locke and coworkers[267] who reported that for the sulfonation of naphthyl- or benzylsilica, both fuming sulfuric acid and concentrated sulfuric acid were too reactive and cleaved the Si-C bond. Better results were obtained by using a 20% solution of chlorosulfonic acid in refluxing acetone. The sulfonyl chloride was hydrolyzed to the free acid with a dilute HCl solution.



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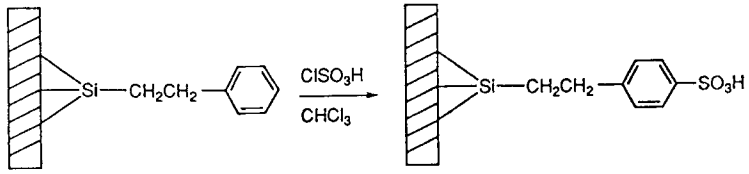
Benzylsilica has been sulfonated in chloroform.[258] Benzylsilylated Davison silica (11.6 g) was suspended in 100 mL of dry chloroform and a solution of 8.8 g of chlorosulfonic acid in 80 mL of chloroform was added dropwise over a 10 minute period. The mixture was then stirred at room temp. for 21 h and the product was washed with chloroform, acetone and water.

Phenylsilylated silica was converted by treating 10 g of the phenyl-modified silica gel with 100 mL of 35% oleum while being stirred for 5 h at room temp.[294] The white reaction product was removed by filtration, washed until the washings were free of sulfate anions and dried for 24 h at 120°.

According to Unger and coworkers[210] who sulfonated phenyl-, diphenyl-, triphenyl- and benzylsilylated silica, chlorosulfonic acid cleaved the Si-phenyl and Si-benzyl groups at a slower rate than oleum. The capacity of their products varied from 0.32 to 1.32 meq/g.

2-Phenylethylsilylated silica gel (Spherisorb S5W) was sulfonated



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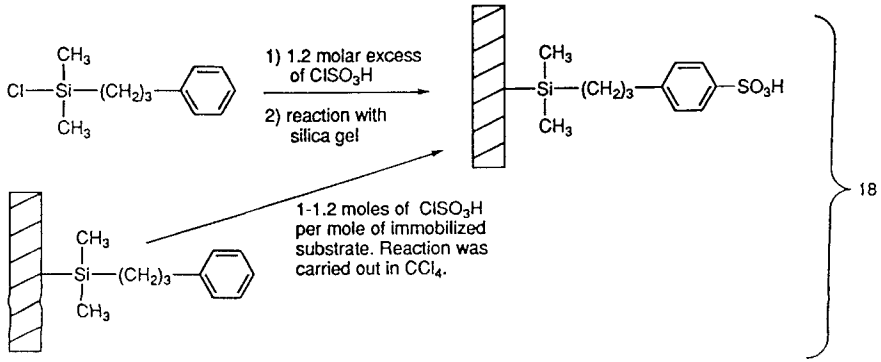
in a boiling solution of chlorosulfonic acid in chloroform.[6] The product capacity was 0.6 meq/g.

Immobilized benzenesulfonic acid



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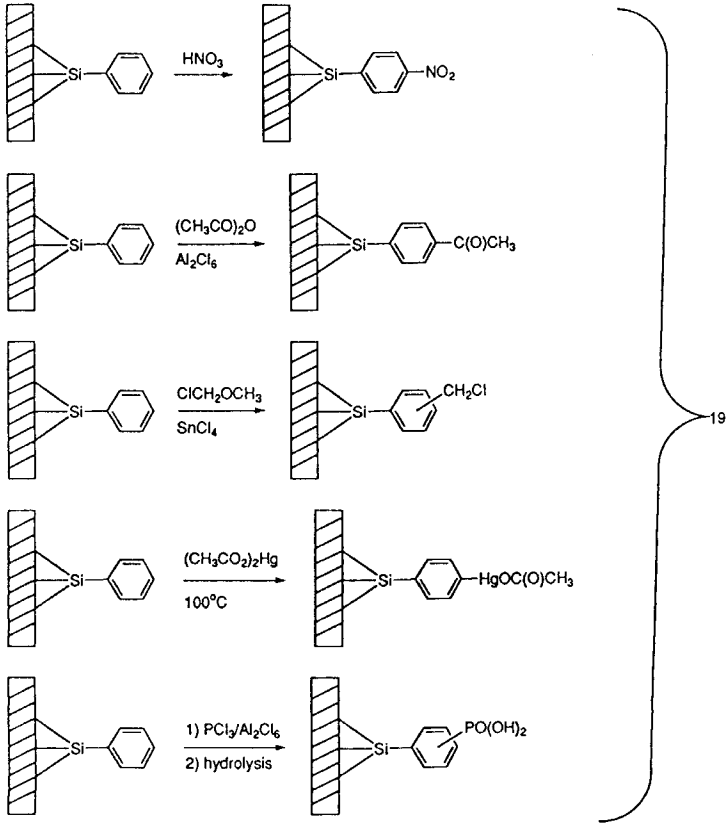
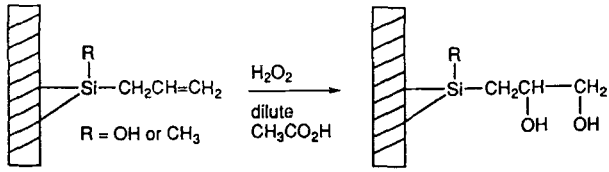
was obtained in two ways as shown in Eq. 18. The reaction conditions were carefully chosen to obtain the best results.[4,296]

Interestingly, silica gel containing graft polymerized styrene, after being sulfonated with 10% oleum for 60 minutes at 40°, had a capacity of 1.9 mmole/g and showed a high exchange rate. A similar product was obtained with alumina as the support.[273] A higher capacity (3.02 meq/g) was achieved by the use of condensation and sulfonation of siloxanes as well as other solid supports.[297] Phenyl substituents immobilized on solid supports undergo other typical electrophilic substitution reactions as shown below (Eq. 33). They include: nitration,[260,298] acetylation (with and without Lewis acid catalysts),[267] chloromethylation using $ZnCl_2$ or $SnCl_4$ as catalysts[210,299] and acetomercuration.[212] The phosphonic group[300] may also be introduced:



3.6.3. Functionalization of Alkenyl Derivatives

Alkenyl residues are precursors to other reactive functional groups. Allylsilica, for example, undergoes mild oxidation with hydrogen peroxide in acetic acid to produce the diol.[301]



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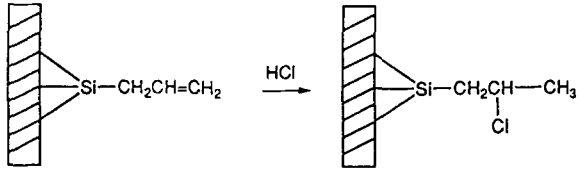
Addition of hydrogen chloride to allylsilica gave the 2-chloropropylderivative.[261]



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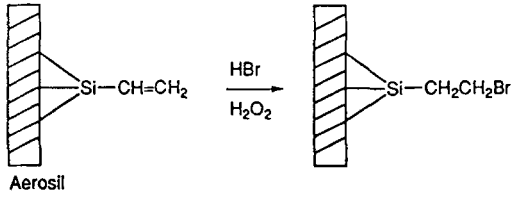
Free radical addition of hydrogen bromide to vinyl-substituted Aerosil gave the terminal bromoethylsilylated Aerosil:[214]



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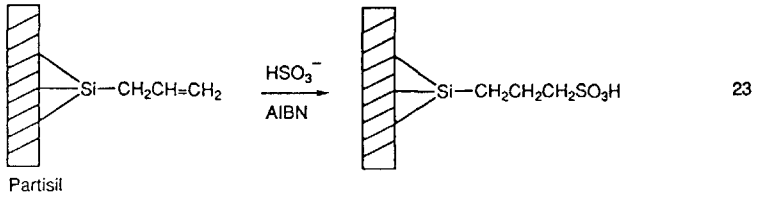
Allylsilylated Partisil, during free radical reaction with hydrogensulfite, gave a terminal sulfonic acid. The procedure is given below (AIBN=azobisisobutyronitrile).[302]



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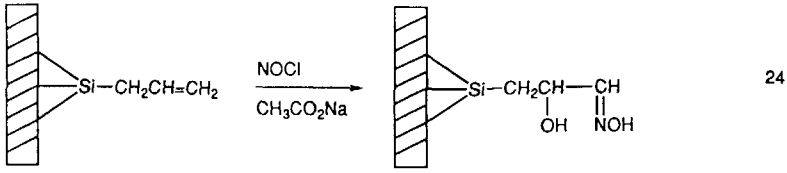
A mixture of 50 mL of methanol-water (1:1) saturated with sodium bisulfite, AIBN and 5 g of allylsilyl bonded silica was heated at 70° for 14 h. The product was washed with water and alcohol and dried at 120°. The capacity (0.48 meq/g) was determined by titration.[302]

Allylsilylated silica undergoes an interesting reaction with nitrosyl chloride in the presence of sodium acetate[220b,261] to form a bonded hydroxyoxime residue.



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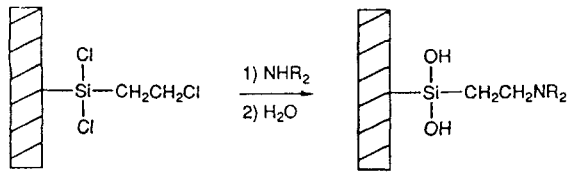
Allyl- or vinyl-bonded silicas have also been used as substrates for copolymerization.[303-305]

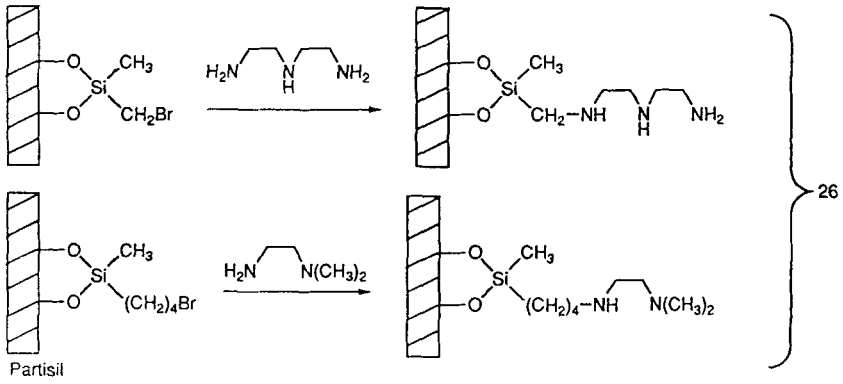
3.6.4. Reactions of Halogen Derivatives

A wide variety of reactions have been performed on the halogenoalkylated derivatives of silica. First, these compounds may be easily converted into amines or into quaternary ammonium salts. This is an alternative way to synthesize immobilized amine derivatives as opposed to direct immobilization. In 1964, Wolf and coworkers[246] performed this type of synthesis as shown below:

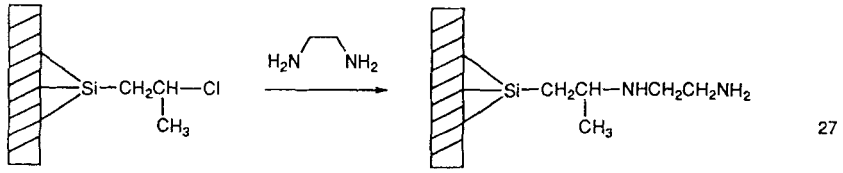


25

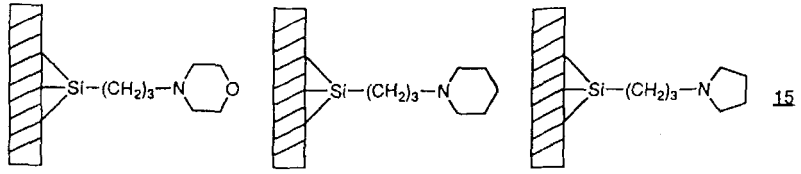
Polyamines were prepared in a similar way from bromoalkylsilica and diethylenetriamine or N,N-dimethylethylenediamine as shown.[2,289]



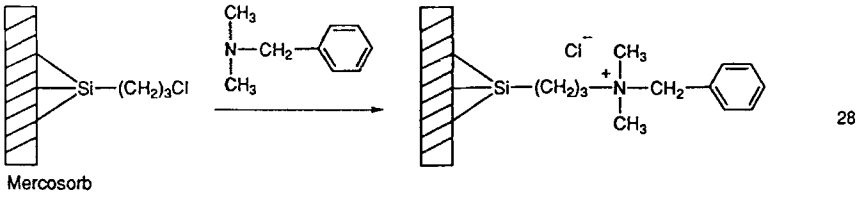
Similar reactions were performed using other straight-chained amines[220b,261]



as well as cyclic amines such as morpholine, piperidine or pyridine.[306]

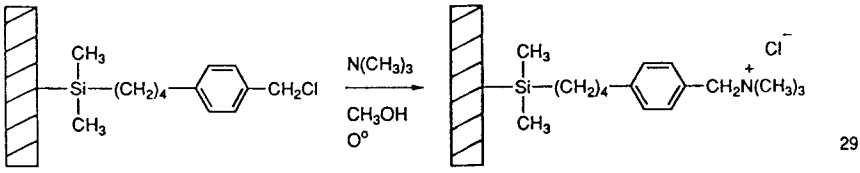


Analogously, when tertiary amines were used, strong anion exchangers were obtained. For example, chloropropyl-substituted silica[217] was refluxed in a mixture of dioxane (25 mL) and benzyldimethylamine (25 mL). The product was collected, washed thoroughly and dried. The capacity (Volhard's method) was 0.6 meq/g for Mercosorb Si-60.[6]



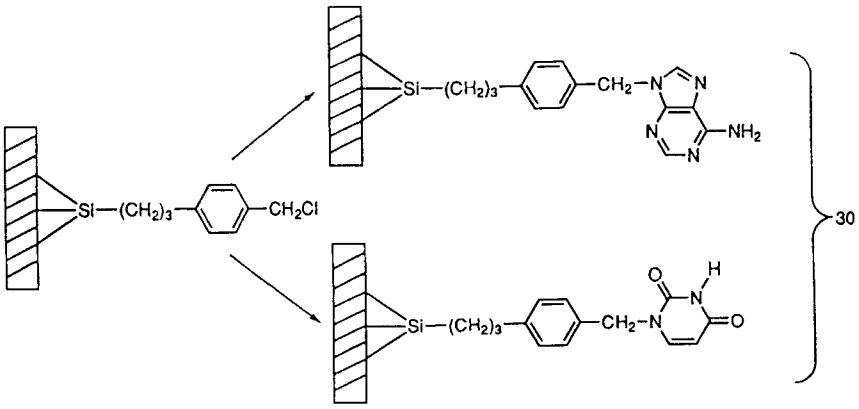
28

Strong anion exchangers were also prepared by the reaction of trimethylamine in methanol at 0° for 1 week.[307]



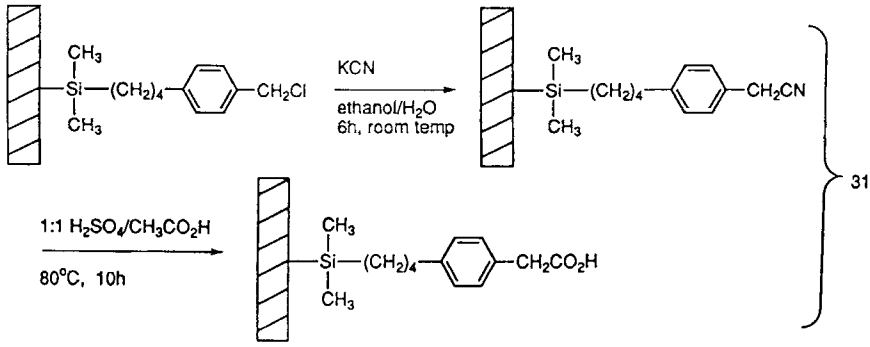
29

Using the chloroderivative shown below, adenine and uracil were bonded to porous silica.[308-309]

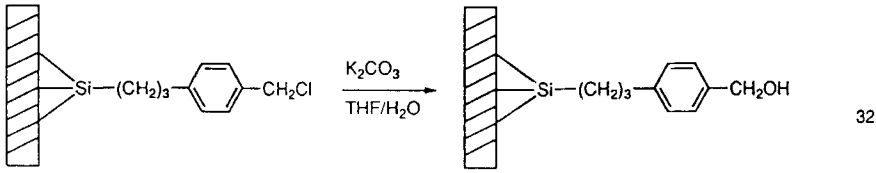


30

A wide variety of other reactions have been performed with chloromethylated starting materials as illustrated in Figs. 31 and 32.[4,301]



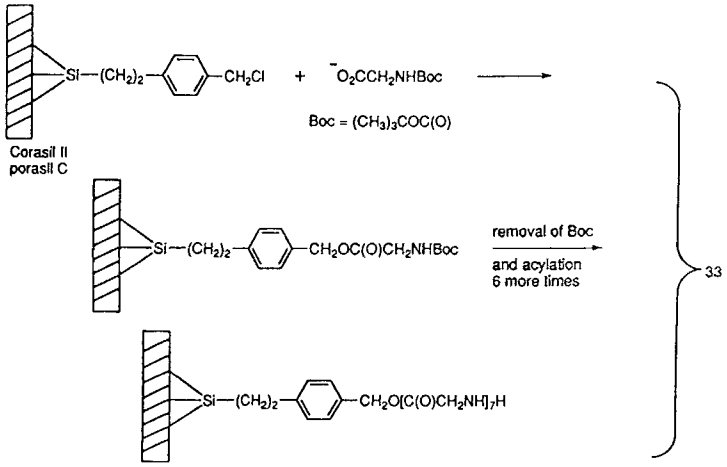
31



32

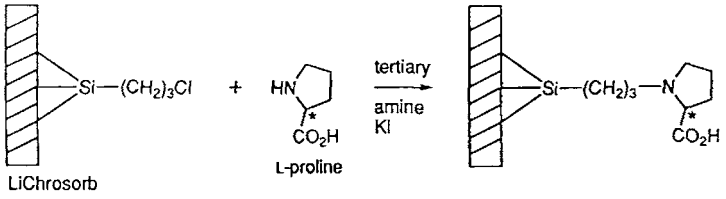
Halogenated silicas react with acylated amino acid salts to form esters. This method is similar to that used in the Merrifield solid phase peptide synthesis. Polypeptides have been anchored to solid supports and used as chromatographic packings.[310]

In a similar way, many amino acids may be attached to silica gel via an ester linkage. Immobilization of L-proline may be performed as follows.[217]



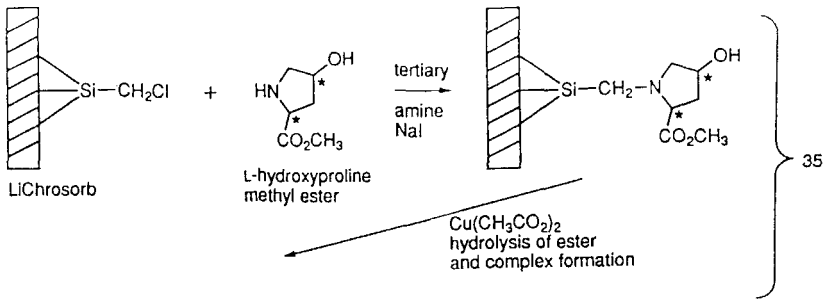
33

Chloropropylsilylated LiChrosorb SI-60 (11 g) was suspended in 200 mL of a chloroform - methanol (85:15) mixture containing 3g of L-proline, 1g of potassium and 2.8 mL of diisopropylethylamine. The mixture was refluxed for 12 h, filtered, washed with methanol and acetone and dried under vacuum.



34

Use of amino acid esters can lead to N-alkylated amino acids as well.[218]

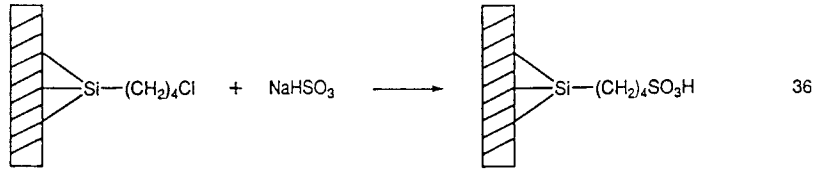


35

Ten grams of LiChrosorb Si-60 (10 μm) and 8 g of chloromethyltrimethoxysilane were heated for 24 h in 300 mL of refluxing n-octane. After the excess silane was removed and the product was washed, a solution of 5 g of L-hydroxyproline methyl ester and 0.5 g NaI in dioxane-methanol (6:1) was added. Heating at reflux was continued for 12 h. After washing, the packing was treated with a copper acetate solution at 50° to hydrolyze the ester.[218]

An interesting concept was patented by Davankov and coworkers.[311] An organosilicon polymer with a molecular weight of 20,000 - 30,000 containing active halogen atoms was reacted with silica gel and then with L-proline or L-hydroxyproline methyl ester to form an optically active support.

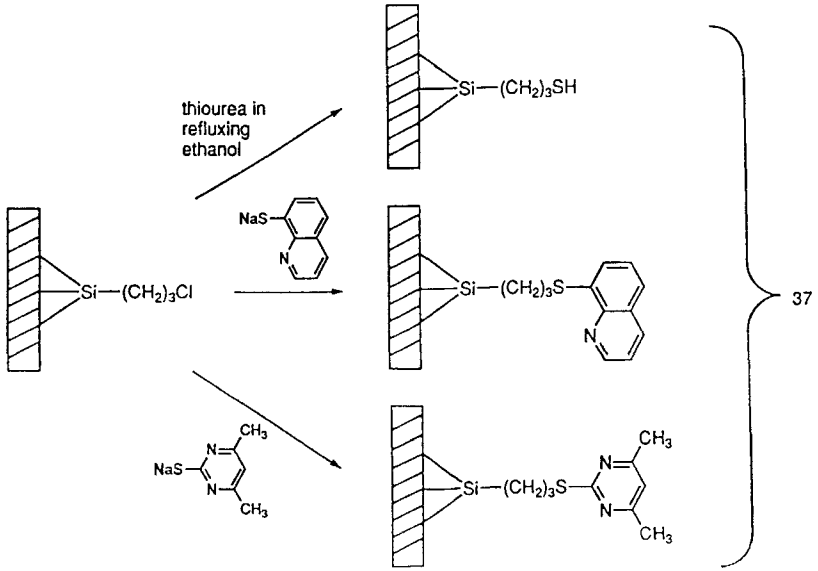
Substitution of a halogen atom by a sulfonyl group according to Eq. 36,[2,289,312]



36

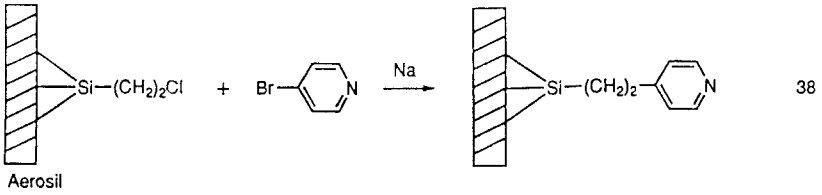
seems to be less frequently used for the synthesis of strong cation exchangers as compared to sulfonation of aromatic derivatives or oxidation of thiols.

Other reactions of halogen derivatives to form C-S bonds are the synthesis of thiols with thiourea and thioethers with sodium sulfides as shown in Eq. 37.[220b,261]



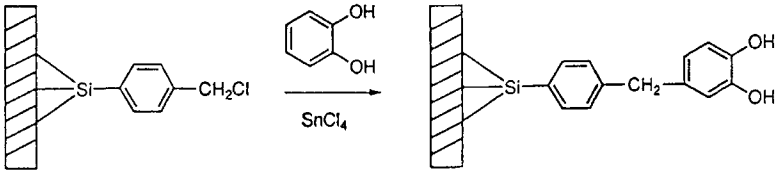
37

Two other reactions are of interest: the Würtz-Fittig reaction of bromoethylsilyl Aerosil with bromopyridine in the presence of sodium.[214]



38

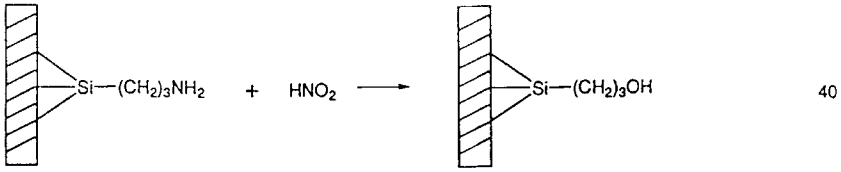
and the Friedel-Crafts alkylation of catechol:[313]



39

3.6.5. Modification of aminoderivatives

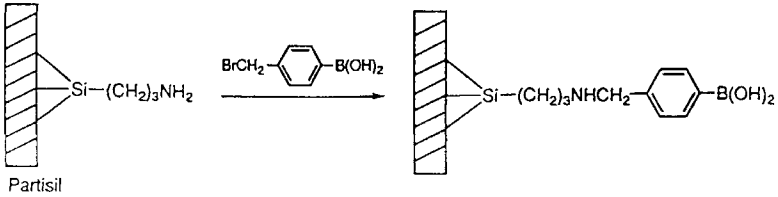
Bonded amines are weak anion exchangers and they are also used to form complexes with metal cations. Bonded amines are also versatile and convenient starting materials for the synthesis of many other useful supports. The primary amine groups may easily be converted into alcohols as shown in Eq. 40.[220]



40

Amines also react with aldehydes and ketones to form Schiff bases.[191,314] These materials are used to form complexes with metal cations or they may be modified in subsequent steps.

As shown below, aminopropylsilylated Partisil was reacted with 4-(bromomethyl)phenylboronic acid to produce a modified support.[315]

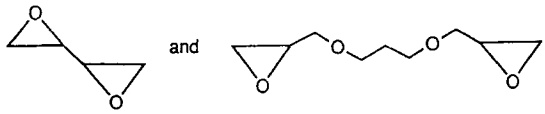


Partisil

41

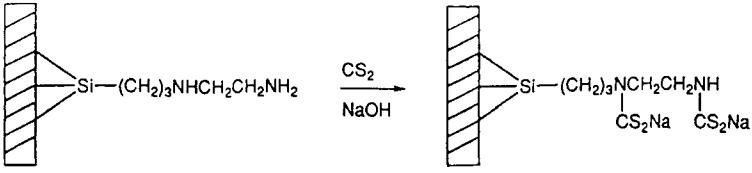
The amine group modifies the acid-base properties of the boronic acid residue.

Similarly, aminopropylsilylated LiChrosphere and Zorbax[211] crosslinked with diepoxides shown in Structure 16 not only increased the number of electron donating groups, but also increased the stability of the immobilized layer.



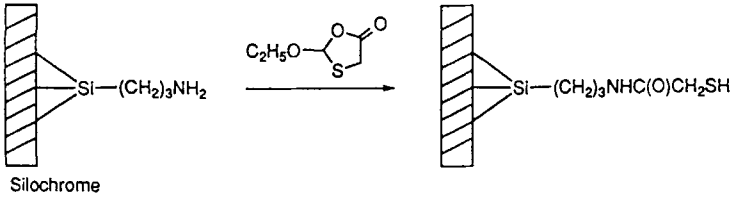
16

Amines can also be transformed into dithiocarbamates, thus changing completely their specificity towards metal cations.[12,316] The synthesis of the dithiocarbamate may be exemplified as follows (Eq. 58): N-(2-aminoethyl)-3-aminopropyl substituted silica gel (20 g) was stirred with 100 mL of water, 25 mL of 0.25 N NaOH, 25 mL of 2-propanol and 2 mL of CS_2 for 15 minutes. The reaction product was collected and the solid material was washed with 2-propanol and air dried.[28,317]



42

The amine group has been used to introduce other functional groups, such as thiols.[318]

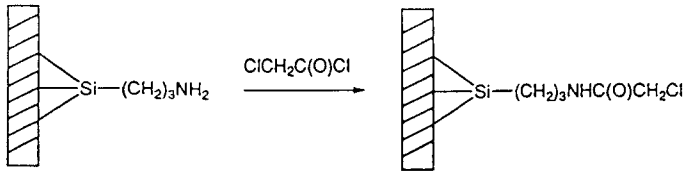


43

Silochrome containing amine residues (1g) was suspended in 1 mL of pure benzene, and a 2 molar excess of 1-oxo-2-ethoxy-3-thiolane-5-one was added. The suspension

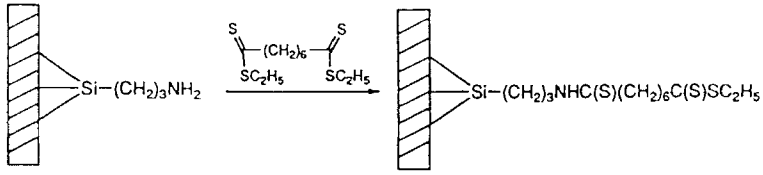
was stirred for 2 h in a stoppered flask under argon. The liquid phase was decanted and the product was washed with pure benzene, dimethylformamide, cold distilled water and used for further reactions.[318]

A reactive chlorine atom may be introduced by chloroacetylation.[319]



44

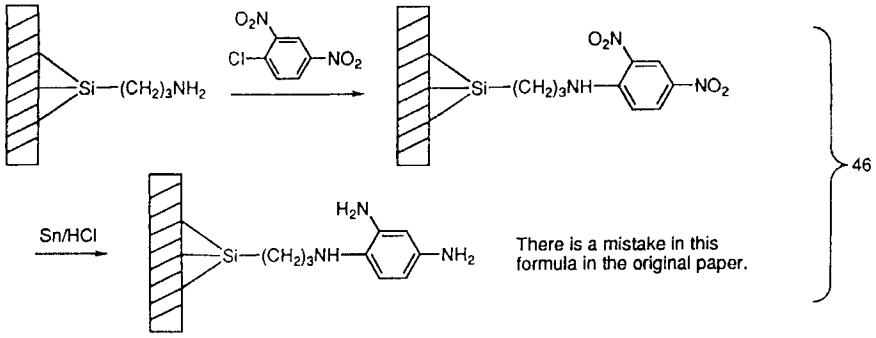
An active ester may be obtained in a similar manner.[320]



45

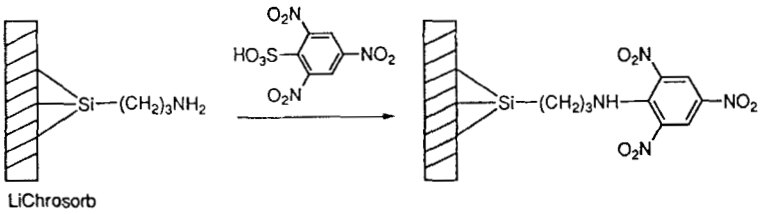
This ester is capable of rapid reactions with amines. The reaction also increases the spacer length. Both materials were used to bind enzymes.

Amines react with chlorodinitrobenzene to form 2,4-dinitrophenyl derivatives (Eq. 46). This product, after reduction, has 2 amine groups per site, each capable of further modification.[321] In principle, this procedure increases the number of chelating groups during modification as compared to the starting material.



46

Reaction of aminopropylsilylated LiChrosorb with 2,4,6-trinitrobenzenesulfonic acid gave the picramide derivative.[322]

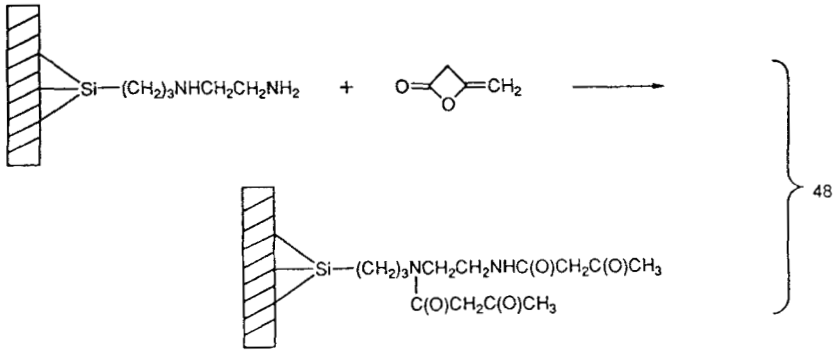


LiChrosorb

47

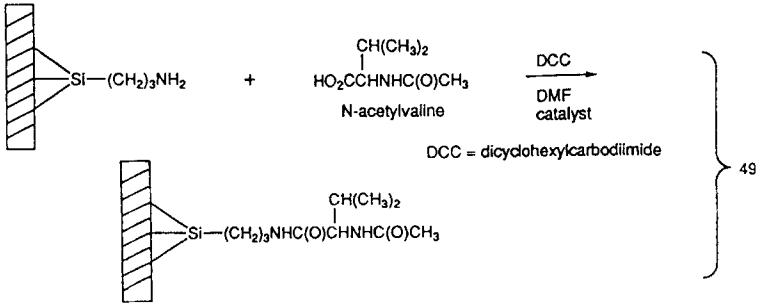
This reaction was performed in a chromatographic column filled with aminopropylsilylated LiChrosorb by flowing a trinitrobenzenesulfonic acid solution through it.

Primary and secondary amines react with many acylating reagents to form N-acyl derivatives. In the case of immobilized amines many such reactions have been performed. For example, reaction of diketene with an aminopropylsilylated silica resulted in the formation of the acetylacetamido derivative, which is a good chelating agent.[229,323]



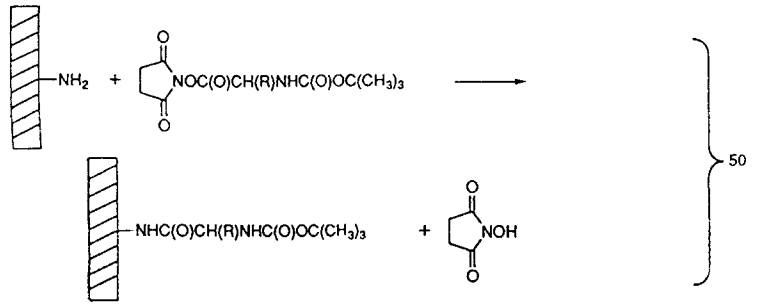
48

Other reactions have been performed with activated derivatives of chiral N-acylated amino acids. Hara and Dobashi[324] attached N-acetyl-L-valine to aminopropylsilylated microparticulate silica using dicyclohexylcarbodiimide (DCC) in the presence of hydroxybenzotriazole as a catalyst.



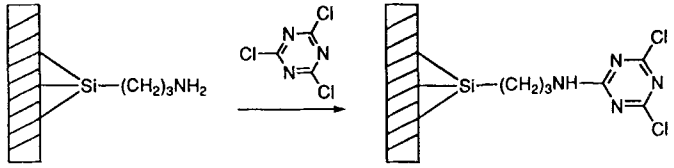
To a suspension of aminopropylsilylated silica (2.2 g) in 8 mL of dimethylformamide (degassed for 5 minutes under vacuum) were added a solution of 1.02 g of 1-hydroxybenzotriazole in 3 mL of DMF and a solution of 0.8 g of N-acetyl-L-valine in 3 mL of DMF. The resulting mixture was stirred with 3 mL of DMF containing 1.14 g of DCC at 0° for 1 h and then at room temperature for 48 h. The modified silica was separated from dicyclohexylurea by centrifugation, washed successively with chloroform, acetone, methanol, and diethyl ether and dried under vacuum. From the nitrogen content, it was estimated that 28.3% of aminopropyl residues were acylated with N-acetyl-L-valine.

DCC was also used by Gimanova, and coworkers[325] for attaching benzyloxycarbonylamino acids. The DCC method is simple, but serious problems arise due to the low solubility of the dicyclohexylurea formed as a side product. Boiling the product with methanol or ethanol may facilitate purification. Many other methods known in peptide chemistry have been adapted.[326-328] The N-hydroxysuccinimide esters of *t*-butyloxycarbonylamino acids were immobilized on aminoalkylated silica gel as follows:



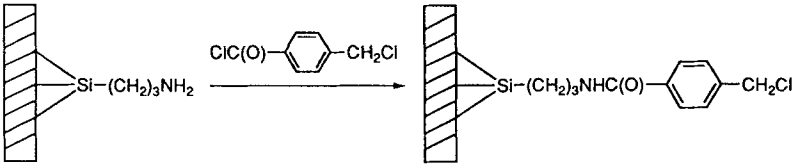
The ester (3 mmole) was dissolved in 10 mL of glyme. This solution was added to a suspension of amine-derivatized silica gel (3 g) in 15 mL of dry glyme. The mixture was gently stirred for 48 h at ambient temperature. The gel was then collected, washed with glyme, dimethylformamide and methanol. Carbonyldiimidazole[329] in combination with N-acylated amino acids or p-nitrophenyl esters of N-acylated amino acids has been used in a similar way.[330]

Aminopropylsilica reacted with cyanuric chloride to form a dichlorotriazine which is able to react with nucleophiles.[331]



51

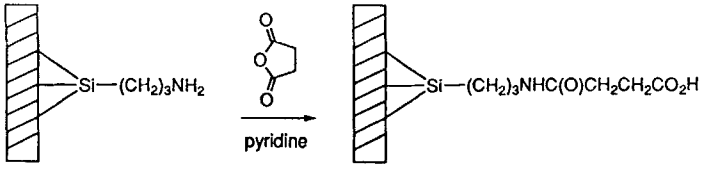
Diisocyanates have also been used for coupling cellulose to aminopropylsilylated silica.[332] An active chloromethyl group may be introduced by acylation of aminoalkyl substitued silica with 4-(chloromethyl)benzoyl chloride.[48]



52

LiChrosorb

The reaction of aminoalkylsilylated supports with succinic anhydride leads to carboxylic acids.[333]

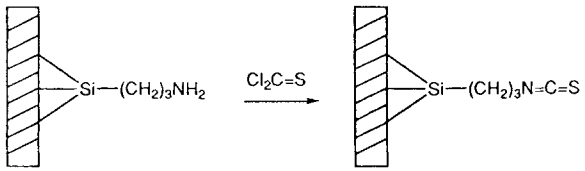


53

These materials are now commercially available.[334] Acylation of aminoalkylsilylated supports with succinimide or its derivatives leads to amides of extended length.[335]

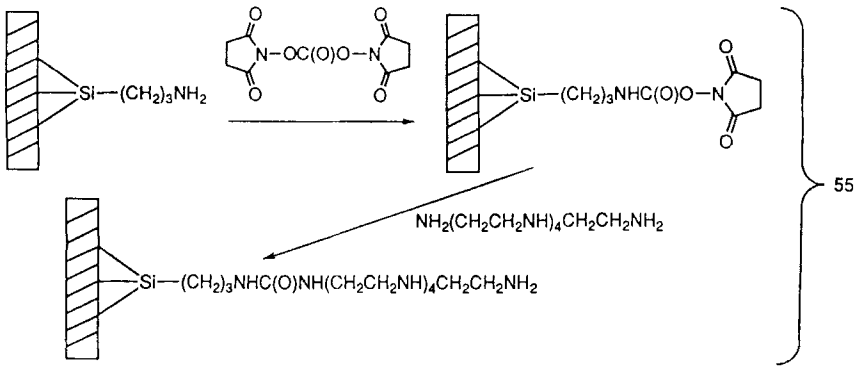
Acylation of aminopropyl-bonded silica gel with acyl chlorides is restricted to acylating agents of a size small enough to penetrate the pores.[336] Alternatively, the remaining free amine groups, after the acylation step, may be acylated with more reactive acid chlorides. Acylation of the aminopropyl residue with long fatty acids produced good "reverse" HPLC phases.[137]

Amine groups are also convertible into other reactive intermediates, making the amine group very valuable in functionalizing solid supports. Treatment of aminopropylsilylated porous glass, alumina or hydroxyapatite with thiophosgene gave bonded isothiocyanates as shown below.[223]



54

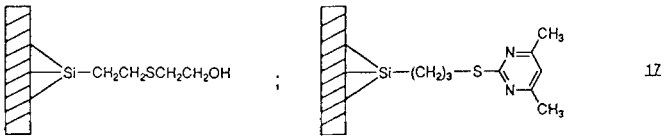
The amine-containing substrate was refluxed in a 10% thiophosgene solution in chloroform overnight. The product was immediately used to immobilize enzymes. Alternatively, isothiocyanates were obtained by thermal decomposition of immobilized dithiocarbamates.[221] Isothiocyanates react with primary and secondary amines to form thioureas. Ureas may also be prepared by the reaction of aminoalkyl silica with disuccinimidocarbonate as shown in Eq. 55.[338]



55

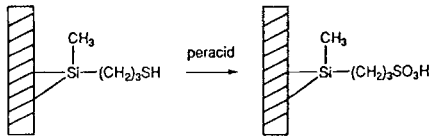
3.6.6. Reactions of Thiol Derivatives

Mercaptans are typically used for the syntheses of thioethers. A few examples are given by Semikolenov and coworkers.[339] Two bonded thioethers prepared by them are shown below.



17

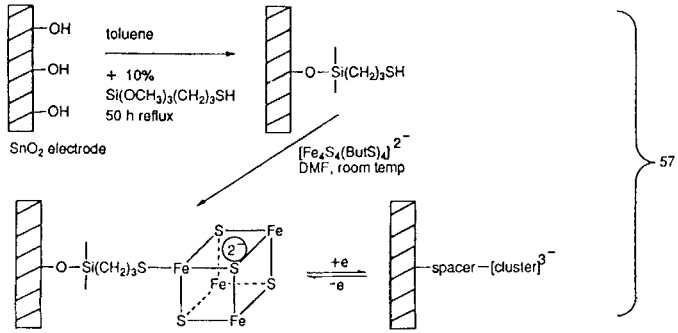
Another obvious modification of a thiol is via oxidation. Sulfonic acids were synthesized by oxidation by Fazio and coworkers.[235] Silica with mercaptopropyl groups immobilized on the surface (and end capped by TMS groups) was oxidized by peroxyoctanoic acid in ethyl ether or by peracetic acid in acetic acid for 6 h at room temperature as shown below.[235]



56

Thiols may also be oxidized to sulfonic acids with sodium hypochlorite.[340]

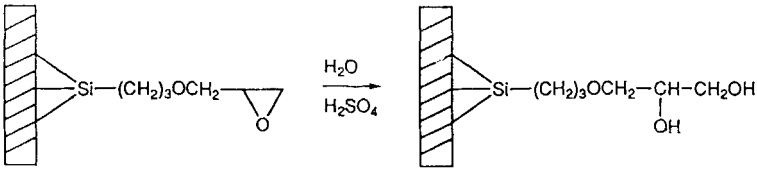
Thiols form stable complexes with heavy metal cations. They also form complexes with ionic clusters, wherein a mercapto group on a SnO_2 surface forms a complex with an Fe-S cluster as shown below.[234]



57

3.6.7. Reactions of Epoxides

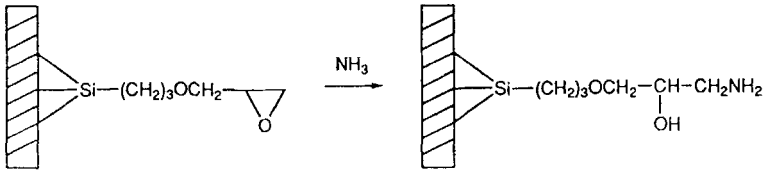
Glycidoxypropyl-bonded supports are not used as packings for chromatography,[341] rather they serve as starting materials for the preparation of many derivatives. Mild hydrolysis in the presence of a catalytic amount of sulfuric acid gave the dihydroxypropoxypropyl support shown in Eq. 58.[239,342,343]



58

Glycidoxypropyl-substituted silica gel was treated with 0.05 M sulfuric acid at 80°. Afterwards, the excess acid was completely removed by washing with deionized water.

A hydroxyamine derivative was obtained by treatment of glycidoxypropyl-bonded silica with concentrated ammonia at room temp.[286]

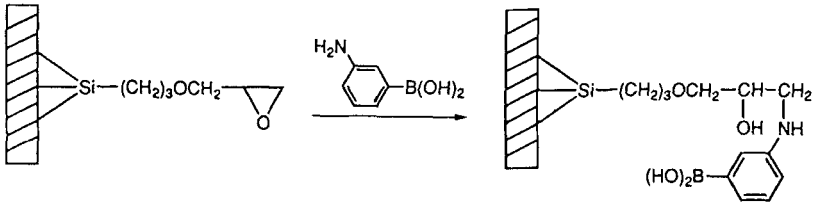


59

Solutions containing primary or secondary amines in DMF react readily with glycidoxypropyl-modified support.[344] As an example, 3-30 g of glycidoxypropyl-substituted silica was treated with an 80% solution of diethylamine in DMF. The suspension was swirled and left at room temperature for 24-48 h. The resulting diethylamine-bonded support was then collected, washed with water and methanol, and dried under vacuum.[239]

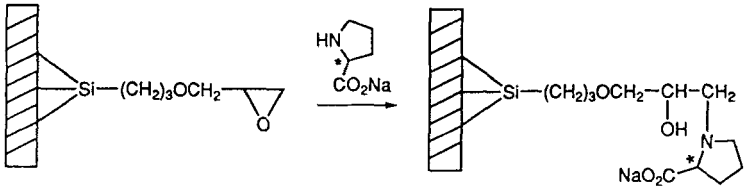
3-Aminobenzeneboronic acid, when treated with glycidoxypropyl-substituted LiChrosorb in aqueous solution at a pH of 8.5 at room temp for 24 h, formed an

immobilized boronic acid:[192,193]



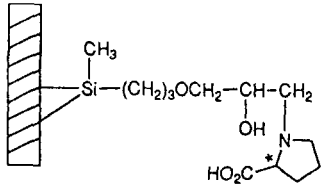
60

Immobilized amino acid derivatives have been prepared by the action of amino acid salts on glycidoxypropylsilylated supports. For example, sodium L-prolinate in dimethylformamide or in methanol was shaken with glycidoxypropylsilylated silica at room temperature for 48 h as shown.[241,345]



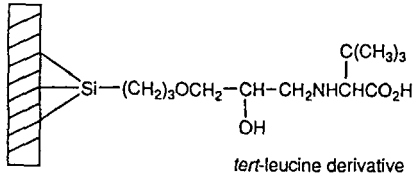
61

Other amino acids were attached to form the products shown in Structures 18 and 19.[346]



18

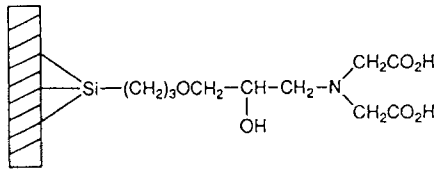
L-proline derivative



19

tert-leucine derivative

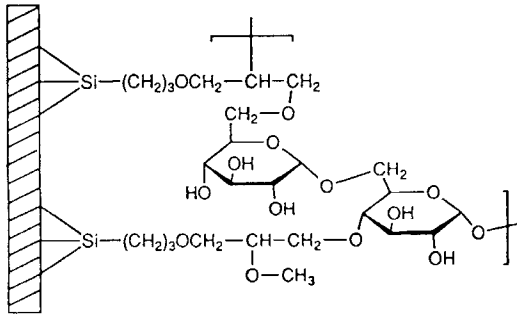
Cibacron Blue F3G-A (dye) was bound to silica using glycidoxypropyl derivatized silica gel.[347] Likewise, nitrilodiacetic acid reacts with glycidoxypropylated silica to form an immobilized chelating agent.[348]



20

Glycidoxypropylated silica also forms ether linkages. For example, 3-30 g of glycidoxypropylsilylated support was added to 50 mL of dioxane containing 40 mmoles of an alcohol or polyethylene glycol and 1 mL of boron trifluoride etherate. After mixing, the suspension was maintained at room temperature for 5 min and then heated at 90° for 30 min. The support was collected, washed with water and acetone and dried.[239]

Another interesting reaction of the glycidoxypropyl-substituted materials is binding bacitracin and gramicidin.[349] Levoglucosan reacts with glycidoxypropyl-substituted macroporous glass in the presence of $BF_3 \cdot Et_2O$ to form a polymer.[350]

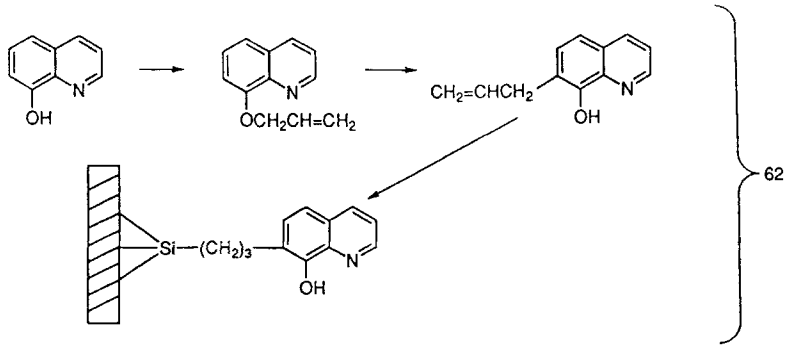


21

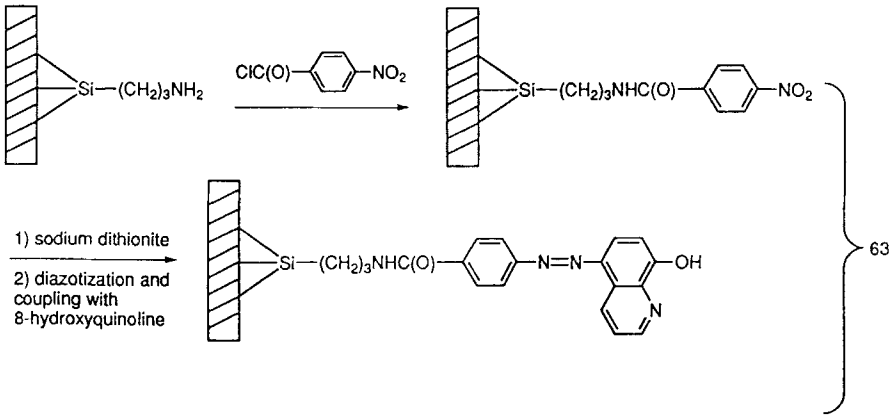
3.6.8. Synthesis of More Complex Immobilized Materials

A good example of a more complex material for immobilization is the chelating ligand 8-hydroxyquinoline. The simplest synthesis of immobilized 8-

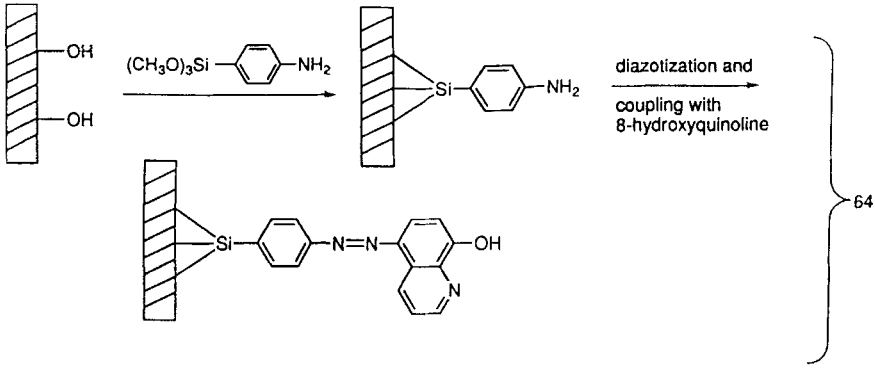
hydroxyquinoline, shown in Eq. 62, has been patented by Plueddemann.[351]



The first procedure leading to the immobilization of 8-hydroxyquinoline was described by Hill[27] as shown in Eq. 63.

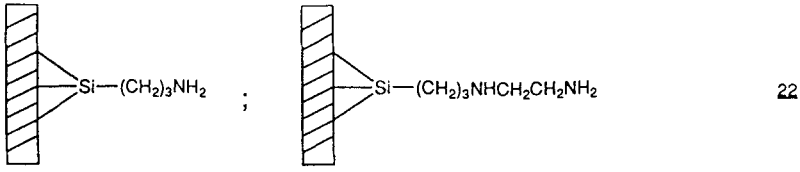


The capacity of the final product was 0.07 mmole/g. The same procedure was repeated to attach 8-hydroxyquinoline to a controlled pore glass[28,317] and Porasil.[225] This procedure was later improved[232,352,353] by the immobilization of aminophenyltrimethoxysilane on silica gel followed by formation of the diazonium salt which afterwards was coupled with 8-hydroxyquinoline.



A 10% solution of aminophenyltrimethoxysilane in dry toluene (20 mL) was added to dry silica and vacuum was applied to remove any trapped air. The reaction mixture was refluxed for 4 h and the product was collected and dried overnight at 80°. To this arylamine-substituted silica, 100 mL of ice cold 2% sodium nitrite in 2 M hydrochloric acid was added and the reaction was allowed to proceed for 30 min. The diazonium salt-silica was collected, washed with three 25 mL portions of ice-cold water, and added to 100 mL of a 2% solution of 8-hydroxyquinoline in ethanol. The appearance of a deep red color indicated the azo-coupling of hydroxyquinoline. The coupling reaction was carried out for 30 min, then the solid was collected and washed sequentially with ethanol, 0.1 M hydrochloric acid and water. The respective capacities for silica gel, Porasil C, and controlled porosity glass, are 0.216, 0.109, and 0.058 meq/g, respectively. This synthesis is shorter requiring 2 fewer steps than the other methods.

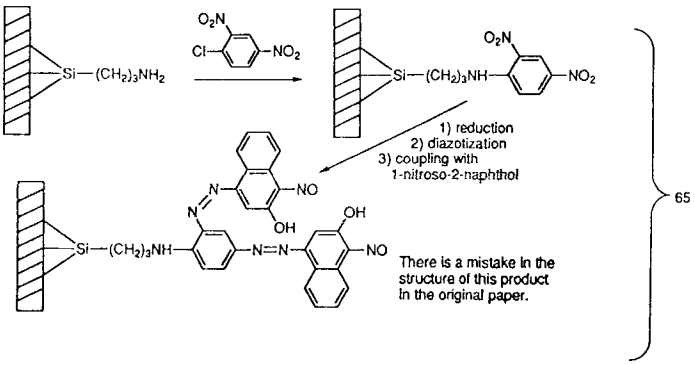
Alternatively, modified silica supports with the following structures



were suspended in methanol. 5-Chloromethyl-8-hydroxyquinoline and triethylamine were added and the mixture was refluxed and stirred for 5 h. The product was

filtered, washed with methanol, water, dilute HCl, water, methanol and then dried under vacuum to give the 8-hydroxyquinoline-substituted silica materials.[355]

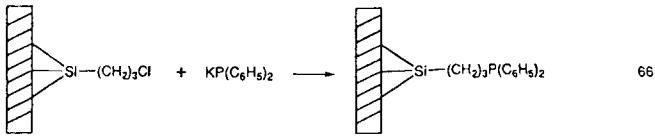
An interesting approach was used by Gennaro and coworkers[321] for the immobilization of 1-nitroso-2-naphthol. Their synthesis giving a bis(1-nitroso-2-naphthol) material is shown below:



This material had a capacity of 0.5 meq/g in complexing Co(II) ions.

A polysulfonic acid phase was prepared as follows. To a suspension of 50 g of polyethyleneimine-bonded silica in 250 mL of toluene, 20 g of maleic anhydride was added with stirring. The reaction mixture was heated to about 65° for 4.5 h. The solid silica was filtered and dried to give 57.7 g of product. Part of the product (20 g) and 13 mL of 1 N NaOH were then mixed with 9.5 g of sodium metabisulfite ($Na_2S_2O_5$) in 100 mL of water and mixed thoroughly. The reaction mixture was placed in a heated bath (80°) open to the air for about 6 h. The mixture was cooled and the product dried to give 20.62 g of silica that had a capacity of 0.634 meq/g of sulfonic acid.[356]

There are two major pathways available which lead to phosphine-containing phases. The first is the reaction of chloroalkylsilylated supports with lithium or potassium derivatives of secondary phosphines.[236]

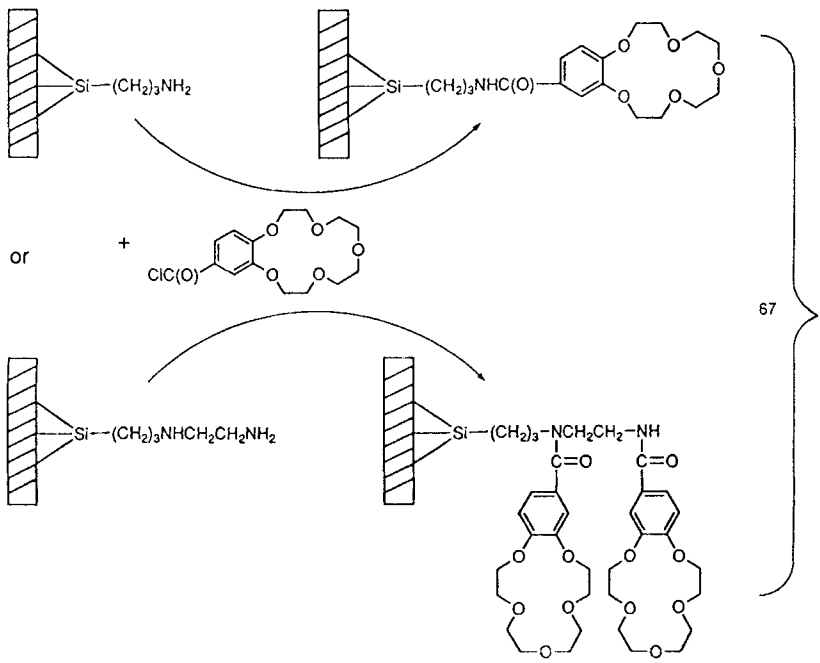


Chloropropylsilylated silica (15 g, 1.2% Cl) was suspended in THF, an excess of $KP(C_6H_5)_2$ in THF was added, and the mixture was brought to reflux for one hour. Methanol was added and the silica was soxhlet extracted with methanol, and then with toluene each for 24 h. Finally, the product was dried in vacuo to give a material containing 0.1% Cl and 0.4% P. The lithium derivative of diphenylphosphine, which reacts analogously,[357] may be obtained from triphenylphosphine and lithium metal in THF. Chiral dimenthylphosphinopropylsilylated silica was obtained from chloropropylsilylated material and the lithium salt of chiral dimenthylphosphine.[238]

In the second method, chlorophosphines react with aminoalkylsilylated supports to give the phosphinoamine derivatives.[358]

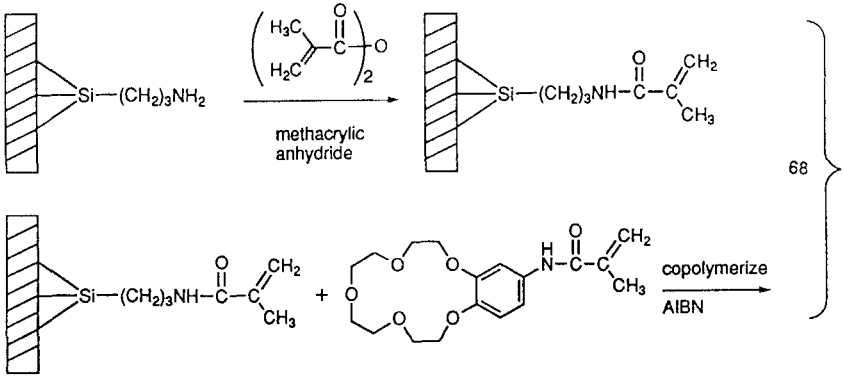
3.6.9. Immobilization of Crown Ethers

The simplest way to immobilize crown ethers onto inorganic supports is depicted in the scheme below.[359,360]



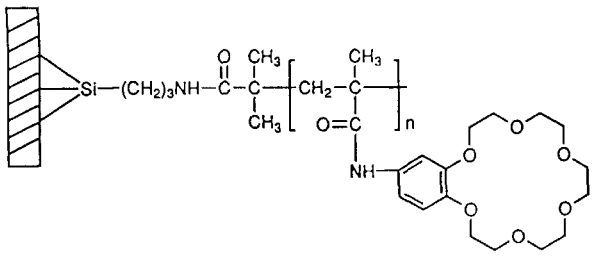
These reactions were performed in chloroform using triethylamine to trap the hydrogen chloride. Another attachement of a crown ether via an amide bond has been reported.[361]

Kimura and coworkers[359] reported the copolymerization of methacrylamidosilylated silica gel and an methacrylamido-substituted crown ether in a manner described by others.[362,363]



68

The crown immobilization was performed as follows: A glass tube containing 6.97 g of methacrylamidopropylsilylated silica gel, 2.5 g of (4'-methacrylamido)benzo-15-crown-5, 40 mg of AIBN as the initiator and 20 mL of dimethylformamide was degassed by the freeze-and-thaw method and then sealed. The polymerization was carried out by shaking the sealed tube in an incubator at 70° for 21 h. After polymerization, the silica was washed successively with dimethylformamide, chloroform and methanol, and then dried overnight in vacuum at 80°. The capacity was 0.09 meq/g. The authors used the same procedure to immobilize benzo-18-crown-6 on silica gel to give the polymer shown below.[364]

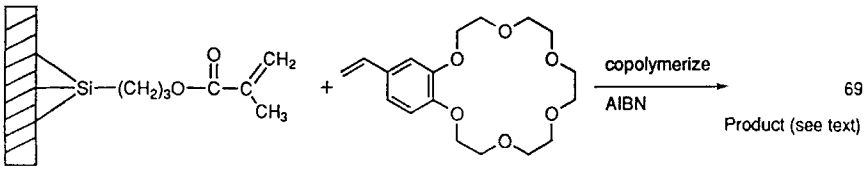


23

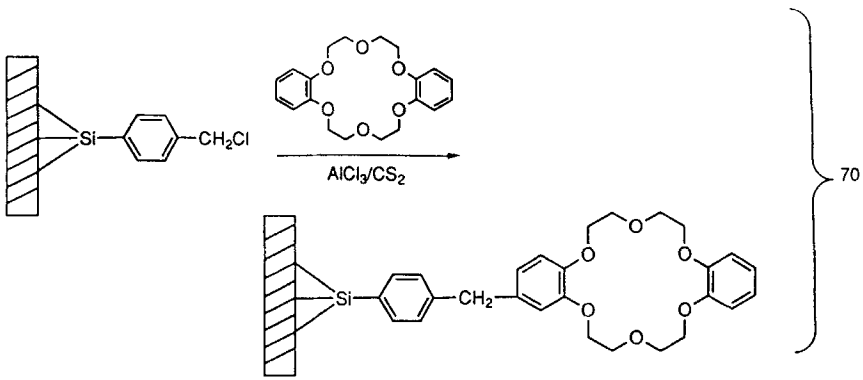
The final capacity of this material was 0.28 meq/g.

Other products were obtained by copolymerization of methacrylamidobenzo-15-crown-5 with methacrylamidopropyltrialkoxysilane followed by immobilization of the prepolymer onto the silica gel surface.[365]

Methacryloyloxymethyl-12-crown-4 and vinylbenzo-18-crown-6 were also attached by copolymerization.[165] Similar copolymerization was performed using vinylbenzo-18-crown-6.[366]



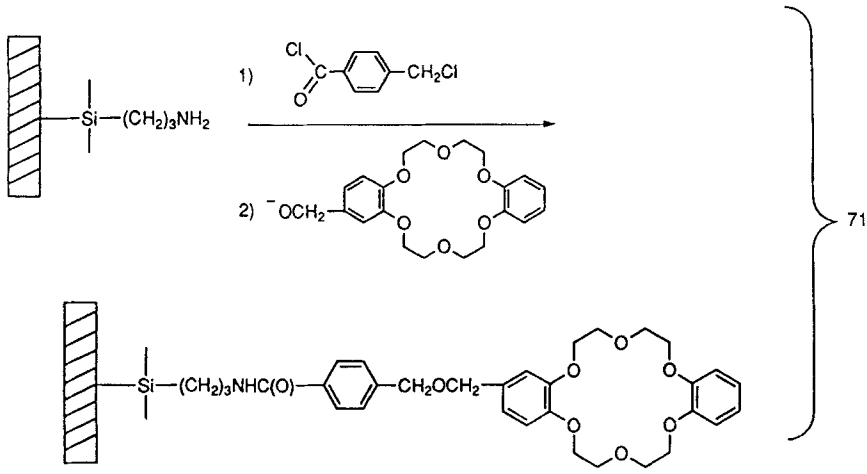
All of the above crown ether derived materials contain at least one hydrolytically unstable bond, i.e. an ester or amide, and hence efforts have been made to find more stable attachments. In 1981, Waddel and Leyden[219] used Friedel-Crafts conditions to attach dibenzo-18-crown-6 to a solid support.

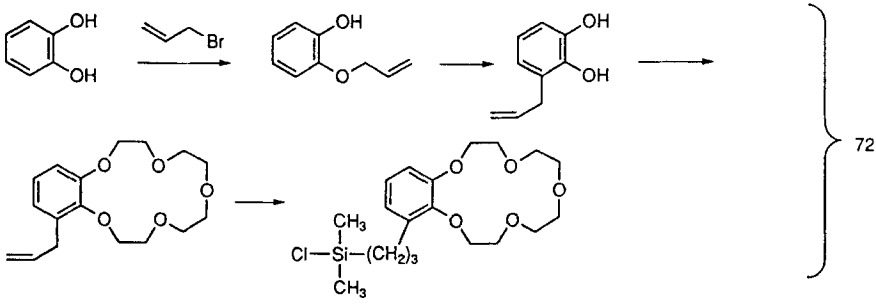


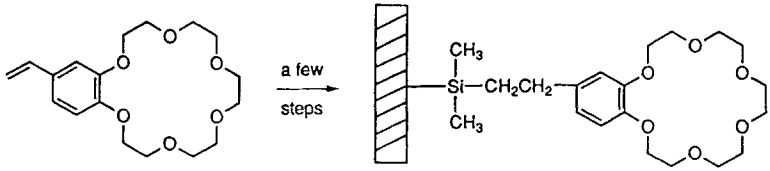
A 0.12 g sample of dibenzo-18-crown-6 in 16 mL of carbon disulfide was stirred at room temp in a stoppered flask. To this suspension, 1.01 g of chloromethylphenylsilylated silica was added, followed by 0.062 g of anhydrous

aluminum chloride. After 1 h the product was isolated. The immobilized dibenzo-18-crown-6 material contained 7.11% of carbon after drying.

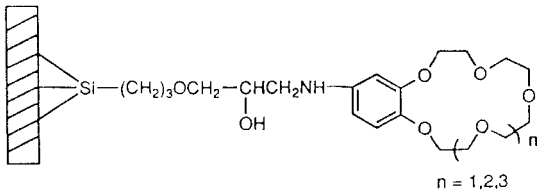
Some procedures lead to the immobilization of crown ethers by ether linkages (Eq. 71)[367] or by stable Si-C bonds (Eq. 72 and Eq. 73).[256,257]





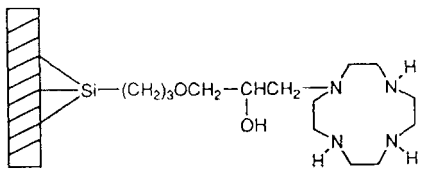


Bradshaw and coworkers reported the immobilization of 18-crown-6 via the allyl group using hydrosilylation.[368] The synthesis of diazacrown ethers bonded to silica gel was patented.[369] A very convenient route to bonded crown ethers was described by Iwachido and coworkers[370] and independedly by Veuthey and coworkers.[316] Their reaction involved glycidoxypropyl bonded Wakogel, LiChrosorb or Polygosil and amine-substituted crown ethers. The capacities of the products were 0.1-0.3 mmole/g.



24

Azacrowns may be bonded to the surface in the same manner, yielding a material with a capacity of 0.1 meq/g.[371]



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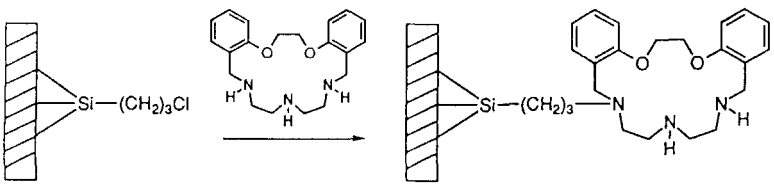
Chloropropylsilylated silica gel also serves as a starting material to immobilize azacrowns.[171]



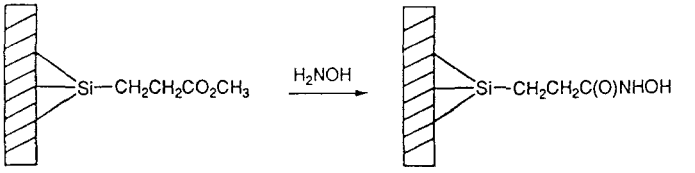
74

A solution of 7.6 g of triazacrown ether shown above, in 20 mL of xylene was added

to 6 g of chloropropylsilylated silica gel and the mixture was placed in an ultrasonic bath for 30 min. The suspension was then refluxed at 150° for 15 h. The product was isolated and repeatedly washed with hot methanol, then dried under high vacuum. This modified silica was stable up to 230° and had a capacity of 0.41 meq/g.

3.6.10. Miscellaneous Immobilized Functional Groups

Surprisingly, only a few reports describe the synthesis of bonded carboxylic acids.[130,372,373] They may be synthesized starting from unsaturated carboxylic acid esters via hydrosilylation, although side products affect the yields. The esters may be hydrolyzed to the respective carboxylic acids, converted into hydroxamic acids (Eq. 75)[372] or reduced to the alcohol (Eq. 76).[130]



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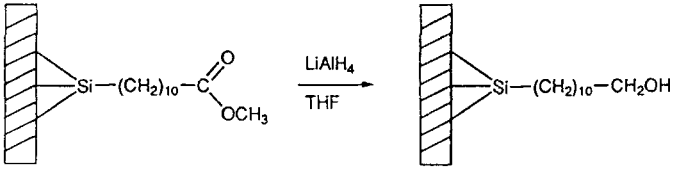
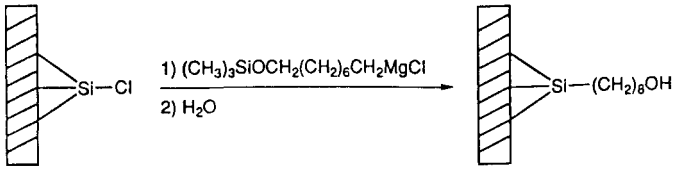


76

Other methods to synthesize immobilized alcohols also have been described.[374] To a stirred, ice-cold solution of 24.2 g (0.15 mole) of 1-chloro-8-hydroxyoctane in 150 mL of dry benzene, 16g (0.15 mole) of chlorotrimethylsilane (TMSCl) followed by 54 mL (0.39 mole) of triethylamine was added dropwise. The mixture was stirred for 30 min at room temperature, filtered and distilled. The silylated chloroalcohol (10.4 g) was converted into a Grignard reagent with 1.3 g (0.05 mole) of magnesium in 20 mL of dry ether and the solution was filtered under

nitrogen. This solution was added under nitrogen to a stirred suspension of Corasil II which had previously been chlorinated with $SiCl_4$. The mixture was refluxed for 3 h and then stirred for two days at room temp. The product was collected and washed with ether. The solid was stirred with dilute sulfuric acid for 2 h, washed with a large volume of water, acetone and ether, and extracted overnight in a soxhlet with chloroform before oven drying at 100°.



77

Alkenols as starting materials were subjected to TMS protection of the OH groups, then reacted with SiH-containing material, immobilized and finally deprotected to give the desired bonded alcohols.[266,378]

4. CHARACTERISTICS OF SURFACE BONDED LIGANDS

4.1. Capacity

To discuss the capacity of chemically modified supports it is necessary to consider two aspects: 1 - maximum available capacity and 2 - methods for its determination.

4.1.1. Maximum Available Capacity

The maximum available capacity of a chemically modified support arises from the number and spatial arrangement of silanol groups on the surface. Since the number of silanol groups is nearly independent of the kind of silica (see silica gel surface in Section 2), the maximum theoretical capacity is a function of the specific

surface area of the support. This statement is limited in fact by at least two factors: not all silanol groups on the surface are available for reaction and, since some of them are located in small pores, their reaction may be hindered for steric reasons. Also, groups bonded inside the pores may, for the same reason, be unavailable to the solutes. Capacity is usually expressed as a function of the number of moles bonded per gram of the modified support. Modified silica gels have capacity from 0.3 - 0.8 meq/g in contrast to less than 0.1 meq/g for porous glass.[375] Other ways of expressing the capacity are: the number of groups bonded to 10 nm^2 of surface or the number of available anchored groups on 10 nm^2 of surface.

Some authors express capacity as a number of miliequivalents per gram. This is not always completely descriptive. If the number of basic atoms is considered, the capacity expressed as a number of moles per kilogram is the same as the number of equivalents for the first example, but one-half in the second example given in Structure 17. When expressing the capacity as a number of bonded groups per 10 nm^2, it is necessary to know the specific surface area. Conversion from one capacity unit to another is not always easy and this may not facilitate understanding of a particular case. In many papers dealing with phases for gas chromatography, the capacities are far from maximum.[200,228] In general, good capacity and high column efficiencies are expected for small porous particles.[4] Increased capacity was observed with decreasing pore size, up to an optimum at about 6 nm (this is affected by the types of molecules to be analyzed).[376] Using modified synthetic methods, capacities up to 3 mmoles/g have been reached.[297]

4.1.2. Experimental Determination of Capacity

The most frequently used method for determining capacity is elemental analysis which yields percentage contents of carbon, hydrogen, nitrogen, sulfur, phosphorous and so on. Calculations based on elemental analysis are inaccurate, because of the low carbon content of the modified support, compared to the large

amount of inorganic material present. Moreover, calculations based on elemental analysis are inconsistent with the results of other methods. For example,[193] the carbon content indicated a capacity of 0.84 meq/g of glycidoxypropyl residues in a certain glycidoxypropyl-substituted phase whereas the periodate oxidation value was only 0.51 meq/g. The search for adequate experimental methods continues.

The number of bonded and free SiOH groups may be determined using methods described in Section 2. The population of free silanol groups in chemically modified supports may be determined by exchanging protons for deuterium under chromatographic conditions[52] or by blocking free silanols with amines and comparing chromatographic behavior of the iron tris β-diketonates, as mentioned in Section 3.2.1.[377]

Another method for the determination of the degree of surface coverage is by photoacoustic spectroscopy. Vibrational overtones in the near infra-red were employed for the examination of modified materials containing bonded aliphatic, aromatic, and aminoalkyl functions. A linear relationship between photoacoustic signal amplitude and carbon or nitrogen content on the chemically-modified surface was obtained.[378] A fluorescence method uses gel beads suspended in an agarose solution. The amount of gel matrix in the suspension was estimated by the intensity of the optical dispersion at 500 nm.[379] Thermogravimetric methods have also been used to determine surface coverage.[331,380-382] Titration is often used for simple ion-exchangers.[383,384]

Serious problems arise for chelating (complexing) ion-exchange supports. The determined capacity may vary with the ion chosen due to the different stoichiometries of the individual complexes. Capacity may also depend on pH, if complex formation is pH dependent. Specific methods using selective chemical reactions have been used. The number of vicinal C-OH groups was determined by periodate oxidation,[193,329] the capacity of immobilized peptide supports was established using the Kjeldahl nitrogen determination method, and Jarrett[334] determined the capacity of a peptide immobilized on silica using a standard amino-

acid analyzer.[218] To characterize a particular support, the exchange capacity is often the easiest to determine.[28] Capacity may be determined with many different reagents, such as hemoglobin.[344]

4.2. CHEMICAL STABILITY

4.2.1. Influence of Radiation

It is generally believed that inorganic materials are more stable in the presence of ionizing radiation than are organic resins, although no direct studies have been carried out. However, it is expected that there are limits beyond which these materials also undergo radiolytic degradation. As an example, inorganic ion-exchangers in combination with organic resins show serious process related problems above 10^6 Gy or more of absorbed irradiation, leading to solubilization, agglomeration, gas generation, channeling, etc.[385]

4.2.2. Thermal Stability

Thermogravimetric analysis was used to study stability of bonded groups by Abel and coworkers.[386] The immobilized phases are significantly more stable than the free, unattached analogs. The first reported value for thermal stability[292] was 300°.[2] Due to the high thermostability of silica-bonded sulfonic acids, they may be used as catalysts (organic resins are unstable above 130°).[246] Sulfonated phenylsilylated silicas[267] as well as chloropropylsilylated silicas[387] decompose at 300°. Compounds which are more temperature sensitive have correspondingly lower thermal stabilities, although these values are still higher than that for the unbounded compound. For example, diaza-17-crown-5 immobilized on silica gel is stable up to 230°[170] and aminopropylsilylated silica heated more than one hour at 150° becomes yellow, indicating oxidation.[12] Oxidation also occurs in solutions containing strong oxidizers.[381]

4.2.3. Acid-base Stability

The stability of immobilized complexing or chelating agents is a multi-faceted problem. First, the silica itself is subject to degradation by both acids and bases. The stability of chemically modified supports is reported over a pH range from 1.5 to 10.5 for time periods from 1 minute to several hours.[12] Many phases are stable to a wide range of pH values and are generally stable in aqueous solutions between pH 1 and 9.[6,27] Sulfophenylated silica gel showed no loss of capacity[294] after 10-fold regeneration with acid. Separation of metal ions on immobilized 8-hydroxyquinoline using 1M HCl, 1M $HClO_4$ or 1M HNO_3 as eluents, caused no measurable loss in capacity.[225] Gennaro and coworkers[321] used concentrations up to 5M HCl, $HClO_4$, HNO_3 and acetic acid with surface bound materials, but concentrated sulfuric or fuming sulfuric acid caused significant loss of the bonded materials (see Section 3.5).

With primary, secondary and tertiary alkylamines and working with acetonitrile-water solutions at pH values < ll, columns can be used for several weeks without appreciable degradation.[388] Many materials are also resistant to 5% ammonia for extended periods. Dudler and coworkers also recommended regeneration procedures, which after 50 cycles showed no reduction of capacity.[170]

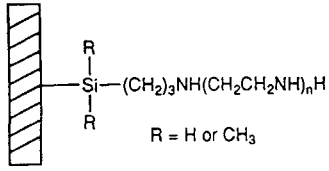
Stability and inertness of bonded silica gel packings were examined from the retention behavior of acidic and basic compounds.[389]

Under alkaline conditions, chemically modified supports are much less stable. When treated with sodium hydroxide or quaternary ammonium bases, the column packings are attacked rapidly, and they become useless within 1-3 days. The alkali metal or quaternary ammonium hydroxides[388,390] rapidly destroy the bond between the immobilized material and the surface. This is one of the reasons that immobilized phases on a variety of mineral supports have been investigated. Celite 545,[386] chrysotile asbestos,[73] or titania covered silica gel, were used to prepare inorganic matrices for the solid-phase synthesis of peptides.[391] Similarly, organosilane coupling agents react with a number of inorganic materials, including alumina,

aluminosilicates, clays, glass, nickel oxide, quartz, silica, talc, and titania.[392] Alumina, magnesia, titania, and zirconia-coated silica, after silanization, are substantially more stable under alkaline conditions than purely silica-based materials. The shape of these supports, specific area, porosity and mechanical stability are similar to the supporting silica.[76]

Unfortunately, the acid-base stability of these chemically modified supports is lower than that of available matrices coated with polymer layers[18] which have a longer life at high pH, but not as long as have the organic polymer gels.[19]

Bonded phases also appear to be more stable with increasing chain length,[393] but the chemical properties of the bonded groups still resembles that of unbound analogues. For example, immobilized dithiocarbamates are intrinsically unstable, especially in acidic solution.[12] An important exception to this statement is the behavior of immobilized 3-aminopropyl groups, and N-aminoethylderivatives of the general structure shown in Stucture 26.



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It was observed that repeated use of these immobilized amines resulted in a steady decrease in capacity. This decrease may be as high as tenfold after 2-3 cycles.[351] A fivefold decrease of capacity was observed by Jezorek and coworkers[394] while other authors observed this phenomenon even on storage of the phases.[124,191,211,352,395,396] Curing of aminopropylsilylated silica[191,211] increased the stability. The instability is common to many derivatives, such as the N-alkyl, N,N-dialkyl, and N-2-hydroxyethyl derivatives of bonded amines and is not affected by the monomeric or polymeric nature of the bonded materials. Two possible reasons have been considered; first, release of the material from the support, and second, oxidation of the amine groups.[352] It is of interest, that N-acyl derivatives of immobilized

aminoalkyl residues are stable.[394] The reported instability seems to affect only amine analogues.

Kinetic analysis of the hydrolytic desorption of chemisorbed, ^{14}C labelled, polymeric aminopropylsilanes from flat silica or borosilicate glass indicated that the polymer probably consisted of short chains, each chemisorbed at one end to the surface with little or no crosslinking.[397] In 1979, Voroshilova[252] found that degradation is slower from Alusil than from Silochrom SCH-2, and also that layers deposited from toluene (monomeric) are lost faster than their polymeric counterparts. Wonnacott and Patton[211] observed the continuous loss of amine from the columns by reaction with ninhydrin. To prevent such losses and to increase the stability of the phases, they crosslinked them with bis epoxides (see Structure 16).

Supports modified with bifunctional ("bidentate") silanes which contain residues of the -Si-$(CH_2)_n$-Si- type are significantly more stable toward hydrolysis then previously described materials.[120]

4.3. PHYSICOCHEMICAL CHARACTERIZATION OF CHEMICALLY MODIFIED SUPPORTS

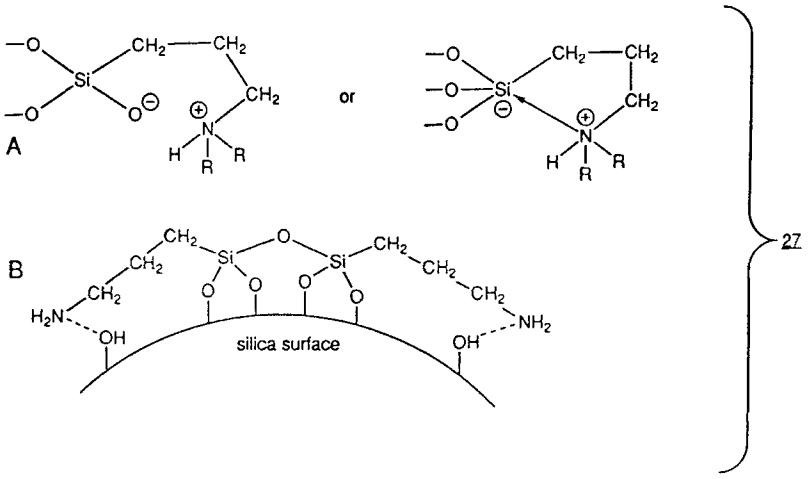
4.3.1. Infrared Spectroscopy

The most commonly used method for studying chemically modified supports is infrared (IR) spectroscopy. IR spectroscopy was applied both to study the silanization progress as well as to characterize the bonded material. In the case of modified solid supports whose spectra are well known,[398] trouble arises from dispersion and low concentration of the organic residues of interest on the surface. Changes in IR spectra have, therefore, become more important. Koelling and Kolb[204] studying the reaction between alkoxysilanes and silica, observed liberation of alcohol in the IR spectra.[205] Consumption of the substrate was also observed by IR spectroscopy during the reaction of vinylmethyldichlorosilane with silica, which demonstrated the rapid binding of 70-80% of the starting material during the first

minute.[215] IR spectroscopy has also been used to obtain direct information on reactions as they proceed.[219,399,400] FT-IR spectra have been used to study the reaction progress,[326] and to characterize the final product.[230] Attenuated total reflection FT-IR spectroscopy was adapted to measure the kinetic rates of reactions with the silica surface.[401]

Use of KBr pellets was unsuccessful in producing IR spectra,[267] however, some successful techniques have been described by Berendsen and De Galan[125] and Fulcher and co-workers.[395]

Structural information was obtained using FT-IR and ^{13}C NMR spectra which showed[402] that hydrolyzed aminopropylsilyl residue exists as represented in Structure 27B below.



The evidence indicates that structures given in Structure 27A are incorrect due to the lack of an NH_3^+ absorption in the IR spectrum. The aminoalkylsilane is bonded[402] onto the high-surface-area silica as a monolayer (Structure 27B) while it formed a multilayer on the E-glass fiber surface.

A strong hydrogen bond of the keto form of acetoacetamidoalkylsilyl residue was also shown by FT-IR and ^{13}C NMR by Leyden and coworkers.[229]

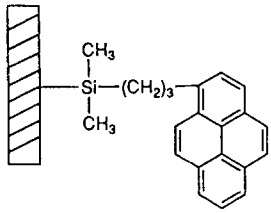
FT-IR determinations enabled Sander and co-workers[403] to specify the conformation of alkyl chains chemically bonded to a solid support. The degree of conformational disorder was shown to be comparable to that observed in the corresponding n-alkanes at room temperature and above.

4.3.2. Photoacoustic Spectroscopy

To study immobilized ligands, photoacoustic spectroscopy was introduced by Lochmüller and co-workers.[354] They characterized immobilized ligands and compared them with the bulk solution.[378] Vibrational overtones in the near-infrared were employed for examination of the modified materials containing bonded aliphatic, aromatic, and aminoalkyl functions. A linear relationship between the photoacoustic signal amplitude and carbon or nitrogen content on the chemically-modified surface was obtained. Field and coworkers[404] studied photoacoustic signal absorption by an immobilized Cu(II) complex. This enabled quantitative determination of metal ions.[405] Urban and Koenig[253] used FT-IR photoacoustic spectroscopy for quantitative surface analysis of silica treated with trifunctional coupling agents such as: methacryloxypropyltriethoxysilane, glycidoxypropyltrimethoxysilane and aminopropyltrimethoxysilane. It was found that the type of orientation of molecules on the surface was a function of the surface coverage. At low coverage, coupling agents tend to be oriented perpendicular with respect to the surface. Increased surface coverage leads to a parallel orientation. Increasing the concentration of coupling agent also causes orientation changes in species which form chemical bonds with the silica surface (hydroxy, carbonyl groups, or water).

Lochmüller and coworkers[139] synthesized a model stationary phase to test predictions based on a lattice-model that would give a unified molecular theory for selectivity. Their results indicated that selectivity follows the order: rodlike solutes > platelike solutes > flexible chains.

Chemically modified chromatographic stationary phases appear to have an active role in solute selectivity. The FT-IR photoacoustic spectrum of



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contains peaks between 1350 and 1725 cm^{-1} which were assigned to the pyrene ring. The peak chosen as diagnostic at 1697 cm^{-1} has a lower intensity for polymeric phases than for brush phases of similar carbon content. This indicates that polymeric phases may interact with the surface to a lesser degree.

Attempts were also made to measure the photoacoustic spectrum of a solid state charge-transfer complex formed between immobilized picramide groups and anthracene molecules.[406]

4.3.3. Nuclear Magnetic Resource Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy, and especially FT-cross-polarization NMR with magic angle spinning (CPMAS-NMR)[407] gave good quality spectra of the surface immobilized ligands. For ^{13}C NMR, the natural abundance ^{13}C is high enough to record spectra. Qualitative analysis of chemisorbed molecular species using the ^{13}C NMR method to determine immobilized silanes on chrysotile asbestos was performed by Chang and co-workers.[408] ^{13}C NMR spectroscopy confirmation of surface structure is a frequently used technique.[190,194,230,409-415] Using the ^{13}C NMR spectra of phenyl groups bonded to silica or alumina, Slotfeldt-Ellingsen and Resing[416] showed that the phenyl groups tend to be oriented parallel to the surface. ^{13}C CP MAS NMR spectroscopy gave information on the variety and quantity of surface species and revealed dynamic properties of the attached alkyl

chains.[417,418] Shinoda and Saito[419] studied the formation of Pt(II) and Rh(III) complexes with aminopropylsilylated and N-(2-aminoethyl)aminopropylsilylated surfaces. The ^{13}C NMR spectra helped to elucidate the structure of some complexes and established the existence of amine to silanol hydrogen bonding in bound aminopropylsilanes.[414] Similarly, ^{29}Si NMR spectra[190,230,411,415] have been used to characterize immobilized products. Boyer and co-workers[130] gave tabulated chemical shifts for both ^{13}C and ^{29}Si NMR spectra of ligands bonded to silica gel. Comparing the ^{29}Si NMR chemical shifts of polymeric siloxanes[420] and the ^{29}Si and ^{13}C NMR shifts of tri-, di- and monochlorosilanes and the respective tri- and dialkoxymethylsilanes with that for the reaction products with silica gel[206,207] made it possible to determine the number of siloxane bonds between the ligand and the silica gel surface. Another study concerning the type of bonding was published by Sudhölter and coworkers[415] and independently by Caravajal.[413] Their results may be summarized as follows: In samples prepared in water, there are no alkoxy groups that remain attached to the silicon atom of the organosilane moiety. The number of siloxane bonds formed during immobilization increases with increasing water content with the largest number obtained for samples prepared in aqueous solution. This study indicates that the amine group in aminopropylsilylated silica gel exists in both a protonated form and a hydrogen bonded form on the silica gel surface in dry toluene. The relative amount of the protonated form increases with the amount of water present at the silica surface.[413]

^{31}P CPMAS-NMR spectra are useful to study immobilized phosphines and their complexes. Nickel(II), palladium(II) and platinum(II) complexes of immobilized phosphines have been studied by high resolution ^{31}P NMR spectroscopy.[421] Their structures are important because the activity of heterogenized catalysts may be related to the structure and activity of homogenous catalysts.[422] Cis-trans isomerism of palladium complexes was elucidated by this technique.[423] There are other sources with additional detailed information on this technique.[208,424,425]

4.3.4. Other Spectroscopic and Miscellaneous Methods

Electron spin resonance (ESR) is frequently used to study paramagnetic complexes. This technique has not been fully exploited in the study of bonded materials. Golubev and coworkers[426] studied complex formation between immobilized aminopropyl-, aminoethylaminopropyl- and higher analogous groups with Cu(II) by the ESR technique. The first support formed a 1:2 metal ligand complex, whereas the ligand tetraethylenepentaamine formed a 1:1 complex.[357,427,428] Tankreda and co-workers[428] showed that the $CuCl_2$ complex with bonded 3-(1-imidazolyl)propyl groups was octahedral with tetragonal distortion. The organization of grafted layers of polyethylene oxide was also studied by EPR.[429]

Spin labelling has been used very little to examine these type of materials. Hall and Waterton[430] introduced a method for determining the spatial distribution of spin-labelled ligands covalently bound to a noncrystalline surface. Lisichkin and coworkers[431,432] used ion-radical salts of tetracyanoquinodimethane as a paramagnetic spin label to study the distribution of immobilized molecules on silica gel. The results were compared with those obtained by Lochmüller and coworkers.[433]

Luminescence spectroscopy has been used in a few cases as well.[434] Ion scattering spectroscopy and secondary ion mass spectroscopy were found to be useful in elucidating the interphase and interface region in composite systems.[435,436]

Lastly, scanning electron microphotography has also been used to study chemically modified surfaces.[409]

4.4. COMPARISON OF LIGAND BEHAVIOR IN SOLUTION AND IN IMMOBILIZED FORM; CHEMICAL PROPERTIES OF LIGANDS BONDED TO AN INORGANIC MATRIX

When comparing properties of functional groups attached via a spacer to a mineral support, it is necessary to consider that bound molecules behave differently

compared to analogous molecules in a bulk solution. First of all, inorganic supports are polar, and thus, affect the dielectric constant and solvation processes on the surface. Due to the hydrophilic nature of silica gel, the immobilized functional groups behave similarly to the same unbounded molecules in aqueous solutions, while the same groups attached to apolar organic resins behave quite differently.

Another factor influencing the behavior of functional groups is the length and nature of the spacer. A long spacer allows better access to the silanol groups inside the pores and will provide higher capacity and better interaction between the functional group and the molecule of interest, especially when the functional group is large (crown ethers, cyclodextrins and enzymes). With longer spacers, the effect of the surface decreased.[245] Ward and Armstrong[437] reported some of the difficulties associated with attaching a large molecule to a support via a short spacer. Steric hindrance usually decreases with increased distance between the functional group and the surface. The spacer length and its chemical nature strongly influence the final product and its utility. A spacer which is too long may decrease the capacity by lowering the reactivity of the ligand to be immobilized during chemical grafting. A length equivalent of about six carbon atoms seems to be optimum. The chemical nature of the spacer is also of prime importance: it influences the swelling (if any) of the grafted phase and thus the resistance to compression.[48] The spacer may also interact chemically with the solute and change the properties of the functional group. This factor is often completely ignored, but some studies have been done.[48] Ward and Armstrong[437] recognized the association of solvent molecules to a long hydrophobic spacer. In some cases, immobilization of small molecules such as 8-hydroxyquinoline do not require long spacers.[232] The effect of immobilization on different functional groups may not be the same.

The facile release of the aminopropylsilyl group from silica gel[124,394] together with the unusually low reactivity of the aminopropyl group bonded to silica gel, makes study of the physicochemical behavior of these and similar ligands very attractive. Moses and coworkers[191,438] found that the reactivity of surfaces modified

with aminopropyltrialkoxysilanes towards acid chlorides was substantially less than anticipated. This was attributed to an intramolecular hydrogen bonded species on the silica gel surface. Previously the lower reactivity of the amine group in aminopropylsililated silicas was ascribed to the formation of the structures shown in Structures 27A[439] and 27B.[402]

The "monomeric" and "polymeric" aminopropylsilylated Silochrom S-120 both revealed by titration[384] that the basicity of the anchored aminopropylsilyl groups at ionic strength close to zero is lower by four orders of magnitude compared to butylamine. Hydrogen bonding of the amine group to the residual silanol groups was again postulated in 1981.[394] According to the authors, the basicity of the propylamine appeared to be about 1000 fold less when bonded to the inorganic surface.

End-capping of the N-(2-aminoethyl)aminopropylsilylated silica gel does not change the unusually low basicity.[440] This is probably due to the fact that only about 5% of the remaining silanol groups react and hydrogen bonding is still possible. Deviations in protonation constants of N,N-bis(carboxymethyl)aminopropylsilica gel are similarly interpreted as a consequence of hydrogen bonded silanol groups.[226]

The properties of other groups have also been changed by the silica gel surface. Watson[441] found that hydrolysis of the oxirane residue in immobilized 3-glycidoxypropyl groups was much slower than the hydrolysis of this group in solution.

It is probable that covalently bonded organic complexing agents will retain their impressive selectivities.[400] When compared with organic ion exchangers where binding strengths are approximately 2-3 kcal/mole, it is easily understood why chelating resins (15-25 kcal/mole) achieve much greater selectivities.[442] Another advantage is that many molecules immobilized on inorganic supports have little, if any, affinity for alkali or alkaline earth ions.[12,124]

Complex formation is pH dependent in the case of many chelating compounds. The same is true when chelating groups are covalently bonded to a solid support.[8] Immobilized 8-hydroxyquinoline, for example,[353] when used for HPLC had

the following retention order:

$$Mn < Zn \sim Ni \sim Co < Cd < Pb$$

This is nearly the same as the order of known stability constants for one-to-one ligand-to-metal ion complexes. The same relationships are also observed in ligand exchange chromatography.[124]

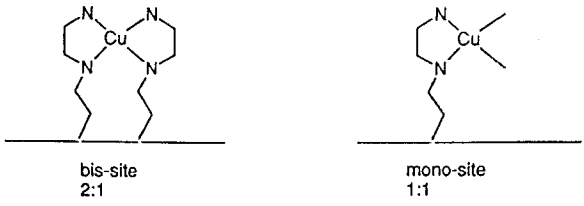
There are a few exceptions to these general observations. Elution of Co(II) ions was impossible from 1-nitroso-2-naphthol immobilized on silica gel[321] whereas the ligand behaves normally towards many other cations such as Cu(II), Pb(II), Cd(II), Zn(II) and Al(III). These effects may be the result of the two azo bonds in the spacer which may significantly participate in complexing metal cations. Another exception is with Hg(II). Although its complex with the free ligand is not very stable, mercury is quantitatively removed from an aqueous solution by functionalized silica.[321] A triazacrown ether immobilized on silica gel[170] showed a loading order Zn(II) > Cd(II) when the opposite is true for the unattached ligand.

4.5. Complex Formation: Stoichiometry and Stability

When reacting with a solute, the quasi-solution behavior depends on the solute size, the spacer and the concentration of the chelating group on the surface. When a chelating group interacts with a cation from the solution, there are steric reasons why only a 1:1 chelate would be formed under most circumstances.[12] Yatsimirskii and co-workers[443] found that aminopropylsilylated silica and its corresponding Schiff's base from salicylaldehyde formed complexes with copper and palladium at a 1:2 stoichiometry, whereas molybdenum formed a 3:1 complex. Stepwise formation of Pd(II) complexes with aminopropyl Aerosil[444] depended on the ratio of the metal cation and ligand concentrations. A 2:1 ligand to Cu(II) stoichiometry was observed for aminopropylsilylated silica[394] and 1:1 stoichiometry for immobilized 8-hydroxyquinoline with Cu(II).

Kvitek and coworkers[445] studied a glass surface modified with $Si(CH_2)_3NHCH_2CH_2NH_2$ by a constant rate thermometric titration with Cu(II) and by manual potentiometric titration with a Gran' plot end-point location. The results indicated that the titrant reacted with the bonded ligand in a two step process, with the thermometric titration responding to the first step, and the potentiometric titration responding to the combined steps.

Complex formation with the same ligand bonded to silica gel with Cu(II) was also studied[446] using photoacoustic and solid-solution distribution measurements. Nearly consecutive formation of bis and mono complexes occured on the surface with increasing Cu(II) concentrations. Evidence for conversion of bis-sites to mono-sites with increasing Cu(II) concentration was not found. Heterogenous distribution measurements fit well with a model which assumes two independent types of binding sites. An approximately 2.5:1 ratio of mono to bis-sites was found. The two types of sites are illustrated in Structure 29.



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Carboxylate ligands immobilized on silica gel demonstrated similar behavior.[447] The sorption isotherms were described in terms of a statistical polydentate model.

Equilibrium constants may be determined by many methods. A review on the stability constant evaluation with immobilized ligands was published in 1985.[448] Kudryavtsev described a statistical method for calculation of the equilibrium concentration of polydentate ligands which was then used to calculate the stability constants of metal ion complexes with ligands bonded to a solid support.[449,450]

4.6. Kinetics of Sorption

Modified silica gels show very fast metal ion-exchange kinetics.[22,23,28] Knox and Pryde[24] showed that ion-exchange modified inorganic supports have efficiencies comparable to those of underivatized silica and alumina. Most papers simply describe the sorption process as rapid for cations like Cu(II), Zn(II), Pb(II) and Hg(II). Slow sorption was observed for Cr(III) and Mn(II) complexation on N-(2-aminoethyl)aminopropylsilylated silica. This is probably due to the slow kinetics of ligand exchange exhibited by the Cr(III), rather than any effect of the surface bound ligand.[451] It is important to note that slow sorption is a relative term and sorption is still much faster than that for organic ion-exchange materials where equilibration times may be hours.[12]

4.7. Qualitative and Quantitative Analysis of Immobilized Phases

The instability of immobilized phases under certain conditions provides an opportunity to remove the phase from the surface for analysis. Thus, Verzele and coworkers[390] stripped an immobilized material from silica gel with a KOH solution. The alkaline solution was trimethylsilylated with the use of trimethylsilylimidazole and the product analyzed by gas chromatography. Later, Genieser and co-workers[452] analyzed several different commercially available modified silica gels. They used fused alkali to cleave the silicon-carbon bond and the ligands released were analyzed by gas chromatography. The determinations revealed structural differences between products of the same ligand type, especially for ion-exchangers. A few products did not conform to the classifications provided by the manufacturers. In 1986, Fazio and coworkers[453] described the acid digestion of an HPLC stationary phase as a method for stripping the immobilized material. Another way for the identification of the kind of immobilized ligand was presented by Blasius and Keller.[454] They found that

pyrolysis GC or pyrolysis MS were useful to characterize polyethers (including cyclic), and enabled the identification of the matrix, bonded group and the crosslinker. Thermal analysis is also used to characterize immobilized groups.[381] A review discussing chemical and physicochemical methods of analysis of chemically modified surfaces has been published.[208] Digestion of modified supports with hydrofluoric acid appears to be a very valuable method to characterize the immobilized material.[455]

5. APPLICATIONS

Although most of the published papers concern different kinds of chromatography and other analytical procedures, there is growing interest in applying chemically modified supports in other areas. Silica-based materials, while not suitable for every application, possess many properties which allow them to perform well in a wide variety of situations. These types of materials are capable of retaining the interactions and selectivities shown by the parent molecule in solution.

The organic network which covers silica gel can subsequently be functionalized to form various kinds of chelating reagents. The choice of chemical reaction involved in chemical modification may be copied from that applicable for organic polymers.[13,14,48] With the wide variety of groups available for attachment to the surface, it is fairly easy to choose one that will have the type of interaction most favorable for the task at hand.[21]

Many of these chemically modified materials are produced commercially. Chromatographic column packings and thin layer chromatography (TLC) supports will be considered first.[456-461] Cis and trans isomers of palladium complexes were separated by TLC on glycidoxypropylated silica gel plates.[462] The manufacturers unfortunately[393,452,463-465] do not provide enough information concerning the structure of the immobilized material. This leads to troubles with interpretation of experimental data.

Few producers are willing to give detailed structural information which prevents a precise interpretation of the observed separations.[452] Some papers describe the studies of retentivity and selectivity of numerous commercially available packings.[393,463] Other reviews on commercially available packings are available.[67,144,145,464,466,467]

5.1. Reverse-phase Packings

In alkylsilylated silicas, the alkylsilane residues behave like organic extractants.[468] The quasi-solution behavior of the bonded alkyl phase is dependent on solute size and bonded chain length.[469] Isolation techniques using bonded-phase silicas (bonded-phase extraction) were evaluated as an alternative to liquid-liquid extraction methods.[470] Hydrocarbons adsorbed on octadecylsilica gel are less degradable by bacteria than in bulk water solution.[471]

Lipophilic column packings have also been used for the preconcentration and determination of inorganic materials.[472-474] Since most inorganic species are strongly hydrophilic, they must first be transformed into derivatives which are compatible with organic phases. 1,10-Phenanthroline,[475] bathophenanthroline[476] or Schiff's base chelates[477] of appropriate cations may serve as an example. Using a pretreatment, selenium was determined in water with the use of LiChrosorb RP-8.[478] HPLC separation of "cis-platin" [cis-dichlorodiamineplatinum (II)] from human physiological fluids was achieved on μBondapak C-18 and on Partisil PXS SAX.[479,480] Various metal ion complexes with 8-hydroxyquinoline were separated on Lichrororb RP-8[481] or on Porasil C18.[482] Selenium and antimony in coastal and ocean water were preconcentrated by a pyrrolidine dithiocarbamate and then passed through a C-18 bonded silica gel Bondapak or Porasil B.[483] Copper dithiocarbamate complexes were determined using an electrochemical method after separation on a Bondapak C-18 column.[484] The separation of other cations using bonded dithiocarbamates has been reported.[485-488] Nisamaneepong and coworkers,[489] separated

arsenite, arsenate and cadmium. Kato briefly reviewed metal complexes as solutes and studied equilibria of Cu(II) on octadecylsilica gel.[490] Inorganic anions were separated using RP chromatography.[491] Alkyl-modified silica Zorbax C-1, Zorbax C-8 and Zorbax C-18 were used to separate inorganic analytes using mobile phase additives. These additives should compliment the LC procedures for ion chromatography.[492] The additive may simply coat the reversed phase used for ion-chromatography.[493] If the additive is a lipophobic crown ether, it enables chromatography of alkali and alkaline earth metal ions.[494]

5.2. Phases with Bonded Complexing Groups

The advantages of silica immobilized complexing agents as substrates for metal ion chromatography are several when compared to the efficient but nonselective ion-exchange resins and to the selective but experimentally tedious liquid-liquid extraction.[225] Also mild elution conditions are sufficient to remove metal ions from such packings (dilute acids, dilute bases or solutions of complexing agents). These materials can be prepared so that their efficiencies are comparable with underivatized silica or alumina.[24]

The most common and impressive application of complexing or chelating agents immobilized on inorganic supports is the rapid sorption of selected cations. The sorption is comparable to the chelating properties of the respective ligands in solution.[495-497]

This technique may be used for concentration or preconcentration of cations especially from water. 8-Hydroxyquinoline[27] immobilized on silica gel has been used for the removal, concentration and separation of trace amounts of copper and other biologically important trace-metal cations from solutions of high ionic strength. It has also been used to separate and remove some transition metal ions from solutions containing salts of the alkali and alkaline earth metals. Controlled pore glass with bound 8-hydroxyquinoline[28] was used to determine the cationic impurities in

laboratory distilled-deionized water. After preconcentration (using 4 liters), iron was not detected (below 0.25 ppb). One liter of the same water was sufficient to determine the level of copper contamination (8 ppb). An automated separation and preconcentration of Cu(II) from natural waters using a column packed with immobilized 8-hydroxyquinoline was described by DaMota, and coworkers.[498] Other types of sample analysis[499] and clean-up have been performed.[500,501] Sturgeon and coworkers[501,502] used chemically modified silica gel for preconcentration of Cd, Pb, Zn, Cu, Fe, Mn, Ni and Co ions from sea water prior to determination by graphite furnace AA. This technique permitted large preconcentration factors to be obtained while providing rapid processing of large volume samples, quantitative recovery of the desired elements, and afforded a matrix free of interfering species suitable for instrumental analysis. ^{90}Sr and ^{90}Y have been preconcentrated and determined using this technique.[503] Most of the commercial supports use 8-hydroxyquinoline to remove and concentrate trace metals for analysis by various techniques.[504,505]

Aminopropyl- and N-(aminoethyl)aminopropylsilylated silicas have frequently been used for analytical purposes. Water, when passed through a short column with this type of packing was freed from iron Fe(II) and Cu(II) ions in preparation of samples for determination of calcium and magnesium as hardness.[506] Preconcentration of heavy metals from coastal seawater has also been studied.[507] On an aminopropylsilylated support, rhodium was separated from palladium, ruthenium, cobalt, copper and iron, preconcentrated and determined by x-ray fluorescence.[508] Immobilized 3-aminopyridine on silica enables sorption of transition metal chlorides from solutions in ethanol and acetone.[509]

Uranium ion in carbonate solutions was preconcentrated on an N-(2-aminoethyl)aminopropylsilylated silica gel and then the concentration was determined.[510,511]

It may become necessary to purify drinking water because of the use of detergents containing ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). These complexones increase the solubility of some metal ions in natural

waters.[488] Problems with purifying waste waters are discussed.[512] The authors showed that immobilized N-(2-aminoethyl)aminopropylsilylated silica has a high enough capacity to be useful in waste water treatment.

Cadmium, copper, lead and zinc were preconcentrated from sea water using mercaptopropylsilylated Kieselgel.[513] Different forms of mercury have been concentrated and determined after sorption on a dimercaptothiadiazole group attached to Silochrome S-80.[514]

An analytical cartridge sampling technique for priority pollutants in waste water has been developed using bonded phase silica adsorbents. This method was compared with that which requires liquid-liquid extraction of the waste water.[515] A microprocessor controlled preconcentration system that permits the automated, off-line preconcentration of several samples at the same time was also described. After stripping the preconcentrated elements, analysis was done by routine techniques.[516]

X-ray fluorescence spectroscopy may also be combined with these preconcentration techniques using the support containing the preconcentrated element in a pelletized form, from which direct multielement[12,517] determinations may be performed.[518-521] ESCA[224] represents an alternative method for trace element analysis without the necessity of stripping them from the column.

Direct methods of determining chemisorbed elements on modified supports are more and more frequently used in trace analysis, and combinations of new techniques have been employed. Leyden[521] introduced quantitative measurements of complexed cations on N-(2-aminoethyl)aminopropylsilicas using photothermal beam deflection detection of the photoacoustic signal.[502,503]

Inductively coupled plasma spectroscopic analysis of solid silica gel samples with preconcentrated metal ions has been described.[522,523]

By introducing fluorescing groups such as diaminomethylnaphthylsulfonyl (dansyl)[524,525] or 8-aminoquinolinyl[526] onto silica gel, it is possible to detect radioactive or nonfluorescing cations on columns or TLC plates.[458] Immobilized luminol chemiluminescence reagent was applied to determine hydrogen peroxide in flowing streams.[527]

The stability of immobilized complexing agents on silica, combined with the potential for higher capacity and efficiency, offers great promise for techniques such as metal ion chelation chromatography[225] and immobilized metal affinity chromatography (IMAC).[528,529] Ligand exchange chromatography has been studied.[217,225,530-533] Applications of immobilized phases for affinity chromatography have been reported.[534-536]

Analytical applications have been reviewed.[14,537] Other examples are in the Tables. These applications have been reviewed.[66,137,142,143,145-147,184,538-547] Reviews on inorganic analytical chromatography have been published.[548-555] There are also some excellent sources dealing with ligand exchange, affinity and ion chromatography.[68,148,530,534,556,557]

5.3. Catalysis

Another obvious application of immobilized complexes is their use as catalysts.[558-561] Immobilized rhodium complexes catalyze the hydrogenation of olefines and dienes in the presence of sulfur compounds.[562] Whitehurst discussed many advantages, disadvantages and benefits, in a review[563] on heterogenized transition metal complexes as catalysts. Studies of heterogenized catalysts also have resulted in a significant number of published papers.[564-571] Rhodium carbonyl complexes on silica gel show good catalytic activity.[572-574] Immobilized complexes have also been used for hydrosilylation,[188,575-578] and "onium" compounds for phase transfer catalysis in liquid-liquid and solid-liquid systems[579,580] and in tri-phase systems.[581]

5.4. Crown Ethers

Crown ethers immobilized on solid supports possess attractive cation-binding ability and selectivity, which differ significantly from those of the other chelating

agents. A wide variety of crown ethers have been prepared synthetically which allows many choices with respect to selectivity.[582] One important advantage is that crown compounds with oxygen donor atoms have affinities for groups IA and IIA cations, whereas most other chelating groups complex transition metal cations.[583,584] The retention times may be changed by varying the composition of the eluent.[360] Chromatographic separations of anions, cations or salts as well as organic compounds are possible on one stationary phase due to the unique selectivity of these materials. Another benefit is that the regeneration of the phase is nearly instantaneous.[257] Three reviews have been published dealing with analytical applications using crown compounds and cryptands.[551,552,554] These materials have been attached to many solid supports,[585] and recently, Izatt and Bradshaw and coworkers have reported a method of synthesis which does not change the Log K value of the macrocyclic complex after it is immobilized.[497] Ion chromatography on supports with immobilized crown ethers has also been studied.[165,360,364]

5.5. Other Applications

Chemical immobilization was applied to modify properties of electrodes.[586-588] The photoelectrochemical generation of hydrogen using chemically modified surfaces has also been studied.[589]

5.6. Large Scale Applications

Chemically modified materials possess very valuable properties from a technical point of view and, in general, these properties resemble those of the inorganic supports. These properties are listed in the following table.[590]

	capacity	flow characteristics	stability
Silica	+	+++	++
Titania	+	+++	+++
Zirconia	+	+++	+++
Alumina	+	+++	+++

+ good, ++ very good, +++ excellent[590]

These inorganic supports with their rigid macroporous structure are nearly ideal for packed-bed reactors.[590] Their back pressure is probably much lower than that of traditional packings.[591] When they are modified with materials containing chelating groups, the binding energy for inorganic species may reach 15-25 kcal/mol.[442] These materials usually retain the amazing selectivities which the parent molecules exhibit in bulk solutions.[495,497] However, their exchange properties are affected by the polar inorganic matrix and its hydrophobic covering, so these types of supports have properties different from those of known polystyrene resins.[4,592]

Methods to remove iron from juices to prevent microbial growth have been developed.[593] A method of preconcentration of silver from water was patented.[594,595] A method for copper and lead ion removal from jet fuels and removal of heavy metals, transition metals and actinides from organic solutions was described[596], as well as removal of uranium from hydrometallurgical processing streams.

A continuous flow system for the extraction of uranium from carbonate solutions containing molybdate was reported in 1981.[231] Recoveries approach 100% of the uranium and molybdenum.

Depending on designation, the sorbent may be specially prepared. Special sorbents for waste water treatment from electroplating were described.[597]

Aminopropyl supports have been used also to remove or to preconcentrate Pd(II), Ir(IV), and Pt(IV) or to separate Fe(III) from other transition elements.[598] Immobilized nitrilodiacetic acid was applied to determine iron in alloys.[599] The removal and concentration of many metal ions have been patented.[600] SuperLig® with crown ethers, cryptands, spherands and calixarenes bonded by different spacers to silica gel are used to isolate valuable inorganic materials.[601]

For some purposes, the back pressure caused by supports discussed here[591] may be too high, and better materials should be found which permit high flow rates. This is possible by the application of fibers. A silylated fiberglass matrix with chelating groups on their surface (dithiocarbamate) was used by Hercules and coworkers[602] for preconcentration of lead, calcium, thallium and mercury. Mineral and organic nonporous fibers with grafted side chains fitted with functional groups are recommended for sorption, since there are no kinetic problems.[603]

Inorganic matricies, unlike resins, cellulose, agarose, and Sepharose do not support microbial growth,[27] and therefore sterile conditions may be more easily maintained.[28]

6. PERSPECTIVES AND CONCLUDING REMARKS

There are many needs for the removal of trace elements from different sources such as in modern powerplants that require high purity water with sodium, chloride and sulfate ion concentrations at the part per trillion level.[591] Ocean water may serve as a prospective source of many deficient materials. Waste water streams should be purified from heavy metals before discharge and mine waters frequently contain radioactive materials which should be removed.

Chemically modified materials with unique selectivities toward selected inorganic species should find application in the solid phase extraction of these species from a mixture containing much higher concentrations of basic electrolytes. To clean up large bodies of water, a selective packing causing low back-pressure

would be required. There are examples of applications of unmodified fibrous materials for such a purpose.

The radioactive metal ions from aqueous nuclear waste streams may be removed using vitrokele compositions - novel, highly effective, metal ion selective and regenerable media.[604] These new materials and their properties have been reviewed.[605,606] Durasil™ has been used on a large scale for removal of radioactive trace elements from aqueous waste streams in light water reactor nuclear power plants.[607-610]

Recovery of trace uranium and radium from uranium mines waste waters using fibrous cation exchangers modified by titanic acid has been described.[611] The adsorbent composed of fibrous material was granular.

Manufacturing of a new fibrous material was patented.[612] It presents a high purity porous TiO_2 fibrous body for filler or catalysts. The fibrous materials obtained by sol-gel preparation of SiO_2 glass fibers and TiO_2 films and their properties have been recently reviewed.[613] Another porous (pores of 10 - 500 Å) alumina - silica fiber has been described recently.[614] Introduction of these fibrous materials seems to be most important for the new industrial applications of chemically bonded stationary phases.[615]

Given the progress that has been made, it may soon be possible and economical to recover valuable materials from very diluted sources like ocean water. It may also become possible (due to high selectivities) to perform environmental clean-up on large bodies of water, particularly where heavy metals are the major problem. Many problems may yet be solved by the ingenious application of this type of technology. J.E. Meinhard's prediction[616] concerning chromatographic separation of ions has proven quite accurate.

7. TABLES

There are many substances attached to inorganic supports. It is simple to organize them when they are only monofunctional. Since the immobilized

compounds frequently possess more than one functional group, it is very difficult to organize the Tables in one uniform mode.

The following rules were used to organize the immobilized ligands in the Tables.

1. Simpler molecules occur first, e.g. one alkyl chain preceeds one branched alkyl chain, etc.
2. One possible point of attachment to the surface preceeds two, etc.
3. Fluoro, chloro, bromo, iodo derivatives preceed alcohols, ethers, aldehydes, ketones and carboxylic acids, and their derivatives.
4. Thiols preceed thioethers, sulfonic acids.
5. Other functions are listed in the following order: amines, substituted amines, ureas (thioureas) and phosphines.
6. The following ligands are collected in a separate part of the tables:
   ·azo compounds possessing -N=N- bonds
   ·glycidoxypropyl derivatives
   ·derivatives of aminoacids and peptides
7. The ligands are arranged according to increasing distance of the functional group from the surface.
8. The type of inorganic support was not considered in ordering the ligands.
9. Information concerning capacity is given when available.
10. In the Tables, many peptides bonded to a mineral support were omitted, except those involved in interactions with inorganic species.
11. The authors did not attempt to distinguish between "monomeric" and "polymeric" immobilized materials. The Tables distinguish between them only when reported by the original authors.
12. The references in the Tables for the same structures are ordered in a sequence corresponding to the order of appearance in the literature.
13. The formulas in the tables are given as published regardless of their correctness or consistency.

14. In all tables the symbols -Si, =Si and ≡Si denote not the actual number of bonds from Si to solid support, but the number of functional groups in the starting silane capable of forming bonds. Comm. means commercial. Alumina means γ-alumina, Bondapack means μ-Bondapack.

Table 1. Solid Supports Containing Alkyl, Alkenyl, Alkynyl, Aromatic, Halogen, Alcohol, Ester, Ether, Cyano, Isocyanate, Carbonyl, Carboxylate, Thiol, Sulfide, Sulfonic Acid and Phosphorous Side Groups

Support	Phase	Capacity	Application	References
ALKYL PHASES				
Silica gel	≡SiH, =SiH_2, -SiH_3	---	lipophilic phase of low SiOH content, substrate for hydrosilylation	173,255
Silica gel	-SiH_2.C_2H_5	---	coverage of silica gel surface is higher than with triple bonding ≡Si-R	128
Silica gel	-SiH_2.C_8H_{17}	---	coverage of silica gel surface is higher than with triple bonding ≡Si-R	128,129
Silica gel	-SiH_2.$C_{18}H_{37}$	---	coverage of silica gel surface is higher than with triple bonding ≡Si-R	128
LiChrosorb	=$Si(CH_3)_2$	---	Separation of As(III), As(V), and Cd(II)	489
Glass beads	=$Si(CH_3)_2$	---	determination of phosphates	474
Chrysotile asbestos	-$Si(CH_3)_3$	---	^{13}C NMR studies	408
Silica gel	-$Si(CH_3)_2CH_2CH_2C(CH_3)_3$	---	study of unreacted silanol groups on retention	52
Silica gel comm.	-$Si(C_4H_9)_3$	---	HPLC of acetylacetonates and other beta-diketonates of Cu(II), Co (II), Cr(III), Al(III), Be(II), Ru(II), Rh(III), Co(III), Fe(III), Ni(II), and Ru(III)	617
Silica gel	≡SiC_6H_{13}		capillary column	618

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel comm.	$\equiv SiC_6H_{13}$	---	HPLC of acetylacetonates and other beta-diketonates of Cu(II), Co (II), Cr(III), Al(III), Be(II), Ru(II), Rh(III), Co(III), Fe(III), Ni(II), and Ru(III)	617
Silica gel comm.	$-Si(C_6H_{13})_3$	---	HPLC of acetylacetonates and other beta-diketonates of Cu(II), Co (II), Cr(III), Al(III), Be(II), Ru(II), Rh(III), Co(III), Fe(III), Ni(II), and Ru(III)	617
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	determination of selenium in water	478
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	determination of Se, Cr, Ni, Co, Pb, Cu and Hg as dithiocarbamates	485
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	separation of metal ion complexes with 8-hydroxyquinoline	481
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	Separation of tetramethylenedithiocarbamates of Se, Te, Fe(III), V, U, Mo, Cr(VI), Sn, Sb, Bi, Zn, and Pb, and of diethyldithiocarbamates of Ag, Ni, Co, Zn, As, Mn, Cd, Pb,Cu, Hg, and Cr(III)	619
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	HPLC of Cr(III) and Cr(VI) ions in waste water as dithiocarbamate complexes	486
LiChrosorb RP-8 comm.	$\equiv SiC_8H_{17}$	---	Simultaneous determination of Cr(III) and Cr(VI) in water by HPLC after chelating with sodium diethyldithiocarbamate	488
Silica gel Merck comm. plates	$\equiv SiC_8H_{17}$	---	TLC separations of tetraphenylporphyrin complexes of Mg(II), Ni(II), and Cu(II), Cd(II), Mn(III), and Fe(III)	620

Support	Phase	Capacity	Application	References
Whatman C-8, LiChrosorb RP-8	$\equiv SiC_8H_{17}$	---	Separation of anions: Br^-, I^-, NO_2^-, NO_3^-, IO_3^-, NCO^- and organic anions	491
Porous silica	$=Si(CH_3)C_8H_{17}$	---	synthesis and DSC studies	127
Develosil	$-Si(CH_3)_2C_8H_{17}$	---	effect of reversed phase structure on retention and selectivity	621
Develosil	$-Si(CH_3)_2CH_2CH_2C_6H_{11}$	---	effect of structure on retention and selectivity	621
Silica gel	$-Si(CH_3)_2C_{14}H_{29}$	---	retention studies of the role of unreacted silanol groups	52
Microbond alphapack C-18 comm.	$\equiv SiC_{18}H_{37}$	---	HPLC separations of Schiff base chelates of Cu(II), Ni(II), and Pd(II)	477
Micro-pack CH comm.	$\equiv SiC_{18}H_{37}$	---	HPLC of β-ketoamine complexes with Co(II), Ni(II), Pd(II), and Cu(II)	622
Corasil II-18 comm.	$\equiv SiC_{18}H_{37}$	---	HPLC separation of cluster complexes $Ir_4(CO)_9[P(Ph)_3]_3$, $HFeCo_3(CO)_{10}[P(Ph)_3]_2$, $Co_2(CO)_6[P(Ph)_3]_2$, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $H_2FeRu_3(CO)_{13}$	623
Silica gel, Partisil, Zipax	$\equiv SiC_{18}H_{37}$	---	HPLC of beta-diketonates of Cu(II), Co(II), Cr(III), Al(III), Be(II), Ru(II), Rh(III), Co(III), Fe(III), Ni(II), and Ru(III)	617
LiChrosorb RP-18 comm.	$\equiv SiC_{18}H_{37}$	---	Chromatographic separation of Se, Te, Fe(III), V, U, Mo, Cr(VI), Sn, Bi, Zn, Pb, Ag, As, Mn, Cd, Ni, Co, Hg, and Cr(III) chelates	619

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
LiChrosorb RP-18 comm.	$\equiv SiC_{18}H_{37}$	---	HPLC of Cr(III) and Cr(VI) ions in waste water as dithiocarbamate complexes	486
RP-18 column	$\equiv SiC_{18}H_{37}$	---	HPLC of Na^+, K^+, NH_4^+, Ca^{2+}, F^-, Cl^-, SO_4^{2-}, NO_2^-, Br^-, $Cr_2O_7^{2-}$, NO_3^-, and I^-	472
C-18 glass beads column	$\equiv SiC_{18}H_{37}$	---	preconcentration of Co(III) as a complex with 2-(2-pyridylazo)-5-(diethylamino)phenol	468
Bondapack C-18 comm.	$\equiv SiC_{18}H_{37}$	---	Separation of 1,10-phenanthroline complexes of Fe(II), Ni(II), and Ru(II)	475
Bondapack C-18 comm.	$\equiv SiC_{18}H_{37}$	---	Cu(II) dithiocarbamate was separated and determined using electrochemical detector	484
Bondapack C-18 comm.	$\equiv SiC_{18}H_{37}$	---	Separation and determination of "cisplatin", *cis*-dichlorodiamine platinum (II), in human fluids	480a,480b
Silica gel	$\equiv SiC_{18}H_{37}$	---	HPLC of Fe, Ru, Co, Mu, Mo, and Ni complexes	624
Porasil	$\equiv SiC_{18}H_{37}$	---	adsorption of Mn and Cu(II) complexes with 8-hydroxyquinoline	482
Silica gel Merck plates comm.	$\equiv SiC_{18}H_{37}$	---	TLC separation of tetraphenylporphyrin complexes of Mg(II), Ni(II), Cu(II), Cd(II), Mn(II) and Fe(III)	620

Support	Phase	Capacity	Application	References
Radial Pak C-18 comm.	$\equiv SiC_{18}H_{37}$	---	HPLC separation of diethyldithiocarbamate complexes of Co(III), Cr(III), Cu(II), Hg(II), Ni(II), Pb(II), Se(IV), and Te(IV)	487
Cosmosil C-18	$\equiv SiC_{18}H_{37}$	---	determination of ppb levels of Pb(II), Ni(II), Co(II), Cu(II), Hg(II), and Bi(III) as pyrrolidinedithiocarbamate chelates	625
Supelco 18 comm.	$\equiv SiC_{18}H_{37}$	---	HPLC separation of Mn(II), Be(II), Co(III), Cr(III), Rh(III), Ru(III), Ir(III), Pd(II), and Pt(II) acetylacetonates and Cr(III) benzoylacetonate	626
Partisil	$\equiv SiC_{18}H_{37}$	---	separation of Br^-, I^-, NO_2^-, NO_3^-, IO_3^-, and NCO^-	491
Silica gel	$\equiv SiC_{18}H_{37}$	---	HPLC of Cu(II) complexes from Estaurine water	627
Silica gel C-18	$\equiv SiC_{18}H_{37}$	---	concentration of Cd(II), Zn(II), Cu(II), Ni(II), Co(II), Mn(II) and Fe(II) from sea water as chelates with 8-hydroxyquinoline using a reversed phase chromatographic technique	502
Glass beads C-18	$\equiv SiC_{18}H_{37}$	---	separation of Fe(II) bathophenanthroline complex	476
Sep-Pak C-18 comm.	$\equiv SiC_{18}H_{37}$	---	removal of Mn(II), Cu(II), and Zn(II) complexes from water	628
Silica gel C-18	$\equiv SiC_{18}H_{37}$	---	separation of As(III), As(V) and Cd(II)	489

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Bondapack, Spherisorb, Partisil, Hypersil	$\equiv SiC_{18}H_{37}$	---	separation of Cl^-, NO_2^- and SO_4^{2-}	473
Bondapak C-18 Porasil B	$\equiv SiC_{18}H_{37}$	---	HPLC separation and determination of Se(IV), Sb(III) and Sb(V) in coastal and open ocean sea water via preconcentration by chelation with pyrrolidine dithiocarbamate and extraction	483
TLC support	$\equiv SiC_{18}H_{37}$	---	Cu complex with chiral additive for TLC resolution of amino acids	629
Silica gel RP-18	$\equiv SiC_{18}H_{37}$	---	ion chromatographic separation of HCO_3^-, Cl^-, NO_2^-, Br^-, HPO_4^{2-}, I^-, SO_4^{2-}, $C_2O_4^{2-}$, and $S_2O_3^{2-}$ on cetyltrimethylammonium bromide coated support	493
Silica gel	$\equiv SiC_{18}H_{37}$	---	adsorption of Cu(II) acetylacetonate, preconcentration of metal ions	490
Partisil	$=Si(C_{18}H_{17})_2$	---	separation of Br^-, I^-, NO_2^-, NO_3^-, IO_3^-, NCO^- and organic anions	491
Zorbax	$-Si(CH_3)_2C_{18}H_{37}$	---	to test predictions of a lattice model based molecular theory for selectivity	138
Silica gel H_3BO_3 modified	$-Si(CH_3)_2C_{18}H_{37}$	---	no phase transformation in the range 0 - 90°	103,630
Silica gel	$\equiv SiO[SiX(CH_3)]_nOSiX(CH_3)_2$ X = H or octadecyl	---	facile synthesis	631
Silica gel	$-Si(iPr)_2R$	---	highly stable bonded phase for HPLC	120

Support	Phase	Capacity	Application	References
Partisil	$-Si(C_{18}H_{37})_3$	---	separation of Br^-, I^-, NO_2^-, NO_3^-, IO_3^-, NCO^- and organic anions	491
ISFET gate, Ta_2O_5, SiO_2	silylated	---	silylated Ion Selective Field Effect Transistor (ISFET) as pH sensors	632
GERMANIUM DERIVATIVE				
Partisil 5	$\equiv GeCH_2CH_2CH_2CH_3$	---	HPLC	203
ALKENYL AND ALKYNYL PHASES				
Glass	$\equiv SiCH{=}CH_2$	---	coverage of capillary columns	618
Chrysotile asbestos	$\equiv SiCH{=}CH_2$	---	^{13}C NMR confirmation of structure	633,408
Silica gel	$\equiv SiCH{=}CH_2$	---	support for chromatography	634
Aerosil	$\equiv SiCH{=}CH_2$	---	further synthesis	214
Partisil	$\equiv SiCH{=}CH_2$	---	copolymerization with acrylonitrile, acrylic acid, butyl methacrylate, 2-hydroxypropylmethacrylate, and diethylaminoethyl acrylate	362
Silica gel	$\equiv SiCH{=}CH_2$	---	copolymerization with methyl methacylate and methyl α-chloroacrylate	303
Aerosil	$=Si(CH_3)CH{=}CH_2$	---	copolymerization with butyl methacrylate	304

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Chrysotile	-$Si(CH_3)_2CH{=}CH_2$	---	^{13}C NMR structure confirmation	633,408
Glass bore	$\equiv SiCH_2CH{=}CH_2$	---	surface modification of capillary column	618
Porasil C	$\equiv SiCH_2CH{=}CH_2$	---	further synthesis	301
Chrysotile asbestos	$\equiv SiCH_2CH{=}CH_2$	---	^{13}C NMR structure confirmation	633,408
Partisil 5	$\equiv SiCH_2CH{=}CH_2$	---	HPLC phases, synthesis and comparison	203
Silica gel	$\equiv SiCH_2CH{=}CH_2$	---	further synthesis	220,261,265
Chrysotile asbestos	$\equiv Si(CH_3)_2CH_2CH{=}CH_2$	---		633
Silica gel	$\equiv Si(CH_2)_3CH{=}CH_2$	---	packing for RP HPLC	203
Chrysotile asbestos	$\equiv Si(CH_2)_{11}CH{=}CH_2$	---		633
Silica gel	$\equiv Si(CH_2)_nCH{=}CH_2$	---	^{29}Si and ^{13}C NMR spectra	130
Develosil	-$Si(CH_3)_2CH_2CH_2$-(4)-cyclohexenyl	---	RP-HPLC	621
Silica gel	≡Si-cyclopentadienyl	---	synthesis of Co(II) and Fe(II) complexes	635

Support	Phase	Capacity	Application	References
Silica gel	-Si(CH_3)$_2$-cyclopentadienyl---		synthesis of Co(II) and Fe(II) complexes	635
Glass	-SiC≡C-CH=CH_2	---	coverage of capillary column	618
PHASES WITH AROMATIC RESIDUES				
Grace-Davison	-Si(CH_3)$_2$$C_5H_5TiCl_2C_5H_5$	.01-.02	hydrogenation catalyst	244
Grace-Davison	-Si(CH_3)$_2$titanoceneCl$_2$Si(CH_3)$_2$-	---	ibid.,	244
Silica gel	-Si(CH_3)$_{3-x}$(CH_2)$_n$titanoceneCl$_2$ x = 1,2; n = 0,1,3	---	catalyst	636
Glass porous membrane	≡Si-C_6H_5	---	further reaction	295
Glass bore	≡Si-C_6H_5	---	surface modification of capillary column	618
Silica gel	≡Si-C_6H_5	---	further reaction	294,637,638
Siliceous materials	≡Si-C_6H_5 monomeric and polymeric	---	further synthesis	639

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel	≡Si-C_6H_5	---	further reaction	259
Mercosorb SI-60 Silica gel	≡Si-C_6H_5	0.6 0.18 meq/g	tridimentional chromatography	264
Silica gel	≡Si-C_6H_5	---	further reaction	210
LiChrosorb	≡Si-C_6H_5	---	comparison of chain length on RP-HPLC	171
Partisil 5	≡Si-C_6H_5	---	further reaction	203
Silica gel	≡Si-C_6H_5	---	synthesis via organometallic compounds	262
Silica	≡Si-C_6H_5	---	synthesis of acetoxymercury derivative for separation of aromatic hydrocarbons	212
Silochrom SI-120	≡Si-C_6H_5	---	intermediate in synthesis of ion-exchangers	640
Wacogel	≡SiC_6H_5	---	further synthesis	260
LiChrosorb SI-100	≡SiC_6H_5	0.907 meq/g	further synthesis	194
Siliceous materials	=Si(CH_3)C_6H_5	---	support for gas chromatography	639
LiChrosorb SI-100	=Si(CH_3)C_6H_5	0.907 meq/g	further synthesis	194

Support	Phase	Capacity	Application	References
Silica gel	$-Si(CH_3)_2C_6H_5$	---	support for gas chromatography	181
Partisil 10	$-Si(CH_3)_2C_6H_5$	---	support for gas chromatography	641
Silica gel	$\equiv SiCH_2C_6H_5$	---	further reactions, evaluation of details of silylation reaction	642
Glass	$\equiv SiCH_2C_6H_5$	---	coverage of capillary columns	618
Porasil	$\equiv SiCH_2C_6H_5$	---	further reactions	267
Aerosil and Porous Silica	$\equiv SiCH_2C_6H_5$	---	further reactions	643
Davison 62 silica	$\equiv SiCH_2C_6H_5$	---	further reactions	258
Silica gel	$\equiv SiCH_2C_6H_5$	---	further reactions	210
Silica gel	$\equiv SiCH_2C_6H_5$	---	synthesis via organometallic compounds	262
Silochrome SI-120	$\equiv SiCH_2C_6H_5$	---	further reactions	640
Mercosorb SI-60 LiChrosorb	$\equiv Si(CH_2)_2C_6H_5$	---	further reactions	6
LiChrosorb	$\equiv Si(CH_2)_2C_6H_5$	---	RP-HPLC phase	171

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silochrom SI-120	$\equiv Si(CH_2)_2C_6H_5$ monomeric and polymeric	---	further synthesis	640
Silica gel	$\equiv Si(CH_2)_2C_6H_5$	---	further reactions	299
LiChrosorb	$\equiv Si(CH_2)_2C_6H_5$	0.972 meq/g	further reactions	194
Silochrome S-80	$\equiv Si(CH_2)_2C_6H_5$	---	further reactions	300
Silasorb, Macroporous glass	$\equiv Si(CH_2)_2C_6H_5$	---	RP HPLC of hydrocarbons, peptides and viruses	644
LiChrosorb SI-100	$=Si(CH_3)(CH_2)_2C_6H_5$	0.906 meq/g	further reaction	194
Develosil	$-Si(CH_3)_2(CH_2)_2C_6H_5$	---	RP-HPLC phase	621
Silica gel	$\equiv Si(CH_2)_2C_6H_4NO_2$	---	separation of dioxins	645
LiChrosorb SI-100	$\equiv Si(CH_2)_3C_6H_5$	---	further reaction	646
LiChrosorb SI-100	$\equiv Si(CH_2)_3C_6H_5$	0.977 meq/g	further reaction	194

Support	Phase	Capacity	Application	References
LiChrosorb SI-100	$\equiv Si(CH_3)(CH_2)_3C_6H_5$	0.896 meq/g	further reaction	194
Silica gel, glass, titania, zirconia, alumina	$-Si(CH_3)_2(CH_2)_3C_6H_5$	---	adsorbents for heavy metal ions	647
Silica gel	$-Si(CH_3)_2(CH_2)_3C_6H_5$	---	further reaction	126
Partisil 10	$-Si(CH_3)_2(CH_2)_3C_6H_5$	---	further reaction	296
LiChrosorb SI-100	$-Si(CH_3)_2(CH_2)_3C_6H_5$	0.83 meq/g	further reaction	194
LiChrosorb	$\equiv Si(CH_2)_4C_6H_5$	---	RP-HPLC support	171
LiChrosorb SI-100	$\equiv Si(CH_2)_nC_6H_5$ n = 4,5,6	0.898 0.879 0.852 meq/g	further reaction	194
LiChrosorb SI-100	$\equiv Si(CH_3)(CH_2)_nC_6H_5$ n = 4,5,6	0.875 0.851 0.832 meq/g	further reaction	194
Silica A	$-Si(CH_3)_2(CH_2)_4C_6H_5$	---	further reaction	307

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Zorbax	$-Si(CH_3)_2(CH_2)_5C_6H_4-C_6H_4(CH_2)_4CH_3$	---	studies of molecular theory of selectivity	138
LiChrosorb	$-Si(CH_3)_2(CH_2)_nC_6H_5$ n = 4,5,6	0.844 0.806 0.804 meq/g	further reaction	194
Porasil	≡Si-1-naphthyl	---	further synthesis	267
$TiCl_4$ treated				
Silica gel	≡Si-1-naphthyl	---	further synthesis	259
Silica gel	≡Si-1-naphthyl	---	synthesis via organometallic compounds	262
Develosil	$-Si(CH_3)_2(CH_2)_2$-2-naphthyl	---	RP-HPLC support	621
Silica gel	$-SiH(C_6H_5)_2$	---	kinetic studies of immobilization	187
Silica gel	$=Si(C_6H_5)_2$	---	further synthesis	637,638,210
Mercosorb Sl-60, Silica gel	$=Si(C_6H_5)_2$	0.96 meq/g 0.6 meq/g	tridimensional chromatography	264

Support	Phase	Capacity	Application	References
Silica gel	$-Si(C_6H_5)_3$	---	further synthesis	637,638,259,210,643
Partisil 5	$-Si(C_6H_5)_3$	---	further synthesis	203
Silica gel	$-Si(C_6H_5)_3$	---	separation of acetylacetonates of Cu(II), Co(II), Cr(III), Al(III), Be(II), Ru(III), Rh(III), and Co(III) and other β-diketonates of Co, Cr, Fe, Cu, Ni, Al, Ru, and Rh	648
Silica gel	$=Si(CH_3)$-3-pyrenyl	---	luminescence spectroscopy studies	434
Develosil	$-Si(CH_3)_2(CH_2)_2$-3-pyrenyl	---	RP-HPLC support	621
Silica gel	$\equiv Si(CH_2)_3$-(9)-10-methyl-anthracene	---	HPLC support for explosives	649
Porasil 10	$-Si(CH_3)_2(CH_2)_3$-3-pyrenyl	---	studies of surface ligand distribution	433
FLUORO DERIVATIVES				
LiChrosorb	$\equiv Si(CH_2)_2(CF_2)_7CF_3$	---	RP-HPLC support	646
Silica support	$-Si(CH_3)_2(CH_2)_2(CF_2)_7CF_3$	---	RP-HPLC support	650
Partisil 10 LC 7	$-Si(CH_3)_2C_6F_5$	0.843 meq/g	RP-HPLC support	641

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
LiChrosorb SI-100	$-Si(CH_3)_2C_6F_5$	0.843 meq/g	synthesis of HPLC phase	190
Nucleosil 100	$=Si(CH_3)(CH_2)_2C_6F_5$ original paper name: "pentafluorophenetyl"	3.45 $\mu m/m^2$	HPLC phase	651
LiChrosorb SI-100	$\equiv Si(CH_2)_3C_6F_5$	---	HPLC phase	646
CHLORO DERIVATIVES				
Xerogel	$\equiv SiCH_2Cl$	---	synthesis	285
Kieselgel	$\equiv SiCH_2CH_2Cl$	---	synthesis of amines	246
Silica gel	$\equiv SiCH_2CHClCH_3$	---	synthesis of amines	261
Zipax Porasil C	$\equiv Si(CH_2)_4Cl$	---	stable up to 300°	387
Mercosorb SI-60	$\equiv Si(CH_2)_4Cl$	---	synthesis of amines	6
Silica gel	$\equiv Si(CH_2)_3Cl$	---	support for chromatography	634
Silica gel	$\equiv Si(CH_2)_3Cl$	---	further synthesis	220, 312, 652

Support	Phase	Capacity	Application	References
LiChrosorb	$\equiv Si(CH_2)_3Cl$	---	further synthesis	217
Silochrom	$\equiv Si(CH_2)_3Cl$	---	further synthesis	653
SnO_2 electrode surface	$\equiv SiCH_2CH_2CHCl_2$	---	study of electrode properties	654
LiChrosorb	$=Si(CH_3)(CH_2)_3Cl$	---	further synthesis	655
Silica gel	$-Si(CH_3)_2(CH_2)_3Cl$	---	packing for RP-HPLC	126
different supports	$\equiv SiC_8H_{16}Cl$	---	HPLC of oligoDNA's	656
Silica gel	$\equiv Si(CH_2)_{11}Cl$	---	further synthesis	657
different supports	$\equiv SiC_{18}H_{36}Cl$	---	HPLC of oligoDNA's	656
different supports	$\equiv SiC_{18}H_{36}Cl$	---	HPLC support	658
column packings	$\equiv SiC_{18}H_{34}Cl_3$	---	HPLC of oligoDNA's	656
column packings	$\equiv SiC_{18}H_{34}Cl_3$ monomeric and polymeric	---	HPLC support	658

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
CHLOROMETHYLATED AROMATIC RESIDUES				
Porasil $TiCl_4$ treated	$\equiv SiCH_2\text{-}C_6H_4(p)CH_2Cl$	---	further synthesis	267
Silica gel	$\equiv SiCH_2C_6H_4(p)CH_2Cl$	---	further synthesis	210
Silica gel TiO_2 covered	$\equiv SiCH_2CH_2C_6H_4(p)CH_2Cl$	---	solid phase for synthesis of peptides	391,299
Corasil	$\equiv SiCH_2CH_2C_6H_4(o)CH_2Cl$	---	HPLC support	659
Porasil C Corasil I	$\equiv Si(CH_2)_3C_6H_4(p)CH_2Cl$ monomeric and polymeric	---	HPLC support, synthesis	269,301,660
Porasil C Corasil I	$=Si(CH_3)(CH_2)_3C_6H_4(p)CH_2Cl$	---	HPLC support, synthesis	269,301,660
Porasil C Corasil I	$=Si(C_4H_9)(CH_2)_3\text{-}\text{-}C_6H_4(p)CH_2Cl$	---	HPLC, synthesis	660
Silica A	$\text{-}Si(CH_3)_2(CH_2)_4\text{-}C_6H_4(p)CH_2Cl$	---	synthesis	307
Porasil C	$=Si(CH_3)(CH_2)_2\text{-}CH(CH_3)C_6H_4(p)CH_2Cl$	---	synthesis	301

Support	Phase	Capacity	Application	References
Porasil C	$-Si(CH_3)_2(CH_2)_2-CH(CH_3)C_6H_4(p)CH_2Cl$	---	synthesis	301
BROMO DERIVATIVES				
Silica gel	$=Si(CH_3)CH_2Br$	---	further synthesis	2
Aerosil	$\equiv SiCH_2CH_2Br$	---	further synthesis	214
Mineral carriers	$\equiv Si(CH_2)_3Br$	---	further synthesis	652
Silica gel	$=Si(R)C_4H_8Br$	---	further synthesis	2
LiChrosorb Si-60	$\equiv Si(CH_2)_nBr$ n = 4-7	---	further synthesis	418
Silica gel	$\equiv SiC_nH_{2n+1}Br$	---	further synthesis	289
Silica or alumina	Halogenation product of $\equiv Si(CH_2)_nCH_2O(CH_2)_mCH_3$ n = 11-23 m = 5-27	---	further synthesis	290
Porasil	≡Si-bromonaphthylene	---	further synthesis	267

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
IODODERIVATIVES				
Porous glass	$\equiv Si(CH_2)_3I$	---	enzyme immobilization	661
ALCOHOLS AND THEIR DERIVATIVES				
Silica gel	$\equiv Si(CH_2)_3OH$	---	synthesis of complexing groups	220
Corasil, Mercosorb Si 60	$\equiv Si(CH_2)_3OH$	1.4 group/100Å^2 1.1 group/100Å^2		266
Silica gel	$\equiv Si(CH_2)_3OCOC(CH_3)=CH_2$	---	support for chromatography	634
Aerosil	$=Si(CH_3)(CH_2)_3OCOCH_3$	---	synthesis	662
Corasil, Mercosorb Si 60	$\equiv Si(CH_2)_8OH$	2.3-2.6 group/100Å^2, two different routes of synthesis 0.8 group/100Å^2		266
Silica gel	$\equiv Si(CH_2)_{10}OCOCH_3$	---	synthesis	657
Corasil, Mercosorb Si 60	$\equiv Si(CH_2)_{11}OH$	2.5 group/100Å^2, synthesis 0.7 group/100Å^2		266

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_{11}OH$	---	packing for chromatography	657,374
Silica gel	$-Si(CH_3)_2(CH_2)_{10}CH_2OH$	---	characterization by ^{29}Si and ^{13}C NMR spectroscopy	130
Porasil C	$\equiv Si(CH_2)_3C_6H_4(p)CH_2OH$	---	synthesis	301,660
Porasil C or Corasil I	$=Si(C_4H_9)(CH_2)_3$-$C_6H_4(p)CH_2OH$	---	synthesis	301,660
Porasil C	$=Si(CH_3)(CH_2)_2CH(CH_3)$-$C_6H_4(p)CH_2OH$	---	synthesis	301
Silica gel	$-Si(CH_3)_2(CH_2)_2CH(CH_3)$-$C_6H_4(p)CH_2OH$	---	synthesis	301
Porasil C	$\equiv SiCH_2CH(OH)CH_2OH$	---	synthesis	301
Porasil C	$=Si(CH_3)CH_2CH(OH)$-CH_2OH	---	synthesis	301
ETHERS				
SiO_2, MgO, Al_2O_3	$-Si(CH_3)_2(CH_2)_3$-$-(OCH_2CH_2)_n$-OH	---	synthesis	663

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
SiO_2, MgO, Al_2O_3	$-Si(CH_3)_2(CH_2)_3-(OCH_2CH_2)_n[OCH(CH_3)CH_2]_m-OCH_2COOCH_3$			663
Silochrom SI-80	$\equiv Si(CH_2)_3OC_6H_5$	---	adsorption of phenols from water	664
LiChrosorb SI-60	$-Si(CH_3)_2(CH_2)_3OC_6H_5$	---	HPLC support	665
Nucleosil	$\equiv Si(CH_2)_3$-O-picryl	---	HPLC support	666
Silica gel	$\equiv Si(CH_2)_3$-O-(4)-$C_6H_4CO_2$-(4)-$C_6H_4OCH_3$		liquid crystalline HPLC phase	780
Silica gel	$\equiv Si(CH_2)_{10}CH_2OC(CH_3)_3$	---	modifier of silica surface	667
LiChrosorb SI-100	$=Si(CH_3)(CH_2)_3$-(4')-benzo-1,3-dioxole	0.79 meq/g	HPLC support	668
Support for gas chrotogr.	$-Si(CH_3)_2(CH_2)_4-O(CH_2)_2OCH_3$	---	GC support	181
Support for gas chrotogr.	$-Si(CH_3)_2(CH_2)_4-[O(CH_2)_2]_4OCH_3$	---		181

Support	Phase	Capacity	Application	References
Silica gel	≡Si(CH$_2$)$_2$-(4)-2,3-epoxycyclohexane	---	support for chromatography	634
Silica gel	≡Si(CH$_2$)$_4$-(4)-2,3-epoxycyclohexane	---	HPLC packing	346a
CYANIDES AND ISOCYANATES				
Glass	≡Si(CH$_2$)$_2$CN	---	coverage of capillary columns	618
LiChrosorb Si-60, Alox T	≡Si(CH$_2$)$_2$CN	---	HPLC and TLC support	669
Porasil C	≡Si(CH$_2$)$_2$CN	---	HPLC support	301
Silica	≡Si(CH$_2$)$_2$CN	---	Rh-complex catalyst	236
Spherisorb Alumina A20Y	≡Si(CH$_2$)$_2$CN	---	HPLC support	24
Silica gel	≡Si(CH$_2$)$_2$CN	0.34 meq/g	Pd-complexes as catalysts	220,261
Partisil 5	≡Si(CH$_2$)$_2$CN	---	comparison of different HPLC phases	203
Glass bore	≡Si(CH$_2$)$_3$CN	---	surface modification of capillary column	618

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel, alumina, glass	≡Si(CH$_2$)$_3$CN	---	Rh, Pd, Pt-heterogenized catalysts for hydrosilylation	188
SnO_2 electrode surface	≡Si(CH$_2$)$_3$CN	---	molibdenum complex Mo(N$_2$)dppe dppe = bisdiphenylphosphinoethane	670
Silica SI-100	≡Si(CH$_2$)$_3$CN	---	exclusion chromatography	671
Bondapack CN comm.	≡Si(CH$_2$)$_3$CN	---	determination of *cis*-dichlorodiamine platinum in urine after conversion into bis(diethyldithiocarbamate)	479
Bondapack CN comm.	≡Si(CH$_2$)$_3$CN	---	separation of 1,10-phenanthroline complexes of Fe(II), Ni(II), and Ru(II)	475
Silica	≡Si(CH$_2$)$_3$CN	---	HPLC of Fe, Ru, Co, Mu, Mo, and Ni complexes	624
TLC Silica gel 60	≡Si(CH$_2$)$_3$CN	---	TLC: various application possibilities	672
Silica gel, glass, titania, zirconia, alumina	Si(CH$_3$)(CH$_2$)$_3$CN	---	adsorbent for heavy metal ions	647

Support	Phase	Capacity	Application	References
Silica gel	$-Si(CH_3)_2(CH_3)_3CN$	1.0 meq/g	RP-HPLC phase	126
Silica gel	$-Si(CH_3)_2CH_2CH_2-C(CH_3)_2CH_2CH_2CN$	---	study the role of unreacted silanol groups on adsorption	52
Silica gel	$\equiv Si(CH_2)_{10}CN$	---	HPLC support	657,667
Silica gel	$\equiv Si(CH_2)_2C_6H_4(p)CN$	0.1 meq/g	Pd complexes for catalytic purposes	220,261
Porasil C	$\equiv Si(CH_2)_3C_6H_4CH_2CN$	---	HPLC packing	301
Silica A	$-Si(CH_3)_2(CH_2)_3C_6H_4-CH_2CN$	0.1 meq/g	further synthesis	4
Porasil C	$=Si(CH_3)(CH_2)_2-CH(CH_3)C_6H_4CH_2CN$	---	HPLC packing	301
Porasil C	$-Si(CH_3)_2(CH_2)_2-CH(CH_3)C_6H_4CH_2CN$	---	HPLC packing	301
Silica gel	$\equiv SiCH(CN)_2$	0.07 meq/g	Pd complexes for heterogenized catalysts	220,261
Silica gel	$\equiv Si(CH_2)_3NCO$	---	used for the resolution of chiral derivatives	673

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
ALDEHYDES, KETONES AND DERIVATIVES				
Silica gel	≡$SiCH_2CH(OH)CH{=}NOH$---		Pd complex as catalyst	220,261
Porasil $TiCl_4$ treated	≡$SiCH_2C_6H_4(p)COCH_3$	---	HPLC support, synthetized via Grignard reagent	267
Silica gel	≡$Si(CH_2)_3CH(COCH_3)_2$	---	Rh-complex	236
Silica gel	≡$Si(CH_2)_3CH(COCH_3)_2$	---	Pd complexes as catalysts	220
Mineral carriers	≡$Si(CH_2)_3CH(COCH_3)_2$	---	comparison of methods of synthesis	652,674,675
Silochrom SI-120	≡$Si(CH_2)_3CH(COCH_3)_2$	0.2 meq/g	Sorption of Zn(II), Cu(II), Co(II), Ni(II), and Mu(II)	226
CARBOXYLIC ACIDS AND DERIVATIVES				
Silochrom	≡$Si(CH_2)_2CO_2H$	---	synthesis	640
Silica gel, controlled pore glass	≡$Si(CH_2)_nCO_2H$ n = 2,3,4	---	separation of organic compounds	373

Support	Phase	Capacity	Application	References
Porous silica gel, spherosil	≡$Si(CH_2)_3CH$-$(CH_3)CO_2H$	2.18-2.26 meq/g	synthesis, comparison with organic ion exchanger	7
Silica gel	-$Si(CH_3)_2(CH_2)_4C_6H_4$-$(p)CH_2CO_2H$	0.095 meq/g	HPLC of organic bases	4
Silochrom SI-80	≡$SiCH_2CH_2CO_2CH_3$		further synthesis	372
Silica gel	≡$Si(CH_2)_{10}CO_2CH_3$		surface modification	657
Silica	≡$Si(CH_2)_nCON(R)$-Alkyl R = H or alkyl	---	HPLC column packing	525
Silica gel	-$Si(CH_3)_2(CH_2)_9CO_2CH_3$	---	^{13}C and ^{29}Si NMR of immobilized ligands	130
Silochrom S-80	≡$Si(CH_2)_2CONHOH$	---	Complexes with Fe(III), Sc(III), Ti, Zr, Hf, and Th	214
Silica gel	≡Si-spacer-CONHOH	---	preconcentration and separation of V(V), Mo(VI), and W(VI)	676
Silica gel	≡Si-spacer-$C(NH_2)$=NH	---	preconcentration and separation of V(V), Mo(VI), and W(VI)	676

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel	≡$SiCH_2CH_2C_6H_4(p)C(NH_2)$=NOH	---	Pd complexes as catalysts	261
SiO_2, MgO, Al_2O_3	-$Si(CH_3)_2(CH_2)_3(OCH_2CH_2)_n$-$[OCH(CH_3)CH_2]_mCH_2CO_2CH_3$	---	metal complexes as catalysts	261

See also, amino acids and glycidoxypropyl derivatives.

XANTHOGENATES

Silica gel	≡$Si(CH_2)_3OCS_2Na$	0.09 meq/g	Pd complexes	220

MERCAPTANS AND DITHIOCARBAMATES

Xerogel	≡$SiCH_2SH$	---	redox and cation exchanger	677
Silica gel	≡$SiCH_2SH$	---	$PdCl_2$ complex as catalyst	570
Silica	≡$Si(CH_2)_3SH$	---	Rh-complex	236,562
SnO_2 electrode	≡$Si(CH_2)_3SH$	---	cluster complexes	234

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3SH$	---	Pd complexes	220
Silica gel	$\equiv Si(CH_2)_3SH$	---	support for chromatography	634
Silica gel	$\equiv Si(CH_2)_3SH$	---	base for preparing composite ion-exchanger with vinyl pyridine	678
Silica gel	$\equiv Si(CH_2)_3SH$	---	Pd(II) complexes as catalysts	339
Silica gel	$\equiv Si(CH_2)_3SH$	---	to synthesize iron cluster catalysts	679
Silica SI-100	$\equiv Si(CH_2)_3SH$	---	exclusion chromatography	671
Adsorbosil, LiChrosorb SI-100, Hypersil WP-300	$\equiv Si(CH_2)_3SH$	1.4-1.5 $\mu m/m^2$ 2.9 $\mu m/m^2$	extraction of Ag(I); 75% recovery with 6 N HNO_3	680
Silica gel	$\equiv Si(CH_2)_3SH$	0.31 meq/g	extraction of Ag(I) and As(III), sulfur content from sea water	250
		0.89 meq/g	silver capacity	
Kieselgel 60	$\equiv Si(CH_2)_3SH$	---	preconcentration of Cd(II), Cu(II), Pb(II), and Zn(II) from sea water. Recoveries > 95%	513

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Kieselgel 60	$=Si[OSi(CH_3)_3](CH_2)_3SH$ $CuCl_2$ complex	---	end-capped with hexamethyldisiloxane	681
Silica gel	$\equiv Si(CH_2)_3SH$	0.022 μm/g	separation and preconcentration of Cu and Cd in water	682
Silica gel	$\equiv Si(CH_2)_3SH$	---	synthesis via thermal decomposition of respective dithiocarbamate	237
Silica gel, glass, titania, zirconia, alumina	$=Si(CH_3)(CH_2)_3SH$	---	adsorbent for heavy metal ions	647
Silica gel	$=Si(CH_3)(CH_2)_3SH$	1.23 meq/g	further synthesis	235
Silica gel	$-Si(CH_3)_2(CH_2)_3SH$	---	synthesis of HPLC support	647
SiO_2,Al_2O_3, MgO, TiO_2,La_2O_3, ZrO_2, Zeolites etc.	$-Si(R)_n(CH_2)_mSH$	---	Rh, Ir, Pd, Ru, Cr, and Ni complexes as catalysts for synthesis of monocarbonic anhydrides	683
Silica gel	$\equiv Si(CH_2)_3$-Tl	---	Pd(II) complexes	339
Silica gel	$\equiv Si(CH_2)_3SCSNHAlkyl$	---	generation of standard gaseous mixtures of alkyl isothiocyanates by thermal decomposition	237

Support	Phase	Capacity	Application	References
THIOETHERS, DISULFIDES AND POLYSULFIDES				
Silica gel	$\equiv SiCH_2CH_2S\text{-}Si(CH_3)_3$	---	complex catalyst synthesis with $Rh_2(CO)_4Cl_2$ and $(C_4H_9)_3P$	684
Silica gel	$\equiv Si(CH_2)_3S\text{-}Si(CH_3)_3$	---	complex catalyst synthesis with $Rh_2(CO)_4Cl_2$ and $(C_4H_9)_3P$	684
Inorganic supports	$-Si(R)_n(CH_2)_mSR$	---	complexes with Rh, Ir, Pd, Ru, Cr, and Ni as catalysts for synthesis of carboxylic acid anhydrides	683
Silica gel, alumina, TiO_2	$-Si(R_2)\text{-}R'\text{-}SR''$ R'= alkylene, phenylene R"= alkyl, cycloalkyl, phenyl	---	platinum or rhodium complexes as hydrosilylation catalysts	576a
Silica gel	$\equiv SiCH_2CH_2SC_6H_5$	0.31-0.65 meq/g	Separation of cations, Rh(III), Ir(III), Au(III), Pd(II), Pt(II), Pt(IV), Os(IV), Ru(III), Cu(II), and Fe(III) from base metal ions	685
Silica gel	$\equiv Si(CH_2)_2SC_2H_4OH$	---	Pd(II) complexes as catalysts	339
Silica gel	$\equiv Si(CH_2)_3$-(2)-thiophene*	---	HPLC support	686
*the original paper gave the wrong formula or wrong name				
Silica gel	$\equiv Si(CH_2)_2SC_6H_4(o)NH_2$	0.31-0.63 meq/g	Separation of Rh(III), Ir(III), Au(III), Pd(II), Pt(II), Pt(IV), Os(IV), Ru(III), Cu(II), and Fe(III)	685

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel	≡Si$(CH_2)_2SC_6H_4(m)NH_2$	0.31-0.63 meq/g	Separation of Rh(III), Ir(III), Au(III), Pd(II), Pt(II), Pt(IV), Os(IV), Ru(III), Cu(II), and Fe(III)	685
Silica gel	≡Si$(CH_2)_2SC_6H_4(p)NH_2$	0.31-0.63 meq/g	Separation of Rh(III), Ir(III), Au(III), Pd(II), Pt(II), Pt(IV), Os(IV), Ru(III), Cu(II), and Fe(III)	685
Silica gel	≡Si$(CH_2)_3$S-(8)-quinoline	0.11 meq/g	Pd complexes	220
Silica gel	≡Si$(CH_2)_3$S-**T2**	---	Pd complexes	220
Silica gel, glass, titania, zirconia, etc.	=Si$(CH_3)(CH_2)_3$S-$N^+(CH_3)_2Cl^-$	---	anion exchanger	647,649
Silica	≡SiCH_2CH_2S-**T3**	---	separation of Pd(II) from Rh(III) and Ir(III) and base ions	685
Silica gel	≡Si$(CH_2)_3$S-quinine-quinidine N-methylquininium iodide	---	chiral stationary phase	687
Silica gel	≡Si$(CH_2)_3$S-S-(3)-5-nitro-benzoic acid	---	separation of thiols	233
Silica gel	≡Si$(CH_2)_3$S-S-2-pyridyl	---	separation of thiols	233

Support	Phase	Capacity	Application	References
Silica gel	≡Si$(CH_2)_3$S-S-S-$(CH_2)_3$Si≡	0.3-0.6 meq/g	separation of Pd(II), Rh(III), In(III) and other metal ions	685
Silica gel	≡Si$(CH_2)_3$S-S-S-S$(CH_2)_3$Si≡	0.31-0.63 meq/g	sorption and separation of Pd(II) from Rh(III) and Ir(IV) from Au(III), Pt(II), Pt(IV), Os(IV), Ru(III), Rh(III), Cu(II), and Fe(III)	685
SnO_2 electrode	≡Si$(CH_2)_3$S-**T4**	---	redox system on working electrode surface	234
Silica gel	≡Si$(CH_2)_3$S-**T4**	---	catalyst	679
Silica	≡Si$(CH_2)_2$S-SnHR_2	---	reducing agent	688
Alumina	≡SiCH(CH_3)S-SnBu_2H Bu = butyl	---	reducing agent	688
Alumina	≡SiCH_2CH_2S-SnBu_2H Bu = butyl	---	reducing agent	688
Silica gel	≡Si$(CH_2)_3$S-$Rh(CO)_2$	---	catalyst	572
Silica	-Si$(CH_3)_2(CH_2)_3$S-$Ru_3(CO)_{10}$H	---	catalyst	689

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica	-$Si(CH_3)_2(CH_2)_3S$-$Os_3(CO)_{10}H$	---	catalyst	689
SULFONIC ACIDS				
Silica gel	$\equiv Si(CH_2)_3SO_3Na$	---	synthesis; product contains 0.6% S	312
Silica gel	$\equiv Si(CH_2)_3SO_3H$	---	synthesis and application as a strong cation exchanger for binding organic bases	340
Partisil	$\equiv Si(CH_2)_3SO_3H$	0.48 meq/g	synthesis; cation exchanger	302
Silica gel	$=Si(CH_3)(CH_2)_3SO_3H$	1.23 meq/g	cation exchanger	235
Kieselgel	$\equiv Si(CH_2)_4SO_3H$	0.25 meq/g	synthesis by sulfochlorination	291
Silica gel, glass, titania, zirconia, alumina	$=Si(CH_3)(CH_2)_4SO_3Na$	---	cation exchanger	647,649
Partisil 5	$\equiv Si(CH_2)_{18}SO_3H$	---	HPLC support	203

Support	Phase	Capacity	Application	References
Porous membrane glass electrode	≡$SiC_6H_4(p)SO_3H$	---	phenylsilylation and sulfonation increased the cation response of the membrane	295
Silica gel	≡$SiC_6H_4(p)SO_3H$	0.46 meq/g	sorption of Ag(I), Zn(II), and Cu(II)	294
Silica gel	≡$SiC_6H_4(p)SO_3H$	0.32 meq/g	ion exchange of Ag(I), Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), Fe(III), and Th(IV)	210
Mercosorb and LiChrosorb SI-60	≡$SiC_6H_4(p)SO_3H$	0.2 meq/g	ion exchange of organic compounds	6
Silochrom SI-120	≡$SiC_6H_4(p)SO_3H$ monomeric and polymeric	---	separation of Na^+, K^+, and NH_4^+	640
Porasil C	≡$SiCH_2C_6H_4(p)SO_3H$	0.0124 meq/g	Pb(II) ion exchanger	267
Silica gel and SiO_2 covered glass beads	≡$SiCH_2C_6H_4(p)SO_3H$	0.05-0.39 meq/g	HPLC of organic compounds	690
Davisil 62, Syloid 74	≡$SiCH_2C_6H_4(p)SO_3H$	0.43 meq/g 0.57 meq/g	HPLC of organic compounds	258

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Aerosil and porous silica	≡$SiCH_2C_6H_4(p)SO_3H$	3.3 μm/m^2	studies of adsorption properties	643
Silochrom SI-120	≡$SiCH_2C_6H_4(p)SO_3H$ monomeric and polymeric	---	separation of Na^+, K^+, and NH_4^+	640
Mercosorb and LiChrosorb SI-60	≡$SiCH_2CH_2C_6H_4(p)SO_3H$	0.6 meq/g	separation of organic compounds	6
Silochrom SI-120	≡$SiCH_2CH_2C_6H_4(p)SO_3H$ monomeric and polymeric	---	separation of Na^+, K^+, and NH_4^+	640
Silochrom SI-120	≡$Si(CH_2)_nC_6H_4(p)SO_3H$ n = 0,1,2	---	separation of titanium and zirconium	691
Silica gel	-$Si(CH_3)_2(CH_2)_3$-$C_6H_4(p)SO_3H$	---	cationic RP-HPLC support	692
Partisil 10	-$Si(CH_3)_2(CH_2)_3$-$C_6H_4(p)SO_3H$	0.24-0.48 meq/g	separation of catecholamines	296
Silica	≡$Si(CH_2)_4C_6H_4(p)SO_3H$	1.14-2.2 meq/g	separation of Ba, Cu(II), Na, K, Ni(II) and Zn	7

Support	Phase	Capacity	Application	References
Silica A	$-Si(CH_3)_2(CH_2)_4-C_6H_4(p)SO_3H$	0.13 meq/g	separation of organic bases	4
Porasil	≡Si-(4)-naphthalene-sulfonic acid	---	cation exchanger	267
Silica gel,	$=Si[C_6H_4(p)SO_3H]_2$	0.51 meq/g	absorption of organic vapours	209
Aerosil		0.26 meq/g		
Silica gel	$=Si[C_6H_4(p)SO_3H]_2$	---	ion exchange of Ag(I), Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), Fe(III), and Th(IV)	210
Partisil 5	$=Si[C_6H_4(p)SO_3H]_2$	---	HPLC phases, comparison of properties	203
Silica gel	$-Si[C_6H_4(p)SO_3H]]_3$	1.32 meq/g	ion-exchange of Ag(I), Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), Fe(III), and Th(IV)	210
Xerogel and similar aluminoxane, titanoxane and zirconoxane	sulfonated polycondensate	3.02 meq/g		297

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
IEX-510SP comm. Toyo Soda	-unknown-SO_3Na	---	separation of crown ethers via complex formation	693
Partisil 10SCX, Nucleosil 10SA comm.	-unknown	---	ion-exchange of lanthanide complexes with hydroxyisobutyric acid	694
TSK-gel SP-2SW	-sulfonic acid type	0.3 meq/g	separation of Mg, Ca and Sr and determination in presence of Arsenazo III	695
See also Amines				
PHOSPHINES AND AMINOPHOSPHINES				
Kieselgel 100	$\equiv SiCH_2P(menthyl)_2$	---	rhodium complex catalyst	238
Kieselgel 40, Kieselgel 100, Sorbosil A	$\equiv Si(CH_2)_nP(Ph)_2$ n = 1 - 6	---	rhodium complexes as catalyst	696,697,238,561
Silica gel	$-Si(CH_3)_2CH_2P(Ph)_2$	---	$PdCl_2$ complex as hydrogenation catalyst	698
Kieselgel 100 Kieselgel 40 Sorbosil A	$-Si(CH_3)_2CH_2P(Ph)_2$	---	Rh immobilized catalysts	696,697
Silica gel	$-Si(CH_3)_2CH_2P(Ph)_2$	---	Pd complex as catalyst for hydrogenations	698

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_2P(C_4H_9)_2$	---	complexes with cobalt carbonyls as catalysts	699
Silica	$\equiv Si(CH_2)_2P(C_6H_{11})_2$	---	RhCl, RhBr, and RhI complexes as catalysts	562
Silica	$\equiv Si(CH_2)_2P(C_6H_{11})_2$	---	Co and Rh complexes as catalysts	700
Silica gel	$\equiv Si(CH_2)_2P(C_6H_{11})_2$	---	complexes with Co carbonyls as catalysts	699
Inorganic supports	$-Si(R)_n(CH_2)_mPR_2$	---	complexes with Rh, Ir, Pd, Ru, Cr, and Ni as catalysts for synthesis of carboxylic acid anhydrides	683
Silica gel, alumina	$\equiv Si(CH_2)_2P(Ph)_2$	---	rhodium, palladium and platinum catalysts	188
Cab-o-sil silica	$\equiv Si(CH_2)_2P(Ph)_2$	0.9 meq/g	rhodium carbonyl complexes	559
Silica	$\equiv Si(CH_2)_2P(Ph)_2]_2RhX$	---	X = Cl, Br, I; Catalysts	562
Silica	$\equiv Si(CH_2)_2P(Ph)_2$-Rh-acac(CO) acac = acetylacetone	---	catalysts	236
Silica gel	$\equiv Si(CH_2)_2P(Ph)_2$	---	complexes with Co carbonyls as catalysts	699
Silica gel	$\equiv Si(CH_2)_2P(Ph)_2$-$(CO)_9Os_3H_2$	---	hydrogenation catalyst, NMR spectra	701,702

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_2P(Ph)_2$-$(CO)_{16}Os_4H$	---	hydrogenation catalyst, NMR spectra	699,701,702
Silica gel	$\equiv Si(CH_2)_2P(Ph)_2$-$(CO)_{11}Os_3$	---	hydrogenation catalyst, NMR spectra	699,701,701
Kieselgel 100, Kieselgel 40, Sorbosil A	$\equiv Si(CH_2)_2P(Ph)_2$	---	rhodium complexes	696,697
Silica gel	$\equiv Si(CH_2)_2P(Ph)_2$	---	Co carbonyl catalysts	703
Silica, Cob-O-sil, alumina	$\equiv Si(CH_2)_2P(Ph)_2$	---	Co and Rh complexes	700
LiChrosorb Si-60	$\equiv Si(CH_2)_2P(Ph)_2$ and endcapped products	0.35-0.4 meq/g	NMR studies	704
Silica	$\equiv Si(CH_2)_2P(Ph)_2Ru_3$-$(CO)_9$-(dppm)	0.022[x] 0.0033[xx]	complex catalyst	705

[x]capacity of material synthetized from the respective immobilized phosphine
[xx]capacity of material when the complex was immobilized

dppm = dis(diphenylphosphino)methane

Support	Phase	Capacity	Application	References
Silica	$\equiv Si(CH_2)_2P(Ph)_2Os_3(CO)_{11}$-(dppm)	0.027[x] 0.0091[xx]	complex catalyst	705
Silica	$\equiv Si(CH_2)_2P(Ph)_2Co_4(CO)_8\{HC[P(Ph)_2]_3\}$	0.027[x] 0.012[xx]	complex catalyst	705
Silica	$\equiv Si(CH_2)_2P(Ph)_2Rh_4(CO)_8\{HC[P(Ph)_2]_3\}$	0.034[x]	complex catalyst	705
Silica	$\equiv Si(CH_2)_2P(Ph)_2Ir_4(CO)_8\{HC[P(Ph)_2]_3\}$	0.017[x] 0.023[xx]	complex catalyst	705
Silica	$\equiv Si(CH_2)_2P(Ph)_2Ir_4(CO)_{11}$	---	complex catalyst	706
Silica	$\equiv Si(CH_2)_2P(Ph)_2$	---	synthesis and structure of Pd complexes, ^{31}P and ^{13}C NMR	423
Porasil C	$\equiv Si(CH_2)_2C_6H_4P(Ph)_2$	---	$CuCl_2$ and $CuBr_2$ complexes as catalysts	707
Silica	$\equiv Si(CH_2)_3P(C_6H_{11})_2$	---	Pd-complexes, synthesis and structure by ^{31}P and ^{13}C NMR	423
Silica gel	$\equiv Si(CH_2)_3P(C_6H_{11})_2$	---	Cu(II) complex synthesis from acetylacetonate	357
Kieselgel 100	$\equiv Si(CH_2)_3P(menthyl)_2$	---	Rh complex as catalyst	238
Glass	$\equiv Si(CH_2)_3P(Ph)menthyl$	---	Rh complex as chiral catalyst	708
Silica	$\equiv Si(CH_2)_3P(Ph)_2$	---	immobilized ligand for the synthesis of catalysts	562

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Aerosil 360	$\equiv Si(CH_2)_3P(Ph)_2$	---	Complexes with $RhCl_3$, $CoCl_2$, $NiCl_2$, $PdCl_2$, and $NiBr_2$	709
Silica gel	$\equiv Si(CH_2)_3P(Ph)_2$	---	Cu(II) complex synthesis from acetylacetonate	357
Aerosil 380	$\equiv Si(CH_2)_3P(Ph)_2$	1.1 group/nm^2	complex with $Rh_6(CO)_{16}$ cluster	710
Kieselgel 40, Kieselgel 100	$\equiv Si(CH_2)_3P(Ph)_2$	---	complex with dicyclooctene rhodium derivative	711
Aerosil A380	$\equiv Si(CH_2)_3P(Ph)_2$-$AuOs_3(CO)_{10}H$	---	complex catalyst	712
Aerosil A380	$\equiv Si(CH_2)_3P(Ph)_2$-$Ru_4(CO)_{12-x}^{II}$	---	complex catalyst	712
Aerosil A380	$\equiv Si(CH_2)_3P(Ph)_2$-$Os_3(CO)_9H_2$	---	complex catalyst	712
Silica	$\equiv Si(CH_2)_3P(Ph)_2$-$Ir_4(CO)_9[P(Ph)_3]$	---	synthesis and characterization	713
Silica	$\equiv Si(CH_2)_3P(Ph)_2$-$Ir_4(CO)_{10}[P(Ph)_3]$	---	synthesis and characterization	713
Kieselgel 100 Kieselgel 40 Sorbosil A	$\equiv Si(CH_2)_3P(Ph)_2$	---	Rh complex catalysts	696,697

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_1P(Ph)_2$	---	Pt-complex as hydrogenation catalyst	714
Silica gel	$\equiv Si(CH_2)_3P(Ph)_2$	---	Pd-complex as catalyst	715
Kieselgel 100 Kieselgel 40 Sorbosil A	$\equiv Si(CH_2)_nP(Ph)_2$ n = 1,2,3	---	Rh-complexes as catalysts	696,697
Silica gel	$\equiv Si(CH_2)_3P(Ph)_2$	---	Rh-complex as hydrogenation catalyst	561
Kieselgel 100	$\equiv Si(CH_2)_5P(Menthyl)_2$	---	Rh-complex as catalyst	238
Silica gel	$\equiv Si(CH_2)_8P(Ph)_2$	---	Co-carbonyl complexes as catalysts	703
Spherosil XOA 200	$\equiv Si(CH_2)_8P(Ph)_2$	0.087 and 0.6 meq/g	synthesis and rhodium acetylacetonate complex	422
Cab-o-sil Silica	$\equiv Si(CH_2)_{14}P(Ph)_2$	1.0 0.9 meq/g	rhodium carbonyl complexes as catalysts	559
Cab-o-sil Silica	$\equiv SiC_6H_4(p)CH_2P(Ph)_2$	---	Pd complex as catalyst	715
Porasil C	$\equiv Si(CH_2)_2C_6H_4$-$(p)CH_2P(Ph)_2$	---	complex with $CuCl_2$ and $CuBr_2$	707

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silica	$\equiv Si(CH_2)_4C_6H_4$-(*p*)$P(Ph)_2$	---	ligand for immobilized catalysts	562
Silica	-$Si(CH_3)_2$-**T5**	---	immobilized ligand for catalysts	716
Silochrome	$\equiv Si(CH_2)_3NHP(Ph)_2$	---	Ni complexes as catalysts for ethylene dimerization	358
DIPHOSPHINES				
Cab-o-sil Silica	$\equiv SiC_6H_4(p)CH_2O$-$CH[CH_2P(Ph)_2]_2$	---	Pd complex as catalyst	715
Kieselgel 100	$\equiv SiCH_2P(Ph)$-$CH_2CH_2P(Ph)_2$	---	Rh complex catalyst	636,717
Kieselgel 100	$\equiv Si(CH_2)_3P(Ph)$-$CH_2CH_2P(Ph)_2$	---	Rh complex catalyst	636,717
Silica gel	$=Si[(CH_2)_4P(C_6H_{11})_2]_2$	0.156 meq/g	Co-carbonyl catalyst	718
Silica gel	$=Si[(CH_2)_4P(Ph)_2]_2$	0.16 meq/g	Co-carbonyl catalyst	718
Macroporous silica	-$Si(CH_3)_2(CH_2)_4$-**T6**	---	Rh complex catalyst for asymmetric hydrogenation	719

Support	Phase	Capacity	Application	References
Silochrome C-120	$\equiv Si(CH_2)_3N[P(Ph_2)]_2$	---	heterogenized Ni complexes for ethylene dimerization	358
Silochrome C-120	$\equiv Si(CH_2)_3$-T7	---		720
Silica gel	$\equiv Si(CH_2)_3$-T8	---		720
Cab-o-sil Silica	$\equiv Si(CH_2)_3O$-$CH[CH_2P(Ph)_2]_2$	---	Pd complex as catalyst	715
ARSINES				
Inorganic supports	$-Si(R)_2(CH_2)_mAsR_2$	---	complexes with Rh, Ir, Pd, Ru, Cr, and Ni, and catalysts for synthesis of carboxylic acid anhydrides	683
PHOSPHINOXIDES				
Davison 56	$\equiv SiCH_2CH_2P(O)(Ph)_2$	---	Pd complexes, synthesis and structure	423
Davison 56	$\equiv Si(CH_2)_3P(O)(C_6H_{11})_2$	---	Pd complexes, synthesis and structure	423
PHOSPHONIC ACIDS & ESTERS				
Silica gel	$\equiv Si(CH_2)_3PO(OC_2H_5)_2$	---	complexes with metal ions	721
Silochrom S 80	$\equiv Si(CH_2)_3PO(OH)_2$	---	sorption of Zr(IV), Hf(IV), Ti(IV), Th(IV), Fe(III), and Sc(III)	300

(continued)

Table 1. Continued.

Support	Phase	Capacity	Application	References
Silochrom	$\equiv SiC_6H_4(p)PO(OH)_2$	---	sorption of Ti(IV), Zr(IV), Hf(IV), Sc(III), Fe(III), and Th(V)	**300**
Xerogel from	$Cl_3SiC_6H_4(p)POCl_2$	---		**288**

See also unnatural amino acid derivatives and glycidoxypropyl derivatives

PHOSPHONIUM SALTS

Silica gel, Alumina 60	$\equiv Si(CH_2)_3P^+(C_4H_9)_3Br^-$	0.34-0.31 meq/g	anion exchanger, phase transfer catalyst	**580,592**
Silica gel, Alumina	$\equiv Si(CH_2)_3NHCO(CH_2)_{10}$-$P^+(C_4H_9)_3Br^-$	0.25-0.11 meq/g	anion exchanger, phase transfer catalyst	**580,592**
Silica gel, Alumina 60	$\equiv Si(CH_2)_3NHCO(CH_2)_{10}$-$P^+(Bu)_3Br^-$		phase transfer catalyst	**580,592**

Table 2. Solid Supports Containing Monoamine, Acylated Monoamine, Urethane, Urea, Quaternary Ammonium, Thioamine, Thioamide, Dithiocarbamate, Sulfonamide, Schiff Base, Oxime and Nitrogen-containing Aromatic Side Groups

Support	Phase	Capacity	Application	References
AMINES				
MONOAMINES AND DERIVATIVES				
Silica gel	≡SiR'-Z R'= alkylene, phenylene Z = amine, alkylamine, ethylenediamine	---	complexes with Na_2PtCl_4, $K[Pt(CH_2{=}CH_2)Cl_3]$ and $Pt_2(CH_2{=}CH_2)Cl_4$ as hydrosilylation catalysts	576b
Xerogel	$\equiv SiCH_2NH_2$	---	confirmation of porous structure and adsorptive properties	285
Silica gel KSK	$\equiv SiCH_2NH_2$	0.3-0.9 meq/g	Pd(II) complexes as catalysts	722
Silica gel, glass, titania, zirconia, alumina	$-Si(CH_3)_2CH_2NHC_6H_4(p)NO_2$	---	anion, cation exchanger, TLC support, adsorbents for heavy metal ions	647
Kieselgel	$\equiv SiCH_2N(C_2H_5)_2$	0.3-0.8 meq/g	synthesis	246

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel KSK	$\equiv SiCH_2N(C_2H_5)_2$	0.57 meq/g	Pd(II) complexes as catalysts	722
Kieselgel	$-Si(CH_3)_2N(C_2H_5)_2$	0.3-0.8 meq/g	synthesis	246
Silica gel KSK	$\equiv SiCH_2N(CH_2CH_2)_2CH_2$	0.5 meq/g	Pd(II) complexes as catalysts	722
Silica gel	$\equiv SiCH_2N(CH_2CH_2)_2Y$ Y = O,S	---	Pt complexes as catalysts for hydrosilylation	577
Silica gel	$\equiv Si(CH_2)_2NH$-T9	---	intermediate in synthesis	526
Kieselgel	$\equiv Si(CH_2)_2N(C_2H_5)_2$	0.3-0.8 meq/g		246
Silica gel	$\equiv Si(CH_2)_2N(CH_2CH_2)_2Y$ Y = O,S	---	Pt complexes as hydrosilylation catalysts	577
Silica gel	$\equiv Si(CH_2)_nNH_2$ endcapped	---	synthesis	289
Silica	$\equiv Si(CH_2)_nNH_2$	---	removal of metal ions (Cu, Pb) from organic solvents	596
Silochrom	$\equiv Si(CH_2)_3NH_2$	---	HPLC of organic compounds	723

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	Rh complex as catalyst	236
SnO_2 electrode	$\equiv Si(CH_2)_3NH_2$	---	electrochemical behavior of the ligand on electrode surface	654
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	HPLC determination of paraquat (T10)	724
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3NH_2$	---	extraction and determination of H_2SeO_4, H_3AsO_4, $H_2Cr_2O_7$, H_2MoO_4, H_2WO_4, H_3VO_4; I^-, Br^-, IO_3^-, IO_4^- and BrO^- were not extracted	495
Partisil 7	$\equiv Si(CH_2)_3NH_2$	---	salts with chiral acids were used for resolution of optical isomers (helicenes)	725
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	Fe(II) and Cu(II) were removed from water samples and in the effluent, the Ca(II) and Mg(II) water hardness was determined	506
Silochrom, controlled pore glass, chromosorb	$\equiv Si(CH_2)_3NH_2$	---	immobilization of tRNA	726
Silochrome, Alusil	$\equiv Si(CH_2)_3NH_2$	---	studies of stability of immobilized ligand	252
Glassy carbon	$\equiv Si(CH_2)_3NH_2$	---	electrochemical behavior of ligand on electrode surface	727

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
LiChrosphere SI-100	$\equiv Si(CH_2)_3NH_2$	---	HPLC separation of carbohydrates	728
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	weak anion exchanger: it separates nitrate anions from interfering ions, analytical method for NO_3^- determination	729
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	support for chromatography	634
Silica Si-100	$\equiv Si(CH_2)_3NH_2$ polymeric(?)	1.74 meq/g	exclusion chromatography of organic compounds	730,671
Partisil 10	$\equiv Si(CH_2)_3NH_2$	3.2 meq/g	HPLC separation of amines on Cu(II) complex (ligand exchange chromatography)	731
SnO_2, TiO_2, glassy carbon	$\equiv Si(CH_2)_3NH_2$	---	electrochemical behavior of the ligand immobilized on electrode surface	732
SnO_2, TiO_2, RuO_2, Pt/PtO, carbon	$\equiv Si(CH_2)_3NH_2$	---	X-ray photoelectron spectroscopy	438
Iron	$\equiv Si(CH_2)_3NH_2$	---	IR characteristics	399
Partisil 5	$\equiv Si(CH_2)_3NH_2$	---	a screen was proposed enabling identification of the bonded support	203

Support	Phase	Capacity	Application	References
Silica gel KSK	$\equiv Si(CH_2)_3NH_2$	1.1 meq/g	complexes with Pd(II) as catalysts	571,722
Silica Si-100	$\equiv Si(CH_2)_3NH_2$	---	exclusion chromatography of organic compounds	671
Merkosorb Si 60	$\equiv Si(CH_2)_3NH_2$	0.19 group/nm^2	support for chromatography	266
Mineral carriers	$\equiv Si(CH_2)_3NH_2$	---	synthesis	652
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	TLC support	458
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	stationary phase for HPLC of aldehydes (or Schiff-bases)	733
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	pH dependence of sorption of Cu(II), Co(II), Mn(II), Ni(II) and Zn(II)	675
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	complex with Na_2PdCl_4 and H_2PtCl_6 as catalysts	734,735
Spherisorb S5-W	$\equiv Si(CH_2)_3NH_2$	---	HPLC separation of glutathione, thiols and disulfides	736
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	$PdCl_2$ complexes as catalysts	737

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	plates for high-performance TLC	738
Silica gel	$\equiv Si(CH_2)_3NH_2$ monomeric polymeric	3.8 μm/m^2 4.7 μm/m^2	complexes with Cu(II), Ni(II), and Zn(II)	124
Wacogel LC-30	$\equiv Si(CH_2)_3NH_2$	---	Cu(II) complex for HPLC separation of aromatic amines	739
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	TLC separation of Cu, Cd, Fe(III), Mn(II), Ni(II), Pb and Zn ions	136
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	complexes with metal ions	721
Silica gel Si-60H	$\equiv Si(CH_2)_3NH_2$	---	^{13}C and ^{29}Si NMR spectra	130
Silochrom Si-80	$\equiv Si(CH_2)_3NH_2$	---	removal of phenols and benzoic acid from water	664
Silochrom S-120	$\equiv Si(CH_2)_3NH_2$	0.7 meq/g	sorption of acids and Zn(II), Cu(II), Co(II), Ni(II), and Mn(II)	226
Silica	$\equiv Si(CH_2)_3NH_2$ polymeric	---	Pt(IV) complex as hydrosilylation catalyst	578
Silochrom S-120	$\equiv Si(CH_2)_3NH_2$	---	separation of Pd(II), Ir(IV) and Pt(IV) from Fe(III) and other transition elements	598

Support	Phase	Capacity	Application	References
Macroporous silica	$\equiv Si(CH_2)_3NH_2$	---	modified with carbohydrates as chromatgraphic support for HPLC	740
Silochrom S-80	$\equiv Si(CH_2)_3NH_2$	---	sorption and separation of Sc(III)	741
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	Pd-complexes as catalysts	742
Alumina, magnesia	$\equiv Si(CH_2)_3NH_2$	---	complexes of cobalt and rhodium as catalysts	703,700
Carbonized silica gel	$\equiv Si(CH_2)_3NH_2$	---	enzyme separation	109
Silica gel LIK-21	$\equiv Si(CH_2)_3NH_2$	---	preconcentration of osmium	743
Silochrom C-80	$\equiv Si(CH_2)_3NH_2$	0.24 meg/q	synthesis and IR characterization	331
Kieselgel 60	$\equiv Si(CH_2)_3NH_2$	0.77	IR spectra	744
Kieselgel 60, alumina	$\equiv Si(CH_2)_3NH_2$	---	complexes with Fe(III), Co(II), and Ni(II)	745
Alumina	$\equiv Si(CH_2)_3NH_2$	---	high enzyme adsorptive capacity	746

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	selective sorption and X-ray fluorescence determination of rhodium in mixtures with Pd, Co, Cu and Fe	**508**
Silica gel	$\equiv Si(CH_2)_3NH_2$	1.18 meq/g	high capacity modified silica	**227**
Silica gel	$\equiv Si(CH_2)_3NH_2$	280 μm/g	affinity chromatography support	**747**
CrO_2 covered by SiO_2	$\equiv Si(CH_2)_3NH_2$	---	---	**113**
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	Cu(II) complex studies by EPR spin probe method	**427**
Silica, Al_2O_3 surface	$\equiv Si(CH_2)_3NH_2$	---	comparison of binding reaction on support	**176**
Silica	$\equiv Si(CH_2)_3NH_2$	---	structural characterization by ^{13}C NMR and ^{29}Si NMR	**414**
Silochrome	$\equiv Si(CH_2)_3NH_2$	---	nickel complexes for dimerization of ethylene	**358**
Silica gel	$\equiv Si(CH_2)_3NH_2$ mixed $\equiv Si(CH_2)_{18}H$ functions	---	HPLC of organic bases	**748**
Silica gel	$\equiv Si(CH_2)_3NH_2$	---	chiral derivatives were used for resolution	**673**
Silica gel	$\equiv Si(CH_3)(CH_2)_3NH_2$	---	studies of release of aminopropyl residue from support	**191**

Support	Phase	Capacity	Application	References
Silica gel	$-Si(CH_3)_2(CH_2)_3NH_2$	---	stability studies	191
Zorbax, LiChrosorb Si-60	$-Si(CH_3)_2(CH_2)_3NH_2$	---	stability studies	211
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3NHCH_3-$	---	extraction of H_2SeO_4, $HMnO_4$, H_3AsO_4, $H_2Cr_2O_7$, H_2MoO_4, H_2WO_4, H_3VO_4; I^-, Br^-, IO_3^-, IO_4^-, BrO_3^- are not extractable	495
Silica gel	$\equiv Si(CH_2)_3NHCH_2-CH(OH)CH_2-Tll$	---	asymmetric HPLC support	749
Zorbax Silica	$\equiv Si(CH_2)NHCH_2-CH(OH)CH_2OCH_2CH=CH_2$	---	stability studies	211
Zorbax Silica	$\equiv Si(CH_2)_3NHCH_2CH(OH)-CH(OH)CH_2NH(CH_2)_3-Si\equiv$		stability studies	211
Zorbax Silica	$\equiv Si(CH_2)_3NHCH_2CH(OH)CH_2O(CH_2)_3O-CH_2CH(OH)CH_2NH(CH_2)_3Si\equiv$		ibid.,	211
Porasil 380	$\equiv Si(CH_2)_3NHC_6H_{11}$	0.11 group/nm^2	complexes with $Rh_6(CO)_{16}$ cluster	710
Silochrom C-80	$\equiv Si(CH_2)_3NH(CH_2)_nX$ n = 2-10; X = Br,I	---	synthesis and IR spectra	331

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Aldrich	≡Si$(CH_2)_3$NH-$CH_2C_6H_4$(*m*)B$(OH)_2$	---	separation of catecholic amino acids	**750**
Partisil 10	≡Si$(CH_2)_3NHCH_2C_6H_4$(*p*)B$(OH)_2$	---	separation of saccharides	**315**
Partisil	-Si$(CH_3)_2(CH_2)_3NHCH_2$-C_6H_4(*p*)B$(OH)_2$		HPLC of sugars	**315**
Kieselgel or Silica Woelm	≡Si$(CH_2)_3NHCH_2$-(4)-8-hydroxyquinoline	---	separation of different cations	**355**
Silochrom C-80	≡Si$(CH_2)_3NHCH(COCH_3)_2$	0.18 meq/g	synthesis and IR spectra	**331**
Silica gel	≡Si$(CH_2)_3NHC_6F_5$	---	HPLC separation of aromatic hydrocarbons	**655**
LiChrosorb	=Si$(CH_3)(CH_2)_3NHC_6F_5$	0.5 meq/g	HPLC support	**655**
Micropar-ticulate silica	≡Si$(CH_2)_3NHC_6H_3$(2,4)$(NO_2)_2$	---	support for "charge-transfer" chromatography	**354**
LiChrosorb Si-60, Silica gel	≡Si$(CH_2)_3NHC_6H_3$(2,4)$(NO_2)_2$	---	support for "charge-transfer" chromatography	**751**
Silica gel	≡Si$(CH_2)_3NHC_6H_3$(2,4)$(NO_2)_2$	---	support for "charge-transfer" chromatography	**321**

Support	Phase	Capacity	Application	References
Hypersil	$\equiv Si(CH_2)_3NHC_6H_2(1,3,5)(NO_2)_3$	---	support for "charge-transfer" chromatography	752
LiChrosorb	$\equiv Si(CH_2)_3NHC_6H_2(1,3,5)(NO_2)_3$	---	support for "charge-transfer" chromatography	322,406
LiChrosorb Si-100	$\equiv Si(CH_2)_3NHC_6H_4(m)B(OH)_2$	0.145 meq/g	separation of *cis*-diols	753
Silica gel	$\equiv Si(CH_2)_3NH$-**T11**	---	ESR and diffuse reflectance spectroscopy of immobilized phases	432
Silica gel	$\equiv Si(CH_2)_3$-NH-**T12**	4.3 μm/g		747
SnO_2 electrode surface	$\equiv Si(CH_2)_3NH$-residue of tetraiodofluorescein	---	photocurrent sensitization to visible wavelength light	754
Microparticulate silica	$\equiv Si(CH_2)_3NH$-2-quinazoline	---	photoacoustic spectroscopy of bonded phase	354
Silochrom S-80	$\equiv Si(CH_2)_3NH$-**T9**	---	intermediate in synthesis	331
Porous glass, Silochrome	$\equiv Si(CH_2)_3NH$-Ciba Blue	---	synthesis of sorbent	755

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NH$-hemin or -bilirubin or -biliverdin	---	synthesis	756
Silica, alumina, glass	$\equiv Si(CH_2)_3N(CH_3)_2$	---	Rh, Pd, and Pt complexes as heterogenized catalysts for hydrosilylation reaction	188
Aerosil	$=Si(CH_3)(CH_2)_3N(CH_3)_2$	---	applied in polymerization of vinyl monomers	662
Silica gel	$-Si(CH_3)_2(CH_2)_3N(CH_3)_2$	0.9 meq/g	HPLC column packing	126
Spherosil comm.	$\equiv Si(CH_2)_3N(C_2H_5)_2$	0.5 meq/g	synthesis, HPLC support	465
Silica	$\equiv Si(CH_2)_3N(C_2H_5)_2$	---	Rh complex as catalyst	236
Silica	$\equiv Si(CH_2)_3N(C_2H_5)_2$	0.51 meq/g	Pd-complexes as catalysts	220,261
Silica gel	$\equiv Si(CH_2)_3N(C_2H_5)_2$	---	Pd-complexes as catalysts	742
Aerosil	$=Si(CH_3)(CH_2)_3N(C_2H_5)_2$	---	used in polymerization of vinyl monomers	662
Inorganic supports	$-Si(R)_n(CH_2)_mNR_2$	---	complexes with Rh, Ir, Pd, Ru, Cr, and Ni as catalysts for the synthesis of carboxylic anhydrides	683

Support	Phase	Capacity	Application	References
Silica	$\equiv Si(CH_2)_3$-(N)-pyrrolidine	---	Rh complex as catalyst	**236**
Silica	$\equiv Si(CH_2)_3$-(N)-pyrrolidine	---	Pt and Rh complexes as catalysts	**306**
Silica	$\equiv Si(CH_2)_3$-(N)-piperidine	---	Pt and Rh complexes as catalysts	**306**
Silica gel	$\equiv Si(CH_2)_3$-(N)-piperidine	---	Pd complexes as catalysts	**742**
Silica	$\equiv Si(CH_2)_3$-(N)-morpholine	---	Pt and Rh complexes as catalysts	**306**
Silica gel	$\equiv Si(CH_2)_nN(CH_2CH_2)_2Y$ n = 1-12; Y = O,S	---	Pt complexes as hydrosilylation catalysts	**577**
Silica gel	$-Si(CH_3)_2(CH_2)_4NH_2$	---	packing for HPLC	**126**
Zorbax, LiChrosorb Si-60	$-Si(CH_3)_2(CH_2)_4NH_2$	---	stability studies	**211**
Silica gel	$\equiv Si(CH_2)_4NH$-residue of uracil, thymine, cytosine, thiouracil	---	HPLC separation of nucleic acids	**757**
Controlled porosity glass	$\equiv Si(CH_2)_nN$ H-glutaraldehyde-hemoglobin and simultaneously -luminol		detection of H_2O_2	**527**
Silica gel	$\equiv Si(CH_2)_{11}N(CH_3)_2$	---	long chain surface modifier	**657,667**

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel, Porasil C, controlled pore glass	≡$SiC_6H_4(p)NH_2$	---	further synthesis	232
Silica gel Wacogel C-200	≡$SiC_6H_4(p)NH_2$	---	intermediate in the synthesis of azo-dye (2-naphthol derivative)	260
Silica gel	≡$SiC_6H_4(p)COC_6H_4(p)N(CH_3)_2$	---	sensitizer for photoisomerization of norbornadiene	758
Silica gel	≡$SiCH_2C_6H_4(p)CH_2NH\text{-}CH_2CH_2OH$	0.68 meq/g	ion exchange of Ag(I), Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), Fe(III), and Th(IV)	210
Silica gel	≡$SiCH_2C_6H_4(p)CH_2N(CH_3)_2$	0.73 meq/g	ion exchange of Ag(I), Zn(II), Mg(II), Ca(III), Ba(II), Sr(II), Fe(III), and Th(IV)	210
Silica gel	≡$SiCH_2C_6H_4(p)CH_2N(CH_2C_6H_5)_2$	---	Rh-complex as catalyst	236
Acylated monoamines				
Silica SI-100	≡$Si(CH_2)_3NHCOCH_3$	1.41 meq/g	exclusion chromatography	730,671
Silica gel	≡$Si(CH_2)_3N(CH_3)COCH_3$	---	sorption of U(VI), Th(IV), and Zr(IV)	153
Hypersil	≡$Si(CH_2)_3NHCOC_6H_{13}$	---	phases for HPLC of organic compounds	752

Support	Phase	Capacity	Application	References
Hypersil	$\equiv Si(CH_2)_3NHCOC_7H_{15}$	---	phases for HPLC of organic compounds	752
Silica gel	$\equiv Si(CH_2)_3NH$-fatty acid residue	---	surface characteristics and comparison with C18 HPLC support	337
Microparti-culate silica	$\equiv Si(CH_2)_3NHCOC(CH_3)=CH_2$	---	further synthesis of immobilized crown ethers	359
Silica SI-100	$\equiv Si(CH_2)_3NHCOCF_3$	1.35 meq/g	exclusion chromatography	730,671
Silochrom S-80	$\equiv Si(CH_2)_3NHCOCH_2Cl$	---	immobilization of enzymes	319
Silica	$\equiv Si(CH_2)_3NHCOCH_2CH_2COO$-succinimide	---	reactive intermediate for immobilization of substances for affinity chromatography	334
Silochrom, controlled pore glass, Chromosorb	$\equiv Si(CH_2)_3NHCOCH_2CH_2CONHNH_2$	---	immobilization of t-RNA	726
LiChrosorb Si-60	$-Si(CH_3)_2(CH_2)_3$-(N)-pyrrolidone		HPLC of aromatic hydrocarbons	759
Nucleosil 200	$\equiv Si(CH_2)_3NHCOCH$-$(OCOCH_3)CH(OCOCH_3)$-COOH[residue of (+)-diacetyltartaric acid]	1.19 meq/g	resolution of chiral compounds	760

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Nucleosil 100	$\equiv Si(CH_3)(CH_2)_3NHCOC_6F_5$	4.068 $\mu m/m^2$	support for chromatography	761
Porous glass	$\equiv Si(CH_2)_3NHCO\text{-}C_6H_4(p)NH_2$	---	intermediate for further synthesis	762
Silica gel	$\equiv Si(CH_2)_3NHCO\text{-}C_6H_4(p)NH_2$	---	intermediate for further synthesis	27
Zirconia covered Silochrome	$\equiv Si(CH_2)_3NHCO\text{-}C_6H_4(p)NH_2$	---	immobilization of enzymes	93
Silica gel	$\equiv Si(CH_2)_3NHCOC_6H_4(p)NH_2$	---	TLC of cations	458
Adsorbosil LC, Polygosil 60-10	$\equiv Si(CH_2)_3NHCOC_6H_4(p)NH_2$	---	intermediate for further synthesis	353
Silica gel	$\equiv Si(CH_2)_3NHCOC_6H_4(p)NH_2$	---	synthesis and characterization, intermediate in the synthesis of quinolinol derivative	395
Zirconia covered silochrome	$\equiv Si(CH_2)_3NHCO(CH_2)_nNHCOC_6H_4(p)NH_2$ n = 2 or 6	---	immobilization of enzymes	93

Support	Phase	Capacity	Application	References
Hitachi gel, 3056	≡Si(CH_2)$_n$NHCOCH_2-**T13** n = 3 or 11 and aryl substituted derivatives	---	HPLC separation of chiral compounds	**763**
Hitachi gel, 3056	≡Si(CH_2)$_{11}$NHCOCH_2-**T14** and aryl substituted derivatives	---	HPLC separation of chiral compounds	**763**
LiChrosorb Si-60	≡Si(CH_2)$_3$NHCOC_6H_3(3,5)(NO_2)$_2$	---	HPLC, "charge-transfer" chromatography	**764**
Silica gel	≡Si(CH_2)$_3$NHCOCH_2CH_2-**T15**	---	fluoresces with Zn(II) and Ca(II) ions	**526**
LiChrospher SI-100	≡Si(CH_2)$_3$NHCOCH_2OCH_2CH_2OCH_2CON(C_2H_5)$_2$	---	synthesis	**765**
LiChrospher	≡Si(CH_2)$_3$NHCOCH_2OCH_2CH_2OCH_2CON(C_2H_5)$_2$	---	HPLC of steroids	**766**
Silica gel	≡Si(CH_2)$_3$NHCOCH_2-T16	---	chiral stationary phase	**749**
Silochrome	≡Si(CH_2)$_3$NHCOCH_2SH	---	synthesis	**318**
Silochrome	≡Si(CH_2)$_3$NHCOCH_2-S-S-2-pyridyl	---	synthesis	**318**
Silochrome	≡Si(CH_2)$_3$NHCOCH_2-S-S-C_6H_4(*o*)NO_2	---	synthesis	**318**

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Silica gel LiChrosorb, controlled pore glass	$\equiv Si(CH_2)_3NHCOCH_2COCH_3$	---	separation of UO_2(II), Cu(II) and Fe(III)	767
Silica gel	$\equiv Si(CH_2)_3NHCOCH_2COCH_3$	---	separation of organic compounds	323
Silica gel	$\equiv Si(CH_2)_3NHCOCH_2COCH_3$	0.7 meq/g	sorption of Fe(III) and Cu(II)	229
Silica gel	$\equiv Si(CH_2)_3NHCOCH_2COCH_3$	---	TLC separation of Cd(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II) and Zn(II)	136
Partisil 5	$\equiv Si(CH_2)_3$-(N)-phthalimide	---	HPLC of polynuclear aromatic hydrocarbons	768
LiChrosorb Si-100	$\equiv Si(CH_2)_3$-(N)-tetrachloro--phthalimide	---	HPLC of aromatic compounds	166
Urethanes				
Hypersil	$\equiv Si(CH_2)_3NHCOOCH_3$	---	phases for HPLC of organic compounds	752
For amino acid and peptide derivatives, see separate part of this table				
UREAS				
Silica SI-100	$\equiv Si(CH_2)_3NHCONH_2$	---	exclusion chromatography	730,671

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NHCONH(CH_2CH_2NH)_4CH_2CH_2NH_2$ and chiral derivatives	---	chiral stationary phases	769
Silica gel	$\equiv Si(CH_2)_3NHCONR_2$	---	synthesis	335b
Aerosil	$\equiv Si(CH_2)_3NHCONH$-**T17**	---	separation and determination of Zn(II), Cd(II), Hg(II), Cr(III),Mn(II),Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(I), and Pd(II)	770,771
Spherisorb	$\equiv Si(CH_2)_nNHCONH$-**T18** n = 3 or 11	---	chiral stationary phase	772
Silica gel	$\equiv Si(CH_2)_3NHCONHC_6H_4(p)HgOCOCH_3$	---	support for sequencing of peptides	773
Silica gel	$\equiv Si(CH_2)_3NHCONH$-spacer-NHCO-cellulose		chiral stationary phase	332
QUATERNARY AMMONIUM SALTS				
Silica gel, controlled pore glass	$\equiv Si(CH_2)_nN^+(CH_3)_3X^-$	---	ion exchanger	525
Kieselgel	$=Si(CH_3)CH_2N^+(CH_3)_3OH^-$	0.3-0.8 meq/g	ion-exchanger	246

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Kieselgel	$\equiv SiCH_2N^+(C_4H_9)_3OH^-$	0.3-0.8 meq/g	ion-exchanger	246
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3N^+(CH_3)_3$	---	separation of H_2SeO_4, $HMnO_4$, H_3AsO_4, $H_2Cr_2O_7$, H_2MoO_4, H_2WO_4, and H_3VO_4	495
Silica	$\equiv Si(CH_2)_3N^+(CH_3)_3$	---	binding of formazanes and their complexes	774
Silochrome S-80	$\equiv Si(CH_2)_3N^+(CH_3)_3Cl^-$	---	sorption of Sc(III)	741
Silica gel alumina, zirconia, glass	$\equiv Si(CH_2)_3N^+(CH_3)_3X^-$ X = I, $CH_3C_6H_4(p)SO_3$	---	anion exchanger	254
Silica gel, glass, titania, zirconia, alumina	$=Si(CH_3)(CH_2)_3N^+(CH_3)_3$	---	TLC support, adsorbent for heavy metal ions, anion exchanger	647
Silica gel, alumina, glass, titania	$=Si(CH_3)(CH_2)_3N^+(CH_3)_3X^-$ X = I or $CH_3C_6H_4SO_3$ polymeric	1.18 meq/g	synthesis of high capacity material	254
Macrosorb	$\equiv Si(CH_2)_3N^+(CH_3)_2CH_2C_6H_5Cl^-$	0.6-0.7 meq/g	strong anion exchanger	6

Support	Phase	Capacity	Application	References
Silica gel	$-Si(CH_3)_2(CH_2)_3N^+(CH_3)_2CH_2C_6H_5$		synthesis	**692**
Partisil	$-Si(CH_3)_2(CH_2)_3N^+(CH_3)_2CH_2C_6H_5$		HPLC of nucleic acids	**775**
Silica gel	$\equiv Si(CH_2)_3N^+(C_2H_5)_3$	---	Pd complexes as catalysts	**742**
Silica gel, alumina 60	$\equiv Si(CH_2)_3N^+(C_4H_9)_3Br^-$	0.16 meq/g	phase transfer catalyst	**580,592**
Silica gel	$\equiv Si(CH_2)_3$-pyridinium	---	Pd complexes as catalysts	**742**
Silica gel	$\equiv Si(CH_2)_3$-pyridinium	---	exchange of Cl^-, Br^-, I^-, SCN^-, and ClO_4^- in ethanol. Affinity order: $NaClO_4^-$ > LiCl > Et_4NCl ~ Et_4NBr > nBu_4NI ~ KSCN	**776**
Silica gel, Alumina 60	$\equiv Si(CH_2)_3NHCO(CH_2)_{10}N^+(Bu)_3Br^-$	0.43 0.14 meq/g	phase transfer catalysts	**580,592**
Porasil C	$\equiv SiCH_2C_6H_4(p)CH_2N^+(CH_3)_3Cl^-$	0.0015 meq/g	strong anion exchanger	**267**
Silica gel	$\equiv SiCH_2C_6H_4(p)CH_2N^+(CH_3)_3Cl^-$	0.75 meq/g	ion exchanger	**210,579**
Silica gel	$\equiv SiCH_2C_6H_4(p)CH_2N^+(C_2H_5)_3Cl^-$	0.55 meq/g	ion exchanger	**210,579**

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
Porous silica	$\equiv SiCH_2C_6H_4(p)CH_2N^+(CH_3)_2CH_2CH_2OH$		ion exchanger for organic compounds	690
Spherosil	$\equiv Si(CH_2)_4C_6H_4(p)CH_2N^+(CH_3)_3Cl^-$	0.6-1.53 meq/g	exchange of Cl^-, NO_3^-, I^-, ClO_4^-	465
Silica gel	$-Si(CH_3)_2(CH_2)_4C_6H_4(p)CH_2N^+(CH_3)_3$	0.2 meq/g	HPLC of organic compounds	307
ISOTHIOTHIOCYANATES, THIOAMIDES AND THIOUREAS				
Silica gel	$\equiv SiCH_2NCS$	---	synthesis via thermal decomposition of dithiocarbamate	221
Porous glass, alumina, hydroxyapatite	$\equiv Si(CH_2)_3NCS$	---	binding of enzymes	223
Silica gel	$\equiv Si(CH_2)_3NCS$	---	binding of enzymes	777
Silica gel	$\equiv Si(CH_2)_3NHCS(CH_2)_6CSSEt$	---	enzyme coupling agent	320
Silica gel	$\equiv Si(CH_2)_3$-NH-**T19** a) Ac,Ac' = benzoyl b) Ac = acetyl, Ac'= 3,5-dinitrobenzoyl	---	HPLC support	778,779

Support	Phase	Capacity	Application	References
Silica gel	≡Si(CH$_2$)$_3$NHCSNH(CH$_2$)$_3$Si≡	---	removal of Br$^-$ and F$^-$ from acidic aqueous solutions	121
DITHIOCARBAMATES				
Silica gel	≡SiCH$_2$NHCSS-Alkyl	---	generation of standard gaseous mixtures of thiol via thermal decomposition	221
Controlled pore glass	≡Si(CH$_2$)$_3$NHCSSNa	---	chelating agent	28
Silica gel	≡Si(CH$_2$)$_3$NHCSSNa	0.5-1 meq/g	X-ray fluorescence determination of Hg(II), Cu(II), Zn(II), Ni(II), Pb(II), Eu(III), and Mn(II)	12
Silica gel	≡Si(CH$_2$)$_3$NHCSSNa	0.059 meq/g	Pd complexes as catalysts	220,261,339,265
Partisil 10	≡Si(CH$_2$)$_3$NHCSSNa	---	chromatographic separation of amines	781
Silica gel	≡Si(CH$_2$)$_3$N(CH$_3$)CSSNa	0.5-1 meq/g	X-ray fluorescence determination of Hg(II), Cu(II), Zn(II), Ni(II), Pb(II), Eu(II) and Mn(II) complexes	12
Silica gel	≡Si(CH$_2$)$_3$N(CH$_3$)CSSNa	---	Ni(II), Zn(II) complex formation, influence of ionic strength	518

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
THIURAMS				
Silica gel	$\equiv Si(CH_2)_3NHCSS\}_2$	---	X-ray fluorescence determination of Hg, Cu, Zn, Ni, Pb, Eu and Mn ions	12
Silica gel	$\equiv Si(CH_2)_3NHCSS\}_2$	---	determination of Pb(II)	782
SULFONAMIDES				
Silica SI-100	$\equiv Si(CH_2)_3NHSO_2CH_3$	1.84 meq/g	HPLC of organic compounds	730,671
Silica gel	$\equiv Si(CH_2)_3NHSO_2$-camphyl	---	HPLC of enantiomers	783
Partisil 5	$=Si[C_6H_4(p)SO_2NH_2]$	---	HPLC phases; comparison of properties	203
SCHIFF' BASES, HYDRAZONES AND OXIMES				
Aerosil	$\equiv Si(CH_2)_3N=C(CH_3)CH_2COCH_3$	---	Cu(II), Pd(II) complexes	784
TLC supports	$\equiv Si(CH_2)_3N=C(CH_3)COOC_2H_5$			458
LiChrosorb SI-60	$\equiv Si(CH_2)_3N=$T20	1 meq/g	HPLC of aromatic compounds	314,785

Support	Phase	Capacity	Application	References
TLC supports	$\equiv Si(CH_2)_3N{=}C(C_6H_5)COOC_2H_5$			**458**
Silica gel	$\equiv Si(CH_2)_nN{=}CHC_6H_4(o)OH$	---	removal of Cu(II) from jet fuel	**596**
Aerosil, Silochrome	$\equiv Si(CH_2)_3N{=}CHC_6H_4(o)OH$	---	complexes with Cu, Mo(V) and Pd as catalysts	**443**
Silica gel	$\equiv Si(CH_2)_3N{=}CHC_6H_4(o)OH$	---	studies of stability of aminopropyl residue	**191**
Silica gel	$\equiv Si(CH_3)(CH_2)_3N{=}CHC_6H_4(o)OH$	---	stability studies	**191**
Silica gel	$\equiv Si(CH_3)_2(CH_2)_3N{=}CHC_6H_4(o)OH$	---	stability studies	**191**
Partisil 10	$\equiv Si(CH_2)_3N{=}C(C_6H_5)CH_2COOC_2H_5$	---	chromatographic separation of amines	**781**
Glass	$\equiv Si(CH_2)_3N{=}CH(CH_2)_3CH{=}[N(CH_2)_6N{=}CH{-}(CH_2)_9CH]_n{=}N(CH_2)_{11}CH_3$		capillary columns	**786**
Glass	$\equiv Si(CH_2)_3N{=}CHC_6H_4CH{=}[NC_6H_4N{=}CH{-}C_6H_4CH]_n{-}NC_6H_5$		capillary columns	**786**
LiChrosorb	$\equiv SiC_6H_4(p)NHN{=}CH$-2-pyridyl	---	ion chromatography of Mn(II), Fe(II), Cd(II), Zn(II), Co(II), Pb(II), and Cu(II)	**787**
Silica gel	$\equiv Si(CH_2)_nNHCO$-spacer-$C(R){=}NHOH$ n = 3,4	---	solid phase oxime reagent for LC	**335a**

(continued)

Table 2. Continued.

Support	Phase	Capacity	Application	References
DERIVATIVES WITH NITROGEN CONTAINING AROMATIC RESIDUES				
SnO_2 electrode	$\equiv Si(CH_2)_2$-2-pyridyl	---	electrochemical behavior of ligand anchored to the electrode surface	654
Glassy carbon	$\equiv Si(CH_2)_2$-2-pyridyl	---	electrochemical behavior of ligand anchored to the electrode surface	727
SnO_2, TiO_2, glassy carbon, glass electrodes	$\equiv Si(CH_2)_2$-2-pyridyl	---	electrochemical behavior of ligand anchored to the electrode surface	732
Alumina	$\equiv Si(CH_2)_2$-2-pyridyl	---	performance and selected applications in HPLC liquid chromatography	24
Silica gel	$\equiv Si(CH_2)_2$-2-pyridyl	---	$PdCl_2$ complex as catalyst	698
Aerosil Khim.	$\equiv Si(CH_2)_2$-2-pyridyl	---	synthesis; cobalt complex and its interaction with oxygen	214,789,790
Silochrom S-80	$\equiv Si(CH_2)_4$-2-pyridyl	---	selective sorption of Sc(III)	741
Silica gel, alumina, glass	$\equiv Si(CH_2)_4$-pyridyl	---	Rh, Pd and Pt complexes as heterogenized catalysts for hydrosilylation	188
Silica gel	$\equiv Si(CH_2)_4$-3-pyridyl	0.32 meq/g	Pd-complexes	220,261

Support	Phase	Capacity	Application	References
Silica gel	≡Si$(CH_2)_4$-3-pyridyl	---	Rh-complex as catalyst	236
Silochrome	≡Si$(CH_2)_3$-T21	---	preconcentration and separation of Hg(II) from alkylmercury compounds	514,791
Silica	≡Si$(CH_2)_3$-N-imidazolyl	---	influence on hydrolysis reaction	565
Davison	≡Si$(CH_2)_3$-T22-L L = Cl,O_2,CO	---	reversible adsorption of oxygen	792
Silica gel	≡Si$(CH_2)_3$-N-imidazolyl	0.357 meq/g, varied, dependent of metal ion	complexes with MX_2 (M = Mn, Ni, Cu, Zn, Cd; X = Cl, Br, I) and $FeCl_3$	793
Silica gel	≡Si$(CH_2)_3$-N-imidazolyl	---	complexes with CoX_2 (X = CH_3COO, Cl, NO_3, ClO_4, SCN)	794
LiChrosorb Si-60	≡Si$(CH_2)_3$-7-theophyline	---	HPLC support	795
LiChrosorb Si-60	≡Si$(CH_2)_3$-1-theobromine	---	HPLC support	796
Porous silica	≡Si$(CH_2)_2C_6H_4(p)CH_2$-adenine or -uracil	0.6 meq/g 0.34 meq/g		308

Table 3. Solid Supports Containing Diamine, Acylated Diamine, Schiff Base, Dithiocarbamate, Triamine and Polyamine Side Groups

Support	Phase	Capacity	Application	References
DIAMINES AND DERIVATIVES				
Silica gel	$\equiv SiCH_2CH(NH_2)CH_2NH_2$ (+), chiral	---	derivatives as chiral stationary phases	797
Silica gel	$\equiv SiCH_2CH(CH_3)NHCH_2CH_2NH_2$	---	Pd complexes as catalysts	261
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	support for chromatography	634
Porasil C	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	synthesis	301
Fiberglass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	further synthesis	224
Silica gel, glass, $TiO(OH)_2$, $ZnO(OH)_2$, $Al(OH)_3$	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	TLC support, adsorbent for heavy metal ions	647
SnO_2 electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	electrochemical behavior of ligand immobilized on electrode surface	654
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$ polymeric	---	rapid sorption of Cu(II), Zn(II), Hg(II), Pb(II), and Co(II) and slow sorption of Cr(III) and Mn(II) from water	451
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	selective or general preconcentration of various anions	495

Support	Phase	Capacity	Application	References
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	extraction of H_2SeO_4, $HMnO_4$, H_3AsO_4, $H_2Cr_2O_7$, H_2MoO_4, H_2WO_4, and H_3VO_4 in the presence of I^-, Br^-, IO_3^-,IO_4^-, and BrO_3^-	**495**
Graphite, glassy carbon	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	electrochemical behavior of ligand immobilized on electrode surface	**727**
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	effect of ionic strength on sorption of Cu(II), Co(II), Ni(II), Mn(II), and Zn(II). Influence of concentration of Ca(II), and Mg(II)	**518**
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.07 meq/g	Pd complexes as catalysts	**220**
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	support for chromatography	**634**
SnO_2, TiO_2 glassy carbon, glass electrode surface	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	electrochemical behavior of ligand anchored to the electrode surface	**732**
PtO, electrode surface	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	electrochemical behavior of ligand on electrode surface	**798**
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	removal of UO_2^{2+} from carbonate solutions	**510**
Controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	sorption of molybdenum under acidic conditions	**133**

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
Partisil 5	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	a screen was proposed to enable identification of the bonded support	203
SnO_2, RuO_2, TiO_2, Pt/PtO, carbon	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	X-ray photoelectron spectroscopic study	438
Aerosil 380	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	1.1 diamine group/nm^2	complex with $Rh_6(CO)_{16}$ cluster	710
Mineral carriers, silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	synthesis of sorbent	652
Silica SI-100	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	exclusion chromatography of organic compounds	671
Silochrom SI-120	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	sorption and separation of Fe(III), Cu(II), Zn(II)), Co(II), and Mn(II)	674
Partisil 10	$\equiv Si(CH_2)_3$-T23	---	HPLC stationary phase	799
Silochrom S-120	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	sorbent for chromatography, and as complexing agent for removal of transition metal cations from solutions	653

Support	Phase	Capacity	Application	References
Silochrom S-120	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	rhodium complexes as catalysts	800
TLC support	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	separation of Fe(III), Cu(II), Ni(II), and Zn(II)	458
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	complex with $[Rhpy_4Cl_2]Cl$ and H_2PtCl_6	734,735
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	pH dependence of sorption of Cu(II), Co(II), Mn(II), Ni(II), and Zn(II)	675
Xerogel, LiChrosorb SI-100	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	synthesis and application to adsorption chromatography	286
Silica	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	determination of protonation constants of anchored diamine	440
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	studies of relation of coverage of the silica gel surface and its HPLC properties	801
Controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.35 meq/g	selective sorption of uranium from carbonate solutions containing molybdate in a continuous flow system	231
Porasil	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	complexes with Co(III) as stationary phases for liquid chromatogrophy	802

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$ monolayer,polymeric polymeric	2.4 μm/m² 3.8 μm/m²	complexes of Cu(II), Ni(II), Zn(II) and aminoacids	124
Silica gel 7	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	further synthesis	459
Silochrom S-120	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.8 meq/g	sorption of Zn(II), Cu(II), Co(II), Ni(II), and Mn(II)	226
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.35 meq/g	metal ion removal from wastewaters	512
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	Co(III) complexes used for ligand exchange chromatography	532
Partisil 10	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	Co(III) complexes used for ligand exchange chromatography	803,804
Partisil 10	$\equiv Si(CH_2)_3$-T24	---	optically active complex for resolution of enantiomers	805
Silochrom S-120	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	Pd(II), Ir(IV) and Pt(IV) separation from Fe(III) and other transition elements	598
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.75 meq/g	quantitative determination of Cu(II) complex using photothermal beam deflection photoacoustic spectroscopy	404
Cosmosil 5SL	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	Cu(II) complexes for ligand exchange HPLC of amines	806

Support	Phase	Capacity	Application	References
Polygosil 60-10	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	Cu complex in precolumn for enrichment of amino acids and carboxylic acids during HPLC separation	807
Porous glass	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	---	anion selective membrane for potentiometric studies	808
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NH_2$	0.1 meq/g	affinity adsorbent for thrombin purification	747
Silica gel	≡Si-spacer-(-)1,2-diamino-cyclohexane	---	resolution of aminoacids on Cu complex (ligand exchange chromatography)	533,809
Silochrom S-120, Silica gel	$\equiv Si(CH_2)_3NH(CH_2)_3NH_2$	---	rhodium complexes as catalysts	800
Silica gel	$\equiv Si(CH_2)_3NH(CH_2)_3NH_2$	---	complex with Na_2PdCl_4, $[Rhpy_4Cl_2]Cl$, and H_2PtCl_6	734,735
Silochrom Si-80	$\equiv Si(CH_2)_3NH(CH_2)_6NH_2$	---	removal of phenol and benzoic acid from water	664
Silica gel	$\equiv Si(CH_3)(CH_2)_4NHCH_2CH_2N(CH_3)_2$	---	HPLC support	2
Silica gel	≡Si(CH$_2$)$_3$-(4)-imidazoline	2.2 μm/m^2	high performance exclusion chromatography of water soluble polymers	671
Silica gel	$-Si(CH_3)_2CH_2CH_2$-T25	---	HPLC support	810

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
Silica	≡Si(CH_2)$_3$NH-3-pyridyl	---	sorption of transition metals from nonaqueous solutions	509
Aerosil	≡Si(CH_2)$_3$NHCH_2-2-quinolyl	---	separation and determination of Zn(II), Cd(II), Hg(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(I), and Pd(II)	771,811
Aerosil	≡Si(CH_2)$_3$NHCH_2-8-quinolyl	---	Cu(II) and Co(II) complexes in nonaqueous solution	811
Aerosil	≡Si(CH_2)$_3$NHCH_2-8-quinolyl	---	separation and determination of Zn(II), Cd(II), Hg(II), Cr(II), Mn(II), Fe(II), Fe(III), Co(II), Mi(II), Cu(II), Ag(I), and Pd(II)	771,811
Aerosil A-175	≡Si(CH_2)$_3$NHCH_2-8-quinolyl	0.42 meq/g	structure of Pd(II) complexes	812
Kieselgel or Silica Whoelm	≡Si(CH_2)$_3$NHCH_2CH_2NHCH_2-5-(8-hydroxy)quinolyl	---	separation of cations	355
Silica gel	≡Si(CH_2)$_3$NHC$_6H_3$(2,4)(NH_2)$_2$	---	intermediate in further synthesis	321
Porasil C	≡Si(CH_3)(CH_2)$_4$NH(CH_2)$_2$N(CH_3)$_2$	---	HPLC support	2
Acylated diamines				
PtO electrode	≡Si(CH_2)$_3$NHCH_2CH_2NHCOC_6H_5	---	electrochemical behavior of ligand anchored to the electrode surface	741

Support	Phase	Capacity	Application	References
RuO_2 electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOC_6H_4(m)NO_2$		electrochemical behavior of ligand on electrode surface	813
RuO_2 electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOC_6H_4(p)NO_2$		electrochemical behavior of ligand on electrode surface	813
RuO_2 electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOC_6H_3(3,5)(NO_2)_2$		electrochemical behavior on electrode surface	813
PtO electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOC_6H_3(3,5)(NO_2)_2$		electrochemical behavior on electrode surface	798
TLC support	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOC_6H_4(p)NH_2$		TLC separation of Fe(III), Cu(II), Ni(II), and Zn(II)	458
Silica gel, LiChrosorb SI-100, Controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCH_3$		complexes with UO_2(II), Cu(II), and Fe(III)	767
TLC supports	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCH_3$		TLC separation of Fe(III), Cu(II), Zn(II) and Ni(II)	458
LiChrosorb SI-100	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCH_3$	1.45 meq/g	separation of organic compounds	323
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCH_3$		Fe(III) and Cu(II) complexes, FT-IR, ^{13}C NMR and photocaustic spectroscopy	229

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
TLC Silica gel 7	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCH_3$		TLC separation of Cd(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II)	**136**
TLC supports	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COCF_3$		separation of Fe(III), Cu(II), Ni(II), and Zn(II)	**458**
SnO_2, RuO_2 TiO_2, Pt/PtO, electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCO$-**T26**	---	electrochemical behavior on electrode surface	**814**
SnO_2, RuO_2 TiO_2, Pt/PtO electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2$-**T27**	---	electrochemical behavior on electrode surface	**814**
TLC supports	$\equiv Si(CH_2)_3NHCH_2CH_2NHCOCH_2COC_6H_5$		TLC separation of Fe(III), Cu(II), Ni(II), and Zn(II)	**458**
Porous glass, Silica gel	$\equiv Si(CH_2)_3$-**T28**	0.316 meq/g 0.378 meq/g	separation of alkaline, alkaline earth cations, ammonia, and organic cations	**400**
Silica and controlled pore glass	$\equiv SiC_6H_4(p)CH_2$-**T28**	---	separation of alkali and alkaline earth cations	**400**

Support	Phase	Capacity	Application	References
SCHIFF' BASES				
Silica gel 7	$\equiv Si(CH_2)_3NHCH_2CH_2N{=}C(CF_3)CH_2COOC_2H_5$		TLC of Fe(III), Cu(II), and Ni(II)	458
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2N{=}C(CF_3)CH_2COOC_2H_5$		HPLC of Cu(II)	459
DITHIOCARBAMATE DERIVATIVES OF DIAMINES				
Fiberglass	$\equiv Si(CH_2)_3NHCH_2CH_2NHCSS^-$	---	detection limit 10 ppb of Pb, Ca, Tl and Hg cations	224
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3NHCH_2CH_2NHCSS^-$	---	effect of ionic strength on complexation of Cu(II), Co(II), Ni(II), and Zn(II). Determination of Pb(II), Au(II) and Fe(III) in redistilled water	518
TLC supports	$\equiv Si(CH_2)_3NHCH_2CH_2NHCSS^-$	---	TLC separation of Fe(III), Cu(II), Ni(II), and Zn(II)	458
Silica gel	$\equiv Si(CH_2)_3N(CSS^-)CH_2CH_2NHCSS^-$	---	X-ray fluorescence determination of complexed Hg(II), Cu(II), Zn(II), Ni(II), Pb(II), Eu(III), and Mn(II)	12
Silica gel, controlled pore glass	$\equiv Si(CH_2)_3N(CSS^-)CH_2CH_2NHCSS^-$	---	effect of ionic strength on complexing of Cu(II), Co(II), Ni(II), and Zn(II). Determination of Pb(II), Au(II) and Fe(III) in redistilled water	518
TLC supports	$\equiv Si(CH_2)_3N(CSS^-)CH_2CH_2NHCSS^-$	---	TLC separation of Fe(III), Cu(II), Ni(II), and Zn(II)	458

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
Polygosil 60-10	$\equiv Si(CH_2)_3N(CSS^-)\text{-}CH_2NH\text{-}CSS^-$	---	separation of Hg(II), Ag(I), Cu(II), Pb(II), Cd(II), and Zn(II)	316
SULFONAMIDES				
SnO_2 electrode	$\equiv Si(CH_2)_3NHCH_2CH_2NHSO_2$-1(5-dimethylamino)naphthyl	---	electrode behavior	524
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2\text{-}NHSO_2$-1-(5-dimethylamino)naphthyl	---	fluorescing support for detection of radioactive and non-fluorescing substances	525
DIAMMONIUM SALTS				
Silica	**T29**	---	photoelectrochemical generation of H_2	589
DIAMINES WITH $\equiv SiC_3$ STRUCTURES				
Silica gel titania, zirconia, alumina	$\equiv Si[(CH_2)_3N(CH_3)_2]_2$	---	anion exchanger, TLC support, and adsorbent for heavy metal ions	647
TRI- AND POLYAMINES AND DERIVATIVES				
Silica gel	$\equiv SiCH_2NH(CH_2)_2NH(CH_2)_2NH_2$	---	HPLC support	815

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_3)\text{-}CH_2NH(CH_2)_2NH(CH_2)_2NH_2$		HPLC phase	2
Silica SI-100	$\equiv Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$	---	HPLC of polymers	671
Silica gel	$\equiv Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ monomeric and polymeric	---	complexes of Cu(II), Ni(II), Zn(II), and amino acids	124
Silica gel	$\equiv Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$	---	preconcentration of Au(III)	816
Cosmosil 5SL	$\equiv Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$	---	Cu(II) complexes for ligand exchange HPLC	806
Silica gel,	$\equiv SiR_2\text{-}Z\text{-}CH_2\text{-}X$ R = OH or organic residues Z = divalent organic radicals $X = NHR'[(CR'_2)_nNH]_m(CR'_2)_nNHR'$ or $N(CH_2CH_2NH_2)_3$	---	removal of heavy metals, transition metals and actinides (Co, Pb, U)	596
Silochrom SI-100	$\equiv Si(CH_2)_3NH(CH_2CH_2NH)_4H$	>1.0 meq/g	complexes with Zn(II), Cu(II), Co(III), Ni(II), and Mn(II)	226
Silochrom SI-100	$\equiv Si(CH_2)_3NH(CH_2CH_2NH)_4H$	---	synthesis of sorbent	652
Silica gel	$\equiv Si(CH_2)_3NH(CH_2CH_2NH)_4H$	---	pH dependence of complexation of Cu(II), Co(II), Zn(II) Mn(II), and Ni(II),	675
Silica gel	$\equiv Si(CH_2)_3NH(CH_2CH_2NH)_4H$	---	sorbent for transition metal ions	817

(continued)

Table 3. Continued.

Support	Phase	Capacity	Application	References
Porous glass	≡Si$(CH_2)_3$-**T30**	---	enrichment of Cu(II), Cd(II), Ni(II), Pb(II), Co(II), Zn(II), Ca(II), and Fe(III)	**818**
Silica, controlled pore glass	≡Si$(CH_2)_3$-**T31**	---	synthesis	**356**
Controlled pore glass, Silica gel	≡Si$(CH_2)_3$[NH$(CH_2)_2$N][$(CH_2)_2$N{$(CH_2)_3$Si≡}-[$(CH_2)_2$NH]$_n$H	---	removal of transition metal cations	**819**
Siliceous materials	≡Si$(CH_2)_n$$(NHCH_2CH_2)_m$$(CH_2)_n$Si≡ n = 2 - 4 m = 2 - 4	---	removal of transition metal cations	**496**
Spherosil	-R{CH(CH_2OH)N[$CH_2CH_2NH_2$]$_2$}$_2$	---	HPLC support detailed structure not reported	**465**

Table 4. Solid Supports Containing Amino Acid, Peptide, Aminophosphonic Acid, Azo, Glycidoxypropyl, Crown Ether and Grafted Polymer Side Groups

Support	Phase	Capacity	Application	References
AMINOCARBOXYLIC AND AMINO ACID DERIVATIVES				
Unnatural amino acid derivatives				
Silica gel	$\equiv SiCH_2N(CH_2COOH)_2$ monomeric	---	Pd complexes as catalysts	742
Silochrom	$\equiv SiCH_2N(CH_2COOH)_2$	---	Cu(II) complex for ligand exchange chromatography of enzymes	820
Silica gel	≡Si-spacer-iminodiacetic acid - Cu (II) complexes	---	electrochemical determination of uric acid in blood	788
Silica gel	$\equiv Si(CH_2)_3NH$-T32	---	affinity for Ag(I), Mg(II), Pd(II), Ni(II), Cd(II), Zn(II), and Cu(II)	821
Silica gel	$\equiv Si(CH_2)_3NH$-T32	---	sorption of Cu(II), Ni(II) and Zn(II). UV-VIS and FTIR spectroscopy	675
Silica gel, mineral carriers	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	immobilization of organic ligands on mineral supports	652
Silochrom S-120	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	separation of Fe(III), Cu(II), Zn(II), Co(II) and Mn(II) on a column	675

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	pH dependence of sorption of Cu(II), Co(II), Mn(II), Ni(II) and Zn(II)	822
Silochrom	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	removal of transition metal cations from solutions	823
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	X-ray fluorescence determination of pre-concentrated Fe, Co, Ni, Cu, V, and Pb ions	520
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	2.4 meq/g	sorption of Cu(II), Ni(II), Zn(II) and amino acids	124
Silochrom S-120	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	sorption of Zn(II), Cu(II), Co(II), Ni(II) and Mn(II)	226
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	determination of iron in alloys	599
Silica gel monomeric	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	Pd complexes as catalysts	742
Unknown	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	determination of Sn in alloys	824
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	quantitative absorption of Ti(IV) in the presence of H_2O_2	372
Cosmosil 5SL	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	Cu complexes for HPLC separation of amines	806
Silica gel	$\equiv Si(CH_2)_3N(CH_2COOH)_2$	---	Concanavalin A was immobilized to the anchored ligand complex via its Cu(II) complex	825

Support	Phase	Capacity	Application	References
Unknown	$\equiv Si(CH_2)_3O(CH_2)_2O(CH_2)_2N(CH_2COOH)_2$		Cu(II) complex as solid phase for affinity chromatography	528
Glass support comm.	$\equiv Si(CH_2)_3N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$		separation and determination of Cu(II), Pb(II) and Zn(II) in sea water	826
Silica gel	ibid.,	---	Fe(III), Co(II), Ni(II), Cu(II), V(V), Pb(II) sorption and determination by X-ray fluorescence	
Silica gel	ibid.,	1.48 meq/g	sorption of Cu(II), Ni(II), Zn(II) and amino acids	124
Unknown	ibid.,	0.161 meq/g	sorption, preconcentration and determination of Cd(II), Co(II), Ni(II), Zn(II) and Mn(II) in coastal seawater	507
Mercosorb Si-60	$\equiv Si(CH_2)_3NHCH_2CH_2COOH$	0.45 meq/g	HPLC of organic compounds	6
Unnatural aminoacids anchored via amide bonds				
Silica gel	$\equiv Si(CH_2)_3[NHCO(CH_2)_5]_nNH_2$ n = 1-4	---	immobilization of trypsine	325
Silica	(poly)carboxymethylaminosiloxanes	---		827
Silica gel	$\equiv Si(CH_2)_3NHCOCH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$			828

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel	≡Si$(CH_2)_1$NHCOCH_2N$(CH_2COOH)CH_2$-$\}_2$			**828**
LiChrosorb	≡Si$(CH_2)_3$NHCO*CH(C_6H_5)NHCO$C_6H_3(3,5)(NO_2)_2$		separation of racemic phosphine oxides	**829**
Natural amino acid derivatives				
Amino acids anchored via amine group				
LiChrosorb Si-100	≡SiCH_2-(N)-proline or hydroxyproline	---	Cu(II) complex for separation of enantiomers	**830,218**
LiChrosorb 60	≡Si$(CH_2)_3$-(N)-L-proline	---	Cu(II) complex for separation of enantiomers	**217**
LiChrosorb Si-100	≡Si$(CH_2)_1$-(N)-proline or hydroxyproline	---	Cu(II) complex for separation of enantiomers	**830,831,218**
Silica gel	≡Si$(CH_2)_3$NHCH(COOH)-$(CH_2)_2NH_2$	135 meq/g	affinity chromatography support	**747**
Silica gel	≡Si$(CH_2)_1$NHCH(COOH)-$(CH_2)_4C(NH_2)$=NH	120 meq/g	affinity chromatography support	**747**
LiChrosorb Si-100	≡Si$(CH_2)_8$-(N)-proline or hydroxyproline	---	Cu(II) complex for separation of enantiomers; study of influence of spacer length	**830,218**

Support	Phase	Capacity	Application	References
Silica gel	≡$SiCH_2CH_2C_6H_4(p)CH_2$-(N)-proline and hydroxyproline	---	Cu(II) complex for separation of enantiomers	**832**
LiChrosorb Si-100	≡$SiCH_2CH_2C_6H_4(p)CH_2$-(N)-hydroxyproline	---	Cu(II) complex for separation of enantiomers	**830,218**
Silica gel	organosilicon polymer-(N)-proline and hydroxyproline	---	optically active support	**311**
Silica gel	-$Si(R)_2$-spacer-(amino acid)$_n$$NRCHCO_2H$		chiral HPLC support	**833**
Aminoacids or peptides anchored via amide bonding				
Silica Si-100	≡$Si(CH_2)_3NHCOCH_2NHCOCH_3$	1.05 meq/g	exclusion chromatography	**730**
Silica gel	≡$Si(CH_2)_3NHCOCH[CH(CH_3)_2]$NH-Acyl Acyl = formyl, acetyl, propionyl, butyryl, valeryl		separation of racemic benzyloxycarbonyldipeptide methyl esters	**834**
Microparticulate silica	≡$Si(CH_2)_3NHCOCH[CH(CH_3)_2]NHCOCH_3$		resolution of enantiomers	**324**
Silochrom Si-80	≡$Si(CH_2)_3NHCOCH[(CH_2)_3CH_3]NHCOCH_2Cl$		further reaction	**835**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silochrom	≡Si(CH$_2$)$_3$NHCOCH[(CH$_2$)$_4$CH$_3$]NHCOCH$_2$NH$_2$		synthesis of reactive diazoacetyl derivative	835
Si-80			for binding of proteins	
LiChrosorb Si-100	≡Si(CH$_2$)$_3$NHCOCH[CH(CH$_3$)$_2$]NHCOOC(CH$_3$)$_3$		separation of chiral amino-acids	327
LiChrosorb Si-100	≡Si(CH$_2$)$_3$NH-**T33**	---	separation of chiral amino acids	327
Kieselgel	≡Si(CH$_2$)$_3$NH-**T34**	---	Co(II) and Cu(II) complexes as stationary phases for chiral recognition	328
Partisil S (Spherosil)	≡Si(CH$_2$)$_3$NH-**T34**	---	Cu(II) complex as stationary phase for chiral recognition	836
Silica gel	≡Si(CH$_2$)$_3$NHCOCH(CH$_2$COOH)-NH$_2$ or residue of phenylalanine or tryptophane		intermediate in synthesis	326
Hypersil	≡Si(CH$_2$)$_3$NHCOCH(CH$_2$C$_6$H$_5$)NH-2,4-dinitrophenyl		chiral stationary phase for resolution of helicenes	752
Develosil 100/10	≡Si(CH$_2$)$_3$NH-histidine residue		synthesis of peptides	329
Unknown	≡Si(CH$_2$)$_3$NHCOCH[CH(CH$_3$)$_2$]NHCONHC(CH$_3$)$_3$		resolution of enantiomers	837

Support	Phase	Capacity	Application	References
Silochrom	$\equiv Si(CH_2)_3NHCOCH(CH_2COOH)NH_2$ and residue of L-asparagine, L-hydroxyproline, L-phenylalanine, D-valine or L-lysine		synthesis of peptides	**330**
Silica gel	$\equiv Si(CH_2)_3NHCOCH[CH_2CH(CH_3)_2]NHCHO$ and $-COCH(CH_2C_6H_5)NHCHO$		HPLC support	**838**
Silica gel	$\equiv Si(CH_2)_3NHCOCH(R)N=T20$ R = H, CH_3, $CH(CH_3)_2$ and $CH_2C_6H_5$			**314,785**
LiChrosorb	$\equiv Si(CH_2)_3NHCOCH(R)NHSO_2$-camphyl R = $CH_2CH(CH_3)_2$ or $CH_2C_6H_5$		separation of enantiomeric drugs	**783**
LiChrospher Si-100	$\equiv Si(CH_2)_3NHCOR$ where COR denotes residue of Boc-L-valine, Boc-L-isoleucine Boc-L-phenylalanine, Boc-L-tyrosine Boc-L-alanine, Cbz-L-valine Boc-D-valine, Cbz-D-valine Boc-L-proline, Boc-L-valine with modified spacer and Boc-peptides		HPLC separation of (*R,S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol	**839**
Hitachi gel 3056	$\equiv Si(CH_2)_nNHCOCH[CH_2CH(CH_3)_2]NHCO$-2-naphthyl or $-COCH(C_6H_5)NHCOC_6H_3(3,5)(NO_2)_2$ n = 3 or 11		chiral stationary phase	**840**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel	-$Si(CH_3)_2(CH_2)_{10}CONHCH[CH(CH_3)_2]COOH$	0.41 meq/g	synthesis of chiral stationary phase	**245**
Amino acids anchored via an ester bond				
Porasil C, Corasil II	$\equiv Si(CH_2)_2C_6H_4(p)CH_2O(COCH_2NH)_nH$ n = 1-7	---	synthesis of support	**310**
Partisil 10	$\equiv SiCH_2CH_2C_6H_4(p)CH_2O$- ester of valyl-phenylalanyl-valine	0.26 meq/g		**841**
BioSil A	$\equiv SiCH_2CH_2C_6H_4(p)CH_2O$- ester of dipeptides	---	HPLC column packings	**842**
Aminocarboxylic acids anchored via glycidoxypropyl silylated supports, including natural amino acids				
Silochrom S-80	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2N(CH_2COOH)_2$		ligand exchange chromatography of nucleases	**820,843**
Silica gel	$\equiv Si(CH_2)_nO(CH_2)_mCH(OH)CH_2$-(N)-tryptophane residue		Cu(II) complexes as HPLC packing materials	**346a**
LiChrosorb	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2$-(N)-residue of L- and D-proline, L-hydroxyproline, L-valine, and L-histidine		Cu(II) complex for HPLC separation of racemic amino acids	**345,241,844**

Support	Phase	Capacity	Application	References
Silica gel	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2$-(N)-valine		Cu complex for chiral separation	346c
Develosil 100-5	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2N(CH_2COOH)$-T35		Cu(II) complex as chiral HPLC phase for ligand exchange chromatography	845
Silica gel	$\equiv Si(CH_3)(CH_2)_3OCH_2CH(OH)CH_2$-(N)-proline		Cu(II) complex as stationary phase	346b
Silica gel	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2$-(N)-proline, azetidine carboxylic acid, hydroxyproline, allohydroxyproline, and respective thiocarboxylic acid derivatives		Cu complexes as stationary phases	846
AMINOPHOSPHONIC ACID DERIVATIVES				
Silica gel	$\equiv Si(CH_2)_3NHCH_2PO(OC_2H_5)_2$	---	metal ion complexes	721
Silica gel	$\equiv Si(CH_2)_3NHCH_2CH_2PO(OC_2H_5)_2$	---	metal ion complexes	721
AZO COMPOUNDS				
LiChrosorb SI-100	$\equiv SiCH_2$-T36		sorption of Rh(III), Ir(III), Ir(IVI), Ru(III), Os(IV), Cu(II), Ni(II), Fe(III), Au(III), Pt (IV) and Pd(II). Only the last three are remarkably bonded.	22

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Adsorbosil LC, Polygosil 60-10	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-**T37**		studies of metal ion retention order as a function of their complex stabilities	**353**
Adsorbosil LC, Polygosil 60-10	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-C_6H_4(p)-N=N-CSNHNHC_6H_5 (dithiazone analogue)		sorption of Mn, Cd, Pb, Ni, Zn, Co, and Cu. Retention order Pb < Zn ~ Cu < Ni < Co < Cd < Mn	**353**
Adsorbosil LC, Polygosil 60-10	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-**T38**		sorption of Mn, Cd, Zn, and Pb	**353**
Adsorbosil LC, Polygosil 60-10	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-**T39**		sorption of Mn, Cd, Zn, and Co	**353**
Silica gel	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-(5)-8-hydroxyquinoline	0.07 meq/g	sorption of Cu(II), Zn(II),and Mn(II)	**27**
Controlled pore glass	≡Si(CH_2)$_3$NHCOC_6H_4(p)-N=N-(4)-1-naphthol	0.017 meq/g	sorption of Ni(II), Co(II), Fe(III), Cu(II), Zr(IV), Ti(IV), V(V), and Al(III). Capacity was determined by column breakthrough	**28**

Support	Phase	Capacity	Application	References
Porous glass	≡Si(CH$_2$)$_3$NHCOC$_6$H$_4$(*p*)-N=N-R R = residue of 8-hydroxy-quinoline, dithizone, neocuproine, o-phenanthroline, salicylaldoxime		sorption of many metal ions was studied	317
Porasil B	≡Si(CH$_2$)$_3$NHCOC$_6$H$_4$(*p*)-N=N-(5)-8-hydroxyquinoline	0.05 meq/g	separation of ion systems: Co(II) - Ni(II); Cd(II) - Pb(II) - Zn(II); La(III) - Gd(III) - Yb(III); Mn(II) - Ni(II) - Co(II)	225
Controlled pore glass	ibid.,	0.022-0.03 meq/g	ibid.,	225
Silica gel, LC Porasil B	ibid.,		preconcentration of Cd, Pb, Zn, Cu, Fe, Mn, Ni, and Co ions from sea water prior to determination by AAS	500
Polygosil, controlled pore glass	ibid.		improved synthesis. The metal ion uptake by controlled pore glass bonded 8-hydroxyquinoline decreases with a decrease in pore size	352
Porous glass	ibid.		enrichment of Cu, Cd, Ni, Pb, Co, Zn, Co and Fe(III) ions	818
Polygosil 60-10	ibid.,		sorption of Mn, Cd, Pb, Zn, Co, Tl(I) and Fe ions	162

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Adsorbosil LC, Polygosil 60-10	ibid.,		elution order Mn < Zn ~ Ni ~ Co < Cd < Pb	353
Silica gel	ibid.,		sorption of Al, Cd, Co, Cu, Fe(III), Mg, Mn, Ni, and Zn and separation by back extraction	505
Adsorbosil LC, Polygosil 60-10	≡Si$(CH_2)_3$NHCOC$_6$H$_4$(*p*)-N=N-(5)-2-methyl-8-hydroxyquinoline		elution order Mn < Zn ~ Ni ~ Co < < Cd < Pb	353
Silica gel	≡Si$(CH_2)_3$NHCOC$_6$H$_4$(*p*)-N=N-(5)-8-hydroxyquinoline		Fe(III) complex stationary phase for HPLC	847
Spheron	ibid.,		mercury (II) complex as a precolumn packing in HPLC	848
Glass	≡SiC$_6$H$_4$(*p*)-N=N-C$_6$H$_4$(*p*)N$(CH_3)_2$		reusable glass-bound pH indicators also attached residues of bromocresol purple, crystal violet, bromocresol green, phenolphthalein, and thymolsulfonphthalein	849
Silica gel, Porasil C, controlled pore glass	≡SiC$_6$H$_4$(p)-N=N-(5)-(8-hydroxyquinoline	0.216 meq/g 0.104 meq/g 0.058 meq/g	fast synthesis	232

Support	Phase	Capacity	Application	References
Unknown	≡SiC_6H_4(*p*)-N=N-(1)-2-hydroxynaphthalene			**260**
Silica gel	≡$SiCH_2CH_2$-**T40**		immobilized fluorogenic ligand which fluoresces with Al(III)	**526**
LiChrosorb Si-100	≡$Si(CH_2)_3N$(-**T41**)CH_2CH_2NH-**T41** lipophilized	0.217 meq/g	preconcentration and determination of ^{90}Sr and ^{90}Y	**503**
Silica gel	≡$Si(CH_2)_3$-**T42** there is a mistake in formula in original paper	0.492 meq/g	sorption of Co(II), Hg(II), Cu(II), Pb(II), Cd(II), Zn(II) and Al(III).	**321**
Inorganic powders	Si-spacer-aza compound analogues of Sudan I, methyl red, naphthyl red and other azo dye derivatives			**850**

See under GLYCIDOXYPROPYL DERIVATIVES for other azo compounds

GLYCIDOXYPROPYLSILYLATED SUPPORTS AND DERIVATIVES

Controlled pore glass,	≡$Si(CH_2)_3OCH_2$-**T43**	---		**239**
Silica gel	≡$Si(CH_2)_3OCH_2$-**T43**	---	support for chromatography	**634**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel Si-100	≡Si(CH$_3$)$_2$OCH$_2$-**T43**	---	support for exclusion chromatography	**730**
Partisil 5	≡Si(CH$_3$)$_2$OCH$_2$-**T43**	---	HPLC support	**203**
Silica SI-100, xerogel	≡Si(CH$_3$)$_2$OCH$_2$-**T43** monomeric and xerogel	---		**342,286**
LiChrosorb Si-100	≡Si(CH$_2$)$_3$OCH$_2$-**T43**	---		**345,241**
Silica gel	≡Si(CH$_2$)$_3$OCH$_2$-**T43**	---	HPLC of Fe, Ru, Co, Mn, Mo, and Ni complexes	**624**
Silica gel Si 60H	≡Si(CH$_2$)$_3$OCH$_2$-**T43**	---	NMR studies	**130**
TLC plates	≡Si(CH$_2$)$_3$OCH$_2$-**T43**	---	TLC support	**242**
Silochrom	≡Si(CH$_3$)$_2$OCH$_2$-**T43**	---		**851**
Silica gel	mixed octadecyl- and glycidoxypropylsilylated support		mixed phase for column chromatography	**341**
TLC silica plates	≡Si(CH$_3$)$_2$OCH$_2$-**T43**	---	TLC of metal complexes	**462**

Support	Phase	Capacity	Application	References
Silica gel	-$SiR_2(CH_2)_3OCH_2$-**T43** R = alkyl or aryl	---	chromatographic support	**663**
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OH$	---	HPLC support	**344**
Silica SI-100	ibid.,	0.76 meq/g	support for exclusion chromatography	**730,671**
LiChrosorb SI-100	ibid., monomeric and polymeric		separation of enzymes and peptides	**342,286**
LiChrosorb SI-100	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OH$		separation of organic compounds	**192**
Silica gel	ibid.,	---	synthesis; derivatization of thiols	**233**
Silica	ibid.,	---	mixed phase for HPLC of many complexes of Ni Fe, Ru, Co, Mn, Mo, and Ni	**624**
Siliceous materials	ibid.,	---	separation of t-RNA	**525**
Support	ibid.,	---	separation of mucopolysaccharides	**852**
Silica gel SI-60II	ibid.,	---	NMR studies	**130**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
LiChrosorb SI-60	ibid., polymeric	---	chromatographic support for size exclusion separation of proteins	853
τ-alumina-	ibid., monomeric	---	high enzyme absorptive capacity	746
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2O(CH_2)_mCH_3$ m = 4 - 18; polymeric		HPLC support and synthesis	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCH_2CH_2C_6H_5$ polymeric		ibid.,	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ polymeric		ibid.,	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCH_2COOH$ polymeric		ibid.,	344
LiChrosorb SI-100	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2NH_2$		HPLC of enzymes, peptides, and proteins	342
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2N(C_2H_5)_2$ polymeric		HPLC support and synthesis	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2(NHCH_2CH_2)_4NH_2$ polymeric		HPLC support and synthesis	344

Support	Phase	Capacity	Application	References
LiChrosorb SI-100	$\equiv Si(CH_2)_3OCH_2CH[OCH_2CH_2N(CH_3)_2]CH_2OH$		Weak anion exchanger. Separation of oligonucleotides	854
Silica gel	ibid.,			855
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCH_2CH_2N(CH_3)_2$ polymeric		HPLC support and synthesis	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCH_2CH_2N(C_2H_5)_2$ polymeric		HPLC support and synthesis	344
LiChrosorb, controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2NH(CH_2)_{10}CO$-(4)-1-bromonaphthalene		phosphorescence detection in HPLC	856
LiChrosorb SI-100	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2NHC_6H_4(m)B(OH)_2$	0.25 meq/g	HPLC of carbohydrates, nucleosides and nucleotides	192
LiChrosorb SI-100	ibid.,	0.375 meq/g	separation of catechols	193
Porous silica	ibid.,		synthesis	308
Porous silica	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2NH$-T44		synthesis	308
LiChrosorb SI-60	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2NH(CH_2)_6$-Cibacron Blue F3G-A residue	6 μm/g	separation of proteins	347,857

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silochrom	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2$-R R = residue of Bacitracin or Gramicidin S			349,747
Macroporous glass MPS 1150	product of addition with levo-glucosane			350
Hypersil 100 and 300	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCOCH_2OCH_2COOH$		variable ligand density supports	858
Hypersil 100 and 300	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCOCH_2CH_2COOH$		variable ligand density supports	858
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCOCH_2CN$ polymeric		HPLC support and synthesis	344
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2OCOC_6H_5$ polymeric		ibid.,	816
Controlled porosity glass	$\equiv Si(CH_2)_3OCH_2CH(OH)CH_2SO_3H$ polymeric		ibid.,	344
CROWN ETHERS IMMOBILIZED ON INORGANIC SUPPORTS				
Kieselgel	$-Si(CH_3)_2(CH_2)_3$-18-crown-6		separation of NaOH, HCOONa, C_2H_5COONa, CH_3COONa and $NaHCO_3$	257

Support	Phase	Capacity	Application	References
Silica gel	≡Si$(CH_2)_3$-(3)benzo-15-crown-5		phase transfer catalyst	859
LiChrosorb	-Si$(CH_3)_2(CH_2)_3$-(3)benzo-		synthesis	256
SI-100	-15-crown-5			
Kieselgel	-Si$(CH_3)_2CH_2CH_2$-(4)benzo--15-crown-5		separation of Na^+ and K^+ and anions ClO_3^-, IO_3^-, ClO_4^- and IO_4^-	257
Silica gel	-Si$(CH_3)_2$-**T45** *R,R*-configuration		resolution of amino acids	860
Silica gel G	≡Si$C_6H_4(p)CH_2$-(4)dibenzo-18-crown-6		X-ray fluorescence determination of potassium after uptake from solution	219
Microparti-culate silica	≡Si$(CH_2)_3$NHCO-(4)benzo-15-crown-5			359
Microparti-culate silica	≡Si$(CH_2)_n$-**T46**: n = 1		separation of alkali metal chlorides, iodides, and bromides. Elution order: LiCl < NaCl < CsCl < RbCl < KCl. The iodides and bromides behave similarly.	360,364
	n = 2	0.33 meq/g	Separation of alkali metal chlorides, iodides and bromides. Elution order: LiCl < NaCl < RbCl < KCl < CsCl. The bromides and iodides behave similarly. Elution order NaCl < NaBr < NaI< NaSCN	

(continued)

Table 4. Continued.

Support	Phase		Capacity	Application	References
Spherical silica gel, silica gel	≡Si(CH$_2$)$_3$NHCO-**T47** copolymer irregular			support for ion chromatography of high sodium affinity. Elution order: LiI < KI < NaI and LiCl < K < Cl < NaCl	**165**
Microparticulate silica	≡Si(CH$_2$)$_3$NHCO-**T48** copolymer	m = 1		separation of alkali metal chlorides, iodides and bromides. Elution order: LiCl < NaCl < CsCl < RbCl < KCl. The bromides and iodides behave similarly,	**360,364,365**
		m = 2	0.28 meq/g	elution order: LiCl < NaCl < RbCl < CsCl and $MgCl_2$ < $CaCl_2$ < $SrCl_2$ < $BaCl_2$	
LiChrosorb SI-100	≡Si(CH$_2$)$_3$NHCOC$_6$H$_4$(*p*)CH$_2$OCH$_2$-(4)benzo-18-crown-6			separation of KSCN - $Ba(SCN)_2$; KCl - $BaCl_2$; $Ca(SCN)_2$ - NaSCN; LiSCN - $SrCl_2$ - $CaCl_2$	**367**
Unknown	ibid.,			separation of $Li^+ < Na^+ < Rb^+ < Cs^+ < K^+$; $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$; and $Cl^- < Br^- < NO_3^- < I^- < SCN^-$	**48**
LiChrosorb	≡Si(CH$_2$)$_3$NHCOC$_6$H$_4$(*p*)CH$_2$O-(4)benzo-18-crown-6			ibid.,	**367,48**

Support	Phase	Capacity	Application	References
Siliceous supports	≡Si(CH$_2$)$_m$NHCOC$_6$H$_4$(*p*)CH$_2$OCH$_2$-(4)benzo-12-crown-4, (4)benzo-15-crown-5, (4)benzo-18-crown-6, (4)benzo-21-crown-7, (4)benzo-24-crown-8 and (4)benzo-27-crown-9 m = 2 - 10			**861**
	≡Si(CH$_2$)$_3$OCO-**T49** copolymer		separation of aromatic compounds	**366**
Wakogel LC -SH and SI-100 LiChrosorb	≡Si(CH$_2$)$_3$OCH$_2$CH(OH)CH$_2$NH-(4)benzo-15-crown-5,		$Li^+ < Na^+ \sim Cs^+ < Rb^+ < K^+$ and $Mg^{2+} \sim Ca^{2+} < Sr^{2+} < Ba^{2+}$	**370**
	benzo-18-crown-6 and		$Li^+ < Na^+ < Rb^+ < Cs^+ < K^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$	
	benzo-21-crown-7		$Li^+ \sim Na^+ < K^+ < Rb^+ \sim Cs^+$ and $Mg^{2+} < Li^+ \sim Ca^{2+} < Na^+ < Sr^{2+} < Rb^+ < K^+ < Ba^{2+}$. Also studies of influence on retention of the following anions: Cl^-, Br^-, I^-, NO_2^-, NO_3^-, $HCOO^-$, CH_3COO^-, ClO_2^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, SCN^-, picrate, SO_4^{2-}, $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_6]^{4-}$	
Silica gel	≡Si(CH$_2$)$_3$-**T50**	0.41 meq/g	complexation of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)	**170**
Polygosil	≡Si(CH$_2$)$_3$OCH$_2$CH(OH)CH$_2$-**T51**		Cu(II) complex. Separation of amino acids and carboxylic acids. Sorption of transition metal cations	**807,316,371**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel KOA 2-997	---CO-NH-(4)benzo-15-crown-5 and benzo-18-crown-6		sorption of KF	361b
Silica gel KOA 2-997	---CONH-(4)dibenzo-18-crown-6-NHCO--		sorption of KF	361a
Controlled pore glass	**-T52**		phase transfer catalyst	863
Silica gel	diazacrown ether derivatives			369
Silica gel	$\equiv Si(CH_3)(CH_2)_3O$-**T53** n = 0,1		quantitative removal and separation of Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} from aqueous solutions	497,368
	-T54 R = benzyl or cyclohexyl		quantitative separation of Hg(II) from Ag(I). Stripping of the cations was performed using EDTA or $S_2O_3^{2-}$ solutions	
Kieselgel Si-300	≡Si/different spacers/-azacrown ether: monoaza-15-crown-5, monoaza-18-crown-6, diaza-18-crown-6, tetraaza-12-crown-4, monoaminodicyclohexano-18-crown-6, monoaminodibenzo-18-crown-6, hydroxymethyl-15-crown-5, hydroxymethyl-18-crown-6, 4-hydroxymethylbenzo-15-crown-5, 4-hydroxymethylbenzo-18-crown-6, and hydroxymethylcryptand [2.2.2]		separation of RNA, and tRNA, affinity chromatography of nucleic acids	862

Support	Phase	Capacity	Application	References
ISFET gate	different modes of binding with crown ethers, calixarenes		changing properties of ion selective field effect transistors as sensors for metal cations	**363**
Silica gel	different modes of bonding with crown ethers, azacrown ethers, cryptands, spherands, and calixarenes		Superlig™ materials for separation of metal ions	**601**
AF-amino-	**-T55**			**864**
-Toyopearl 650 gel				
MISCELLANEOUS				
Support	≡Si-**T56** n = 1 or 0 R = $-(CH_2)_1-$ or $-CH_2-CH(CH_3)-$	---	sorption of metal ions	**351b**
Solid support including inorganic	≡Si-different spacers or linear ferrioxamine, cyclic ferrioxamine, ferrichromes, citrate hydroxamate derivatives, rhodotorulic acid, mycobactins, fusarinines, enterobactin, aerobactins, or pseudobactins	---	removal of iron, uranyl and thorium from water (juices)	**593**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel	≡Si(CH_2)$_a$NH-spacer-phthalocyamine dye Cu(II) complex and (blue silica gel)		removal of mutagnic substances from environmental and food materials	865
Support	≡Si-mercaptopropyl + spacer + dye Cibacron Orange, Cibacron Brilliant, Blue FBR-D, Blue F3G-A, and 25 other dyes		HPLC affinity chromatographic supports	866
Support	≡Si-glycidoxypropyl + + spacer + Cibacron Orange, Cibacron Brilliant, Blue FBR-D, Blue F3G-A, and 25 other dyes	---	HPLC affinity chromatographic supports	866
Glass covered with ZrO_2 or NiO	alkyl, azo or sulfonamido+ spacer+ residue of dialkylaniline, phenophthaleine, Erichrome T, methylene blue, and others	---	reusable pH indicators	867
Silica gel	≡Si(CH_2)$_4$-T57	---	Cu complex as HPLC packing materials	346a
Durasil™	unknown	---	large scale removal of radioisotopes from water streams in light reactor nuclear power plants (Cs, Co, Mn, Cr, Ag, and Sr)	607
SiO_2, MgO, Al_2O_3	≡Si-T58	---	separation of organic compounds	663

Support	Phase	Capacity	Application	References
Silochrom S-80	-Si-spacer-cyanuric acid - different groups			**331**
Silica gel	unknown	---	toxic metal removal from electroplating wastewater using silylated silica gel	**868**
Silica gel	ferroin type chelating agent		metal ion chromatography	**869**
Silica gel and xerogel	≡Si-spacer-polyoxazoline	---	hydrophilic and amphiphilic support	**287**
GRAFTED LAYERS OF POLYMERS AND COPOLYMERS				
Silica gel	grafted n-alkyl residues	---	existence of a critical n-alkyl chain length with maximum flexibility was shown by ^{13}C NMR	**870**
Silica gel	polybutadienes or polysiloxanes	---	were immobilized on non- or specially presilanized silica particles by using different dose rates of gamma-radiation and by addition of different amounts of allylmethacrylate as a radical stabilizer	**871**
Silica gel, white carbon, silicic acid anhydride,	vinyl monomers	---	radiation induced polymerization of monomers adsorbed on supports	**278**

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Macroporous silochrome	acrylonitrile	---	grafted using gamma-irradiational induction	270
Silica gel	$\equiv Si(CH_3)CH{=}CH_2$ and polyethylene glycol monovinyl ether	---	graft polymerized. Increase in binding capacity in the order $Cs^+ < K^+ << Na^+$	872
Aerosil and Chrysotile asbestos	Immobilized copolymers of $CH_2{=}CHSi(OCOCH_3)_3$ $CH_2{=}CHSiCl_3$ and $CH_2{=}CClSiCl_3$ with styrene			276
Silochrome S-80	vinyl silylated support grafted material		factors affecting stability	305
Partisil	vinyl silylated support		copolymerization with acrylonitrile, acrylic acid, butyl methacrylate, 2-hydroxypropyl methacrylate, diethylaminoethyl acrylate	362
Bentonite, glauconite, kaolin, silica	acrylonitrile, vinyl acetate methyl methacrylate		supports were modified by grafting polymers	274,280
Silica gel, kaolinite, calcite	Methyl methacrylate and styrene - the supports were preirradiated and used to form graft copolymers			277
Silica gel	methyl methacrylate		polymerized photoinductively on silica surface containing dithiocarbamate residue	271

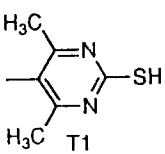
Support	Phase	Capacity	Application	References
Silica gel	methyl methacrylate		synthesis of isotactic polymethyl methacrylate covalently bound to silica	873
	(Trimethoxy silyl)propyl methacrylate and poly(triphenylmethyl)methacrylate		optically active copolymer for HPLC	874
Silica gel	butyl acrylate		monomer was graft polymerized onto silica gel modified with gammaaminopropyltrialkoxysilane and 4,4'- azobis(4-cyanovaleric acid)	875
Zeolite, activated alumina	styrene		both graft and homopolymers were obtained	876
Silica gel	grafted polystyrene	---	further reaction	273
Inorganic support	styrene, divinyl benzene and silylating agent		grafting on support packing for chromatography	634
Silica gel and alumina	grafted sulfonated polystyrene	1.9 meq/g	very high exchange rate	273
Silica gel	styrene-methyl methacrylate		graft polymerization with dithiocarbamate initiators	877
Silica gel, Chromosorb W	polyethylene glycol, dinonyl phthalate and tribenzylphosphate		cold plasma grafting	282

(continued)

Table 4. Continued.

Support	Phase	Capacity	Application	References
Silica gel	polyethylene oxide		EPR study of spin labelled material	429
Macroporous silica gel	2-vinylpyridine, 2-methyl-5-vinylpyridine 4-vinylpyridine		radiation-chemical grafting	279
Silochrom S-80	$-CH_2CH_2COOH$ grafted		complexation of Cu(II), Zn(II), Cr(III), and La(III)	878
Macroporous glass	levoglucosane		biocompatible chromatographic sorbent was obtained by graft polymerization on ethoxylated surface of glass	350

Formulas for the Tables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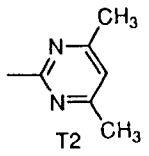
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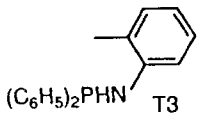
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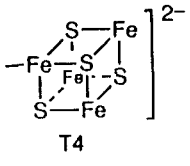
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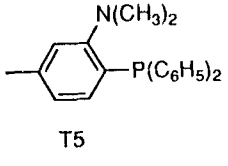
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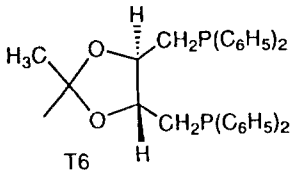
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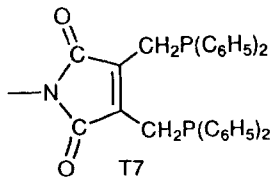
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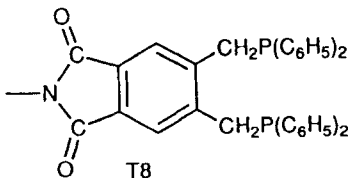
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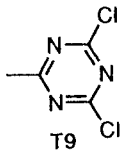
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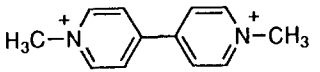
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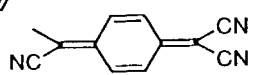
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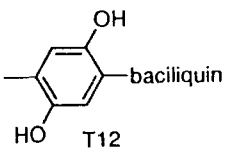
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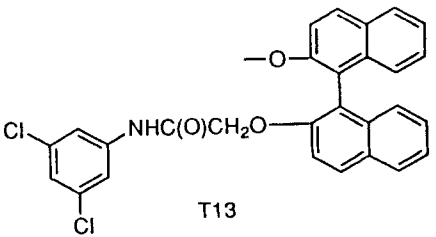
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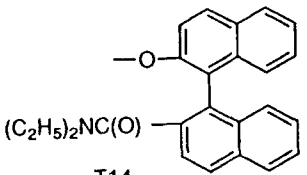
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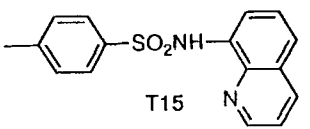
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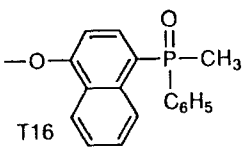
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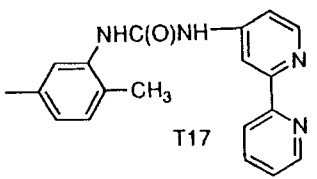
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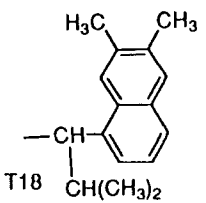
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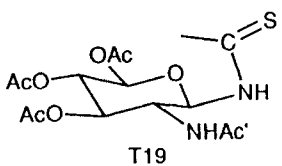
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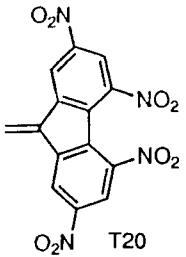

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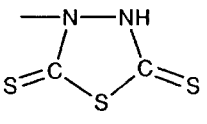

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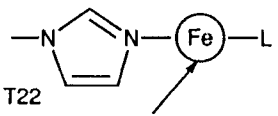

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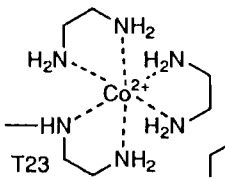

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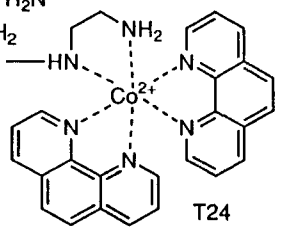

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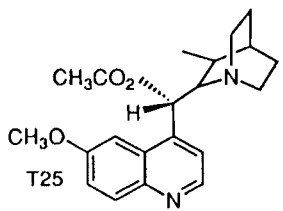

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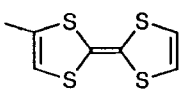

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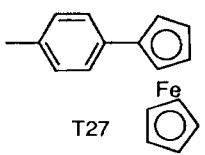

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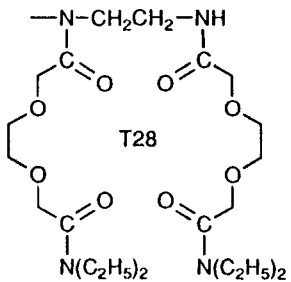

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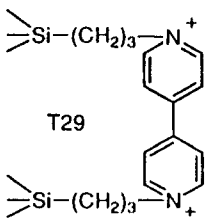

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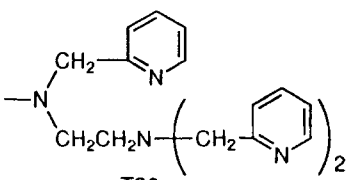

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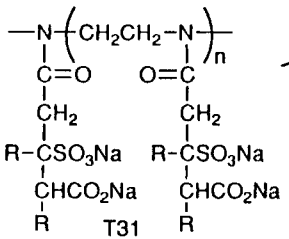

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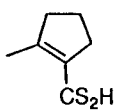

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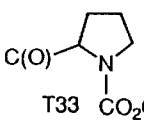

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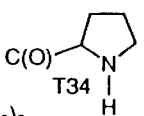

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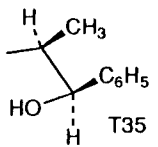

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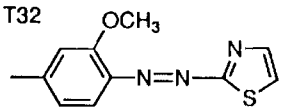

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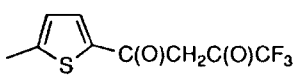

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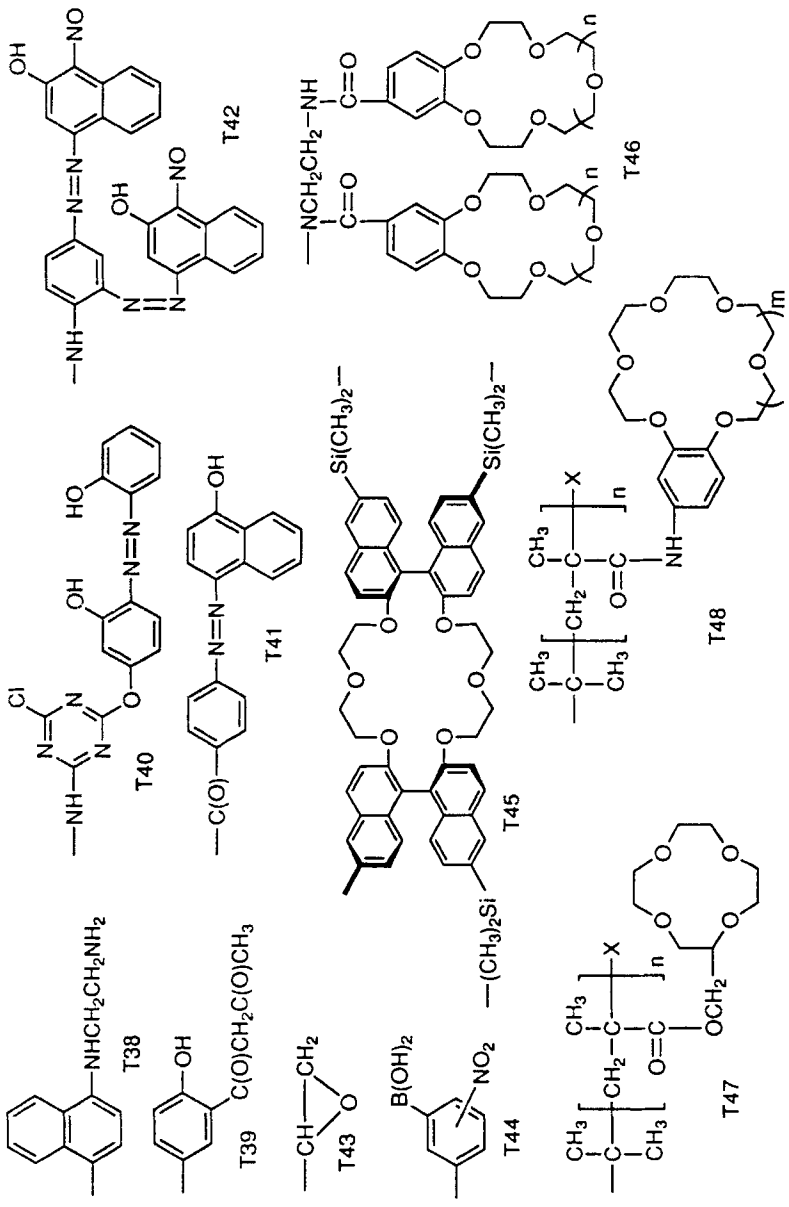

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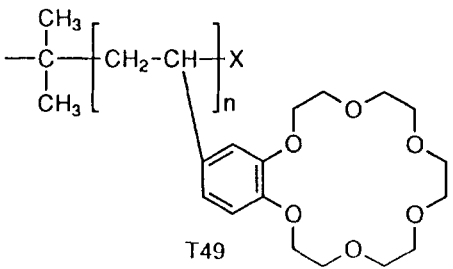

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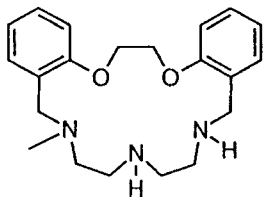

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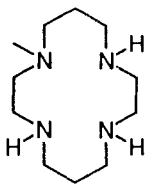

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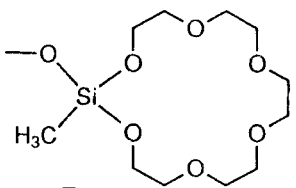

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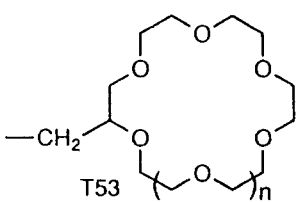

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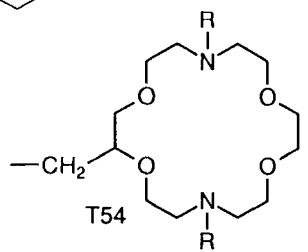
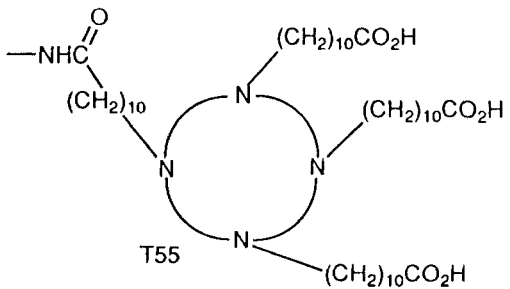
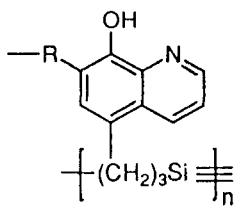


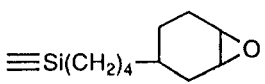
T54



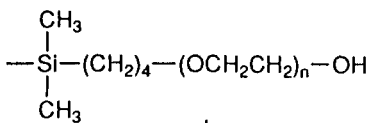
T55



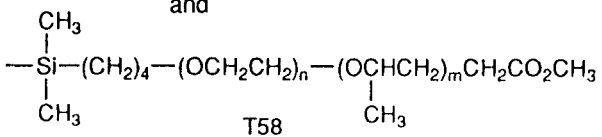
T56



T57



and



T58

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