

Review

A review on polysiloxane-immobilized ligand systems: Synthesis, characterization and applications

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Abstract

The immobilized silica gel ligand systems made by modification of silica surfaces have been briefly summarized. Short background was described based on the synthesis methods and their applications. In this review more attention towards the functionalized polysiloxane xerogels and their postmodification has been given. Polysiloxane-immobilized ligand systems bearing organofunctionalized ligand groups of general formula $P-(CH_2)_3-X$ (where P represents a three-dimensional silica like network-matrix and X is an organofunctional group) were prepared through the sol-gel process by hydrolytic polycondensation of $Si(OR)_4$ and the appropriate silane coupling agent $(RO)_3Si(CH_2)_3X$ (where R is an alkyl group, e.g. CH_3 or C_2H_5). There are many other immobilized ligand systems, which were prepared by treatment of post-polysiloxane precursors with an appropriate organofunctional ligand. Variety of functionalized materials ranging from simple up to macrocyclic immobilized ligand systems were prepared and well characterized. These materials have the advantage over the functionalized silica, as they can be prepared using different molar ratios of $Si(OR)_4$ and $(RO)_3Si(CH_2)_3X$ silane agents, and therefore their metal uptake capacities can be altered. A mixture of two different ligand groups can also be achieved on the same matrix. Analytical and environmental applications of these materials have been reported including extraction, separation and preconcentration of metal ions. A variety of physical chemistry techniques that were employed to characterize the surface and the bulk of the immobilized systems were reported. These included high-resolution solid-state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR).

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1. Synthesis of immobilized ligand systems

These immobilized ligand systems have been made by two different routes: the silica gel route and the sol–gel route.

1.1. Silica gel route

Much work has been carried out with ligand grafted onto silica surface by chemical treatment in which silica gel was especially immobilized with various organic compounds with metal chelating ability. In this process organic reagent or synthesized organic molecule containing the required organic functional group is directly attached to the support, or to the original chain bonded to the support to produce the required immobilized ligand system [1–21]. These modified silica materials have many applications in catalysis [6–11], chromatography [12–18] and biotechnology [19–21]. In this review we will limit our concerns with the immobilized ligand systems made by the sol–gel route, their characterization and applications. Therefore, we will briefly describe the silica gel, its synthesis, the chemistry of silica surface and the chemical reactions of silica, because these were intensively examined and reviewed by many authors [1–21].

1.1.1. Silica gel

Silica is the most common substance on earth. It is a constituent of most rocks. Its name comprises a large class of products with the general formula SiO_2 or $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Most forms of silica have the tetrahedral structure in

which each silicon atom is surrounded by four oxygen atoms [22]. Silica occurs in nature as a crystalline phase, which is present in minerals as quartz, and in plants such as bamboo, rice and barley. Most of the silica used in chemical applications, however, has a synthetic origin [23]. A crystalline substance is one whose atoms form a regular pattern over large distances [22]. Quartz, the major natural crystalline form of SiO_2 , is a periodic structure of tetrahedra where Si occupies the center and the oxygens are on the apex in a regular form. The active surface, which may participate in any chemical or physical interaction, is limited to the external surface of the crystalline particles. Silica is also found in amorphous forms (silica glass), in which the atoms are not found in regular arrays even though the atomic ratios are the same in crystalline forms and have the elemental tetrahedron structure. Porous amorphous silica has an interesting role in many applications. Porosity introduces a large surface area inside the silica particles, which gives superiority over crystalline counterparts for chemical and physical applications. Amorphous silica can be transformed into crystalline forms such as tridymite and cristobalite by heating to high temperatures (approximately 870 °C and 1470 °C, respectively) [24]. The process is very dependent upon pressure and chemical environment.

1.1.2. Synthesis of silica gel

The formation of silica gel, in general, involves two major steps: the formation of a wet gel, and drying of the

wet gel to produce many forms of silica. Originally, wet gels were made by the aqueous condensation of sodium silicate, or a similar material.

While this process worked well, the reaction formed salts within the gel that were to be removed by many repetitive washings (a long, laborious procedure) [25]. Silica is also regarded as a polymer of silicic acid consisting of interlinked SiO_4 tetrahedra. Polysilicic acid is produced when silicon tetrachloride is hydrolyzed [26] (Scheme 1). The polysilicic acid condenses further to produce a cross-linked gel. Over the last few decades, with the development of sol–gel chemistry, the alkoxy silanes such as $\text{Si}(\text{OR})_4$ have been used with $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ or C_3H_7 as precursors for silica synthesis. However, many other alkoxides, containing various organic functional groups, can be used to impart different properties to the gel. Alkoxide-base sol–gel chemistry avoids the formation of undesirable salt by-products, and allows a much greater degree of control over the final products. Silica sols are formed first by mixing tetrachlorosilane or tetraalkoxysilane with water. By condensation, stable particles of colloidal size are formed. As condensation proceeds, small three-dimensional siloxane networks are gradually formed, which are accompanied by an increase in the viscosity of the medium, reaching the gel point. The formed gel is termed as hydrogel (or alcogel) if an alcohol has been used as the solvent).

The resulting gel (alcogel) is constituted by a coherent continuous solid silica network impregnated by a liquid phase representing the solvent and the reaction by-product.

The hydrogel structure is controlled by temperature, the pH of the medium, the nature of the solvent, the water content, the concentration, the nature of the added electrolyte and the type of the starting salt or alkoxide and the drying conditions. Hopefully all these parameters give additional degree of freedom to tailor specific properties such as pore volume, pores size, and specific surface area. Aging or drying of the hydrogel results in a loss of the pore-filling liquid.

A xerogel is formed, with narrowing pores by capillary forces exerted by the liquid. Porosity and surface area

depend on the aging and drying conditions such as temperature, pH and concentration of the hydrogel particles. Xerogels may retain their original shape, but often crack. The shrinkage during drying is often extreme ($\approx 90\%$) for xerogels.

Aerogel is formed by drying an alcogel under supercritical conditions, the pore narrowing by capillary attraction is excluded, and so large pores volume is formed without damaging the solid part [27].

Xerogels and aerogels have a porous structure. Aerogel is a low-density, nanoporous solid that is typically composed of 95–99% air. Typically, aerogels can withstand hundreds of times their weight in applied force, with surface areas of several hundred square meters per gram and densities ranging from 0.1 to 0.001 g/cm^3 . Ordinarily, if the alcogel is allowed to dry out by evaporation, it will collapse and form a dense polymer. It is possible, however, to extract the liquid from a gel without collapsing the gels solid matrix. This is typically done by supercritical drying of the alcogel. Once the gel has been dried the remaining solid is aerogel.

Other types of silicas can also be formed, which include pyrogenic, arc and precipitated silicas. The preparation methods of the latter are patented [28–30].

By changing the method and specific parameters of the silica preparation, surface area, pore volume, pore size and particle size are, to some extent, independently controllable. These factors govern the chemical and physical behavior of silica [23].

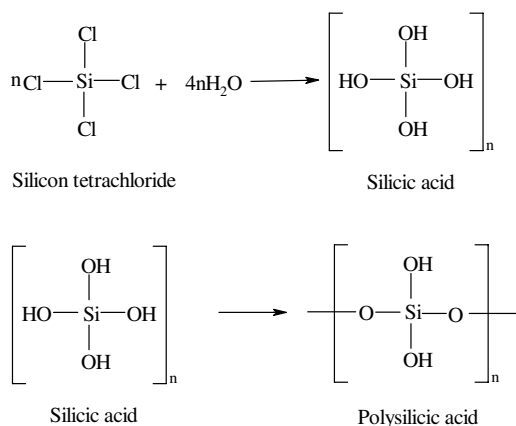
1.1.3. Modification method of surface silica

Silica particles of small particle size (2–5 nm) have an extraordinarily large surface-to-volume ratio ($\approx 2 \times 10^9 \text{ m}^{-1}$) and a corresponding high specific surface area ($\approx 900 \text{ m}^2/\text{g}$). It is not surprising, therefore, to note that the chemistry of the interior surface of silica gel plays a dominant role in its chemical and physical behavior. It is this property that makes silica gel an attractive material for use as catalysts, catalyst substrates, and adsorbents. The nature of the surface groups of a silica gel is strongly dependent on the conditions used in its preparation.

As with most hydroxyl surfaces, the surface of silica gel can show strong hydrogen-bonding effects. Because of this, silica gels with hydroxyl surface are extremely hygroscopic. Dry silica will absorb water directly from moist air, with mass increases of up to 20%.

Silica has been investigated by many workers to determine its properties. Silica can be regarded as a polymer of silicic acid, consisting of interlinked SiO_4 tetrahedra. The structure terminates at the surface in either a siloxane group ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) with the oxygen on the surface, or one of several forms of silanol groups ($\equiv\text{Si}-\text{OH}$).

The silanols can be divided into isolated groups (or free silanols), where the surface silicon atom has three bonds in the bulk structure and the fourth bond is attached to a single OH group, and vicinal silanols (or bridged silanols), where two single silanol groups, attached to different

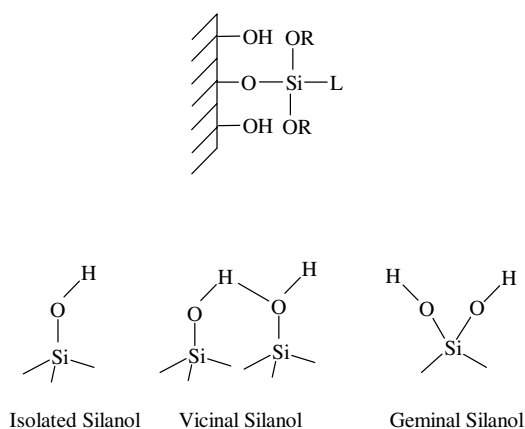


Scheme 1.

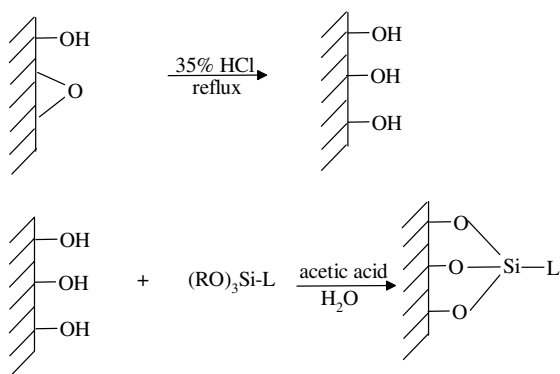
silicon atoms, are close enough to the hydrogen bond. The third type of silanols, geminal silanols, consists of two hydroxyl groups that are attached to one silicon atom and that are too close to form hydrogen bond between each other [31] (Scheme 2).

1.1.3.1. Chemical reaction of silica. The enhanced acidity of silica surface gives it a high degree of chemical reactivity, so it can react with many coupling agents to immobilize organo-functionalized silanes [32] (Scheme 3), in which Lisichkin and Zaitsev's teams have made an important contribution [33,34].

It has been observed that bond formation with silica matrix is not complete [32]. So some alkoxy groups survive the silylation reaction, e.g.;

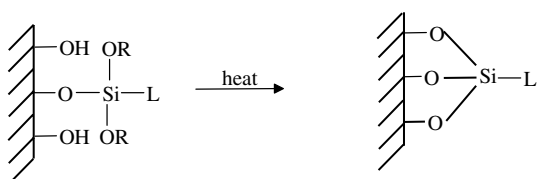


Scheme 2.



Where L is an organofunctional group.

Scheme 3.



Scheme 4.

This problem could be overcome by oven curing to ensure complete bond formation between the silica matrix and the silane. This would increase the strength of bonding and decrease the degradation or washing of the silane from the silica surface (Scheme 4).

1.2. The sol-gel route

It is a one spot reaction in which the tetraalkoxy silane $\text{Si}(\text{OR})_4$ and the silane coupling agent $(\text{RO})_3\text{Si}(\text{CH}_2)_3\text{X}$ (where $\text{R} = \text{Me}$ or Et , $\text{X} =$ complexing ligand group) mix together in an alcoholic solution in the presence of an acid or a base catalysis, where hydrolysis and condensation occurred simultaneously [35–42]. In acidic condition, hydrolysis is relatively faster than condensation, and weakly branched polysiloxane network is formed. In basic condition, condensation accelerates relative to the hydrolysis and more siloxane linkages are formed [43]. There are two strategies for the preparation of the immobilized polysiloxane ligand systems. The first strategy is to prepare the silane with the complexing group and then to immobilize the complexing ligand by hydrolytic condensation reaction with tetra ethoxy silane.

The second strategy is post-treatment of the polysiloxane with the complexing ligand. The first strategy frequently results in a high amount of complexing ligand than the post-treatment of the polysiloxane, provided that the ligand is stable in the hydrolytic-condensation step. Therefore, the immobilized polysiloxane ligand systems can be prepared by two different methods, which are briefly surveyed.

1.2.1. Obtaining functionalized xerogels

Hydrolytic polycondensation of a mixture of tetraethylorthosilicate (TEOS) and the appropriate silane coupling agent in a definite mole ratio [41] is done through the sol-gel process [38]. Acid or base catalysis can be used to enhance the two-step process, which takes place at room temperature [39].

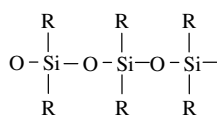
1.2.2. Modification method of functionalized polysiloxane xerogels

As a limited number of silane coupling agents were available, modification of pre-prepared polysiloxane precursors with the appropriate organic compounds, forming new immobilized ligand systems is reported [44–48]. Therefore, the organic chelating groups containing the desired functional groups can be attached to the original chain via a sequence of reactions to increase the main chain where other basic centers can be added to ensure the enhancement of specific adsorption.

1.2.2.1. Polysiloxanes. Polysiloxane-immobilized ligand systems, functionalized polysiloxane sorbents, polyorganosiloxanes, or simply polysiloxanes are insoluble spatially cross-linked organosilicon polymers with a con-

trollable porous structure. They are intermediates in composition between the pure inorganic silica and organic polymers such as polystyrene. These materials have been available for several decades in the form of liquids, gels, greases and elastomers that exhibit good stability. They are the most thoroughly studied and highly commercialized class of inorganic polymers.

Although the chain is entirely inorganic, with alternating Si and O atoms, organic side groups are attached to the silicon atoms. Many applications of polysiloxanes were derived from the extraordinary flexibility of the siloxane backbone. The Si–O bond is significantly longer than the C–C bond, the oxygen atoms are unencumbered by side groups, and the Si–O–Si bond angle of 143° is much more open than the usual tetrahedral angle of 110° . These combined structural features increase the dynamic and equilibrium flexibility of the chain [49].



Most work on polysiloxanes seems to be hidden in patents. Important applications include high-performance elastomers, membranes, electrical insulators, water repellent sealants, adhesives, protective coatings, and hydraulic heat transfer, and dielectric fluids [50,51]. They also find use in other important applications, such as, biomaterials [52–57], catalyst supports [40,58–60], chromatography [61–63], extraction and uptake of metal ions from aqueous solutions [44–48,64] and encapsulation of organic compounds [65–70].

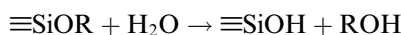
1.2.2.2. Sol–gel process. The sol–gel process is a method for the production of inorganic materials at ambient temperature, and was first reported some 150 years ago [71,72]. The process is gaining renewed interest because it provides a convenient way for incorporation, immobilization, entrapment, and encapsulation for a large variety of materials including organic, inorganic, biomolecules, microorganisms, tissue and indicators [38,65–70,73–75].

The synthetic method of polysiloxanes by sol–gel process, as its name implies, involves the formation of a colloidal suspension (sol) and gelation of the sol to form a wet gel (a globally connected solid matrix), which after drying forms “dry gel” state (xerogel) [76,77].

The following steps summarize the preparation of polysiloxane by the sol–gel process.

1.2.2.2.1. Hydrolysis. Most sol–gel techniques use water and low molecular weight tri- or/and tetra-alkoxysilanes as gel precursors. Because alkoxysilanes are not miscible with water, a common solvent is used for homogenization, although in some cases the released alcohol can provide sufficient homogenization. Generally, the hydrolysis reaction is promoted by the addition of a catalyst.

Hydrolysis leads to the formation of silanol groups. Soluble intermediates produced in the alcohol–water medium include silanols, ethoxy silanols and oligomers of low molecular weight which were formed at the first stages of the process [38].



Two models for the hydrolysis reaction have been proposed: one in which a trivalent [78] and another in which a pentavalent transition state is formed [79]. Raman spectroscopic studies on the hydrolysis of TMSO indicate that the model involving a pentavalent transition is correct [38].

Hydrolysis can be readily occurred under acidic or basic catalysts.

1.2.2.2.2. Acid catalyzed hydrolysis. In general, acids accelerate the hydrolysis process of alkoxysilane, the most frequently used acid being hydrochloric acid. Other acids such as acetic acid, phosphoric acid or sulfuric acid have been used [80,81]. It has been suggested that the resulting gels are much the same irrespective of the acid that is used [82].

It is proposed that the mechanism of hydrolysis under acidic condition is proceeded as follows (Scheme 5).

The proton is attracted by the oxygen atom of the OR group. This causes a shift of the electron cloud of the Si–O bond toward oxygen, and the result is the positive charge of the silicon atom increases. A water molecule can now attack the silicon atom, and a transition state is formed [38].

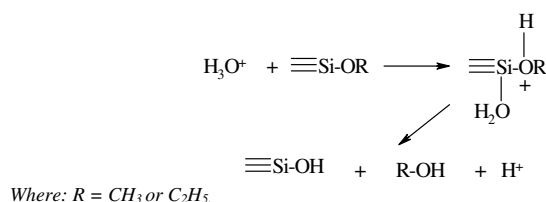
1.2.2.2.3. Base catalyzed hydrolysis. In case of base catalysis ion, the reaction is caused by a hydroxyl ion (Scheme 6).

The OH^- ion has high nucleophilic power and is able to attack the silicon atom directly. These attacks are aimed toward the silicon atom as the Si atom carries the highest positive charge.

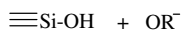
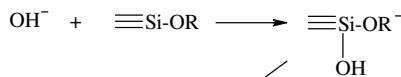
1.2.2.3. Polycondensation. The polycondensation of alkoxysilanes can be summarized in terms of two reactions: silanol–silanol condensation and silanol–ester condensation [38] (Scheme 7).

For example the formation of the solid product from TMOS (Scheme 8) [38].

Further polycondensation occurs to produce SiO_2 network (Scheme 9).



Scheme 5.



Where: $R = \text{H}_3$ or C_2H_5 .

Scheme 6.



or



Where: $R = \text{CH}_3$ or C_2H_5 .

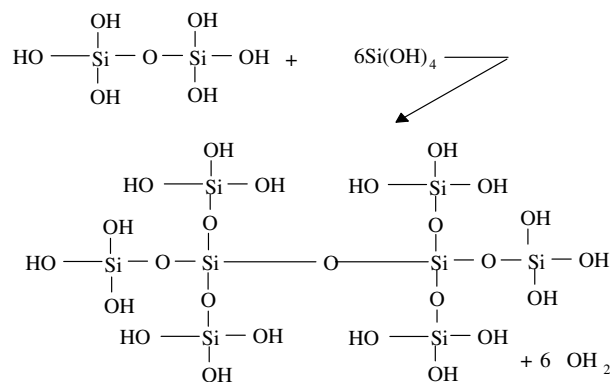
Scheme 7.

Many different intermediates are possible. This means that it is very hard to give an exact thermodynamic description of what might be possible or not, in the sol-gel reaction paths. The effect of the different reaction parameters (Organic radical of the OR group, solvent, catalyst, temperature and concentration) has to be investigated experimentally, and the conclusions have to be drawn from these results [83].

The H_2O and alcohol expelled from the reaction remain in the pores of the network.

The hydrolytic ability of the Si–O–Si bond is responsible for the differences between organic and inorganic polycondensation. Organic polymers evolve through the formation of dimers, trimers, and linear chains, which cross-link to form the gel state. Inorganic particles, however, evolve either through aggregation of small colloids or by addition of low molecular weight particles to larger ones [84].

1.2.2.4. Gelation. Gelation of the sol occurs when interconnection between particles of the sol increases forcing the sol to become more viscous (gel-point) thereby losing its fluidity. At the initial stages of polymerization, the silanol functional groups at the surface of the growing particles are partly deprotonated and their negative charge provides a repulsion barrier that stabilizes the sol. Later,



Scheme 9.

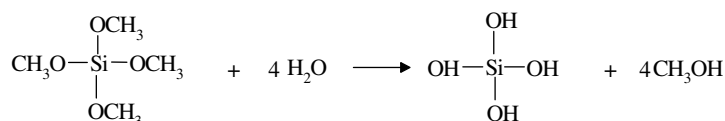
solvent evaporation and water consumption by alkoxy silane hydrolysis concentrated the solution and destabilized the suspension [84].

1.2.2.5. Drying. During the last stages of gelation, water and the organic solvent evaporate from the pores of the glassy material and the volume of the solid shrinks gradually (in some cases, the final volume of the xerogel is <10% of the initial volume of the gel). During the drying phase, some of the larger pores are emptied while smaller pores remain wetted by the solvent, creating large internal pressure gradients. This process causes cracking and fracture in large monoliths. Addition of surfactants, such as Triton-X, was suggested to prevent these fractures [84]. Drying the wet gel under monitored conditions also gives free cracks monolith [85].

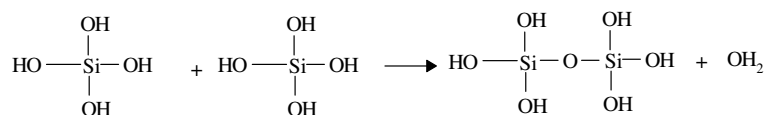
1.2.2.6. Aging. In this stage, the polycondensation reactions, formation of new bonds, water and alcohol still occur as a function of time [86]. Additional cross-linking and spontaneous shrinking occur. As a result composition, structure and properties of the gel continue changing with time [87,88]. The gel is aged to complete the reaction, which includes further hydrolysis and reesterification. The strength of the gel increases with aging (Scheme 10).

When the pore liquid is removed at or near ambient pressure by thermal evaporation, the dry gel is called a

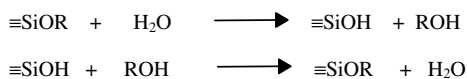
Hydrolysis:



Condensation:



Scheme 8.



Scheme 10.

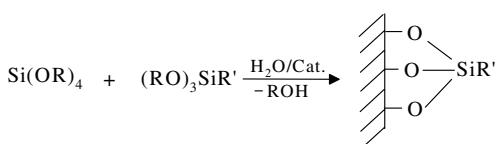
xerogel. The generic term gel usually applies to either xerogels or alcogels, whereas aerogels are usually designated as such. A gel is defined as dried when physically adsorbed water is completely evacuated, which occurs at temperatures between 100 and 180 °C [38]. A dried gel still contains a very large concentration of chemisorbed hydroxyls on the surface of the pores. Thermal treatment in the range 500–800 °C desorbs the hydroxyls and thereby decreases the contact angle and the sensitivity of the gel to rehydration stresses, resulting in a stabilized gel. Densification is complete at 1250–1500 °C, in which the number of pores reduces and so the density of the gel increases [74]. Silica glass made by densification of porous silica gel is amorphous and nearly equivalent in structure and density to silica made by fusing quartz crystals or sintering of SiO₂ powders made by chemical vapor deposition (CVD) of SiCl₄ [89–91].

The basic synthetic method of functionalized polysiloxane through the sol–gel process is the hydrolytic polycondensation of a mixture of tri- and tetra-silane agents (monomers): [R'Si(OR)₃ and Si(OR)₄] [35]. More than two components of alkoxy silane may be used to form the functionalized polysiloxane. Tetraalkoxy silane (TEOS) is the base component which gives the polysiloxane its rigidity due to the cross-linking polymerization [35] (Scheme 11).

Silane coupling agents have been used widely to modify surfaces for chemical applications [92], to immobilize chelating functional groups on silica gel and to prepare organofunctionalized polysiloxanes [35].

1.2.2.7. Silane coupling agents. Silane coupling agents have the general formula X₃SiR, where X is a hydrolyzable group and R represents an organo functional group [93]. The organofunctional groups are chosen for reactivity with the polymer, while the hydrolyzable groups X (Cl or OR) are merely intermediates in the formation of silanol groups for bonding to mineral surface [94].

Ordinarily, trialkoxy silane is used because it is easier to handle than the trichlorosilane and the corrosive HCl formed as a by product of hydrolysis is undesirable.



R = Me or Et R' = Organofunctionalized ligand

Scheme 11.

Silane coupling agents combine the organic chemistry of organofunctional groups with inorganic chemistry of silicates to bridge the hydrophilic interface between mineral substrate and organic polymer.

To form a bond between a ligand and the surface of silica, a molecule containing an organofunctional ligand group is reacted with the surface silanols [95]. In principle this can be achieved in several ways, all of which have been used to bond organofunctional groups to structures.

The porous structure of the functionalized polysiloxane can be modified by varying the conditions of gelation, such as pH of the reactants sol, temperature during gel sedimentation and drying conditions of the gel [96].

The first preparation of functionalized polysiloxane was by Neimark and co-workers [97,98]. It was based on the hydrolytic polycondensation of TEOS and 3-aminopropyltrimethoxysilane in the presence of methanol as a solvent in alkaline media.

Solid ligands were firstly prepared by Khatib by hydrolysis and condensation of tetraethylorthosilicate with alkoxy silane agents carrying functional groups in appropriate molar ratio of the mixture [35].

Recently, during the last 25 years several functionalized xerogels have been prepared and their structures have been characterized. Different applications based on the prepared polysiloxanes have been studied, e.g. preconcentration, extraction and separation of metal ions from aqueous solutions [99–116].

1.2.2.8. Advantages of polysiloxane-immobilized ligand systems. The polysiloxane-immobilized ligands have certain advantages [37,84]:

1. The physical rigidity of their structures.
2. High resistivity.
3. Negligible swelling in both aqueous and organic solutions.
4. Chemical inertness (low interaction with analytes).
5. Slower poisoning by irreversible side reactions.
6. High biodegradation, photochemical and thermal stability.
7. High amount of functionalized groups.
8. Uniform distributions of ligand sites within the polymer particles.
9. Readily modified by a variety of functional groups to be immobilized either before or after polymerization.

1.2.2.9. Drawbacks of polysiloxanes. Polysiloxane matrices and functionalized systems have some notable drawbacks [46,54] including

1. Hydrolysis at low and high pH.
2. Leaching of the functional groups from the support surface into the solution upon treatment with acidic solutions.

1.3. The sol–gel route (functionalized xerogels)

The sol–gel technology and surface chemistry of silica, particle size have been recently reported by Bergna and Reborts [117]. The preparation of sols, stability of sols, surface chemistry of silica, particle size and characterization techniques have also been described [117].

1.3.1. Immobilized halide systems

Polysiloxanes bearing halide groups (I or Cl) were prepared by hydrolytic condensation of a mixture of TEOS and 3-halopropyltrimethoxysilane to give functionalized 3-halopropyl polysiloxane. The reaction was catalyzed by $\text{Bu}_2\text{Sn}(\text{OAc})_2$ or HCl [35–37]. The optimum ratio of TEOS/halopropyltrimethoxysilane is 2:1 (Scheme 12).

1.3.2. Immobilized amine ligand systems

Polysiloxane immobilized monoamine, diamine and triamine ligand systems have been prepared using the hydrolytic polycondensation of a mixture of TEOS and the appropriate silane agent bearing the amine functional group in the presence of alcoholic solvent and stoichiometric amount. No catalyst was used as the amino groups considered a self-catalyzed component. El-Nahhal and co-workers [35,36,45,46,100] gave a detailed description of the preparation of these ligand systems (Scheme 13).

The hydrolysis of amino–ligand system alone (under these conditions) results in the formation of oligomers which are completely soluble in water [35]. Condensation, using TEOS in the optimum ratio of TEOS/aminopropyltrimethoxysilane (2:1), minimizes the formation of soluble oligomers to a very small extent. The immobilized monoamine ligand exhibits high potential for metal uptake of divalent metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). Maximum metal uptake capacities are obtained at pH 5–7. Lower metal uptake occurs at low pH \ll 4 due to protonation of the amino groups [39,46]. The immobilized monoamine ligand exhibits high potential for separation of copper(II) from aqueous solution containing Co^{2+} , Ni^{2+} and Cu^{2+} . The ligand system has been shown to be an effective solid-phase preconcentration agent for copper(II) ion at pH 5.5 [62].

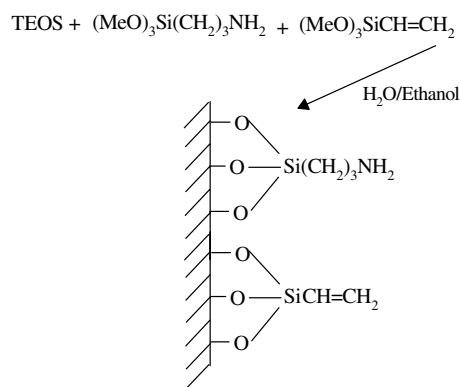
The immobilized diamine and triamine ligand systems exhibit higher potential for the extraction of divalent metal ions (Co^{2+} , Ni^{2+} , Cu^{2+}) than that of the immobilized monoamine ligand system [46]. Generally, all the immobilized amine ligand systems undergo substantial degradation upon treatment with acidic and basic solutions [39,45,46,100]. It is found that small oligomer species of the amine ligand containing groups are oozed out under acidic treatment [99].

Three component systems were used to prepare amine functionalized polysiloxane ligands by hydrolytic condensation of mixtures of $\text{Si}(\text{OEt})_4$, $(\text{MeO})_3\text{SiCH}=\text{CH}_2$ and $(\text{MeO})_3\text{Si}(\text{CH}_2)_2\text{NH}_2$ [36]. The amine functionalities also act as excellent basic catalysts, and gelation occurs rapidly. The vinyl silane was included simply as a non-ligand diluent (Scheme 14).

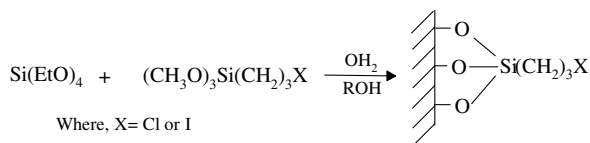
Functionalized polysiloxane containing thiol ligand was prepared by hydrolytic polycondensation of TEOS with $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{SH}$ (Scheme 15) [115]. In an effort to enhance the capacity of the bulk of SiO_2 -based materials to bind Hg^{+2} ions, novel mesoporous materials grafted

1.3.3. Immobilized thiol ligand systems

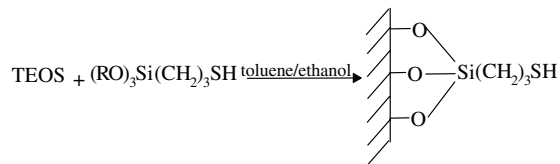
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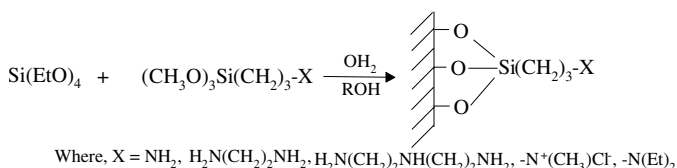
Scheme 14.



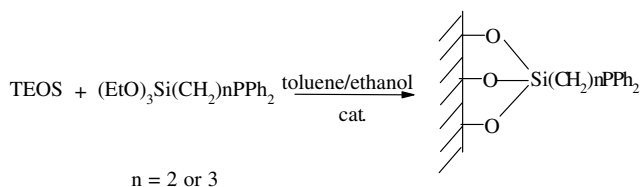
Scheme 12.



Scheme 15.



Scheme 13.



Scheme 16.

with mercapto ligands have been developed [111]. The mesoporous mercapto ligands with and without surfactant templates have been prepared by one step process to give ligand-grafted silica gels with high affinity and capacity for metal uptake [112].

1.3.4. Immobilized phosphine ligand systems

Functionalized polysiloxanes containing phosphine ligand have been prepared by hydrolytic polycondensation of $(\text{EtO})_3\text{Si}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2, 3$) with TEOS in the ratio of 1:2 using non-aqueous solvents (toluene, ethanol) and $(n\text{-Bu})_2\text{Sn}(\text{CH}_3\text{COO})_2$ as a catalyst (Scheme 16) [40]. The solid ligands form metal complexes having significant activity as hydrogenation catalysts [40].

1.3.5. Immobilized glycinate ligand systems

These ligand systems have been prepared using a multi step reaction [102]. The first step is the functionalization of 3-aminopropyltrimethoxysilane agent with ethylchloroacetate, followed by co-polymerization of the prepared silane agent with TEOS. The appropriate immobilized ligand was then obtained by hydrolysis of ethylacetate immobilized-polysiloxane system with HCl (Scheme 17). The immobilized glycinate ligand system extracts copper(II) ions from aqueous solutions. It might be expected that the maximum copper(II) loading would correspond to one metal per two glycinate groups [102]. This stoichiometry was not achieved and low metal uptake was found. This low metal uptake may be due to irregularity of the distribution of glycinate groups on the polymer matrix [102].

1.3.6. Immobilized iminodiacetate ligand systems

This ligand system was also prepared by two methods. The first method by functionalization of 3-iodopropyltrimethoxysilane agent with diethyliminodiacetate, then copolymerization of the prepared diethyliminodiacetate silane agent with TEOS (Scheme 18). The second method, by functionalization of the 3-aminopropyltrimethoxysi-

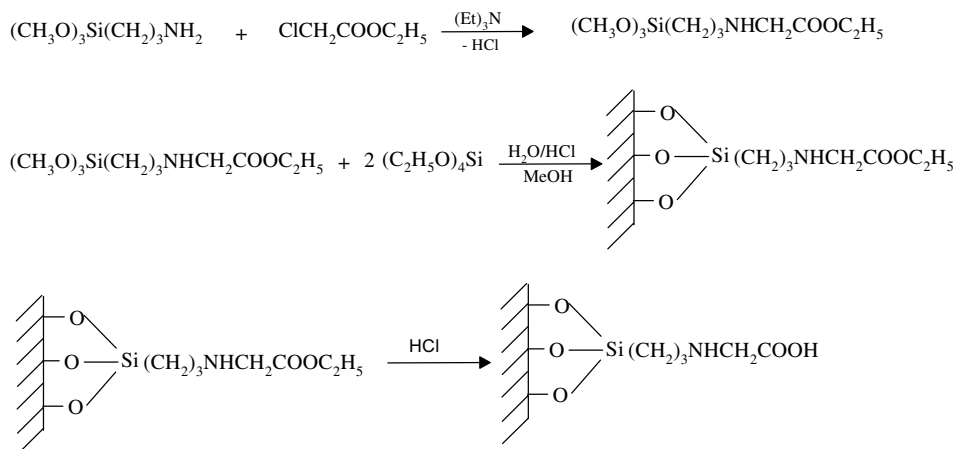
lane by ethylchloroacetate, then copolymerization with TEOS (Scheme 18). The produced diethyliminodiacetate ligand system then hydrolyzed by HCl to produce the iminodiacetic acid ligand system (Scheme 20). The immobilized ligand system prepared by hydrolytic polycondensation reaction of $\text{Si}(\text{OEt})_4$ and $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CO}_2\text{Et})_2$ exhibits higher potential for extraction of metal ions than the analogous material in which the iodopolysiloxane was treated with diethyliminodiacetate [47,103]. In the two systems the maximum metal uptake capacities suggest that 1:1 metal-to-ligand ratio complexes were obtained [103].

1.3.7. Immobilized bi-ligand systems [42,115,116]

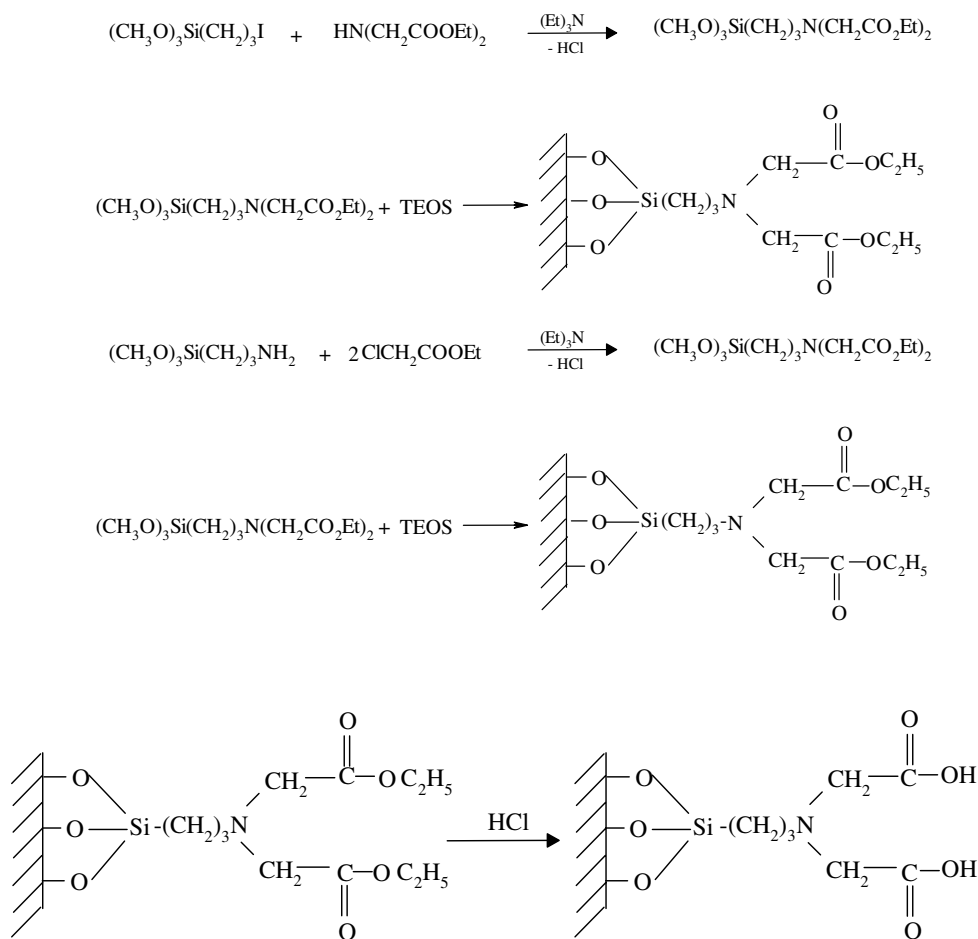
Thiol-amine ligand systems have been prepared by hydrolytic-polycondensation of a mixture of TEOS and $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{SH}$ and $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$, $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ or $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ [42,116]. In these systems the amine groups can apparently serve as an internal catalyst (Scheme 19).

Immobilized-polysiloxane phosphine-monoamine, phosphine-diamine and phosphine-thiol ligand systems are prepared by hydrolytic-polycondensation of mixtures of $\text{Si}(\text{OEt})_4$, $(\text{R}'\text{O})_3\text{Si}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2$, $\text{R}' = \text{Me}$, $n = 3$, $\text{R}' = \text{Et}$) and $(\text{R}'\text{O})_3\text{Si}(\text{CH}_2)_3\text{X}$ ($\text{X} = \text{NH}_2$, $\text{R}' = \text{Et}$; $\text{X} = \text{NHCH}_2\text{CH}_2\text{NH}_2$, $\text{R}' = \text{Me}$) or $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{SH}$ [115]. In these systems, two types of ligand groups are introduced into the polysiloxane matrix during the sol-gel process [115,116]. The sol-gel process permits the preparation of relatively homogeneous polysiloxane-immobilized ligand systems containing two types of ligand groups, with specific molar ratios, on the same polysiloxane framework. In these systems the amine groups can apparently serve as an internal catalyst and the gelation occurred rapidly. In the preparation of phosphine-thiol systems, $(n\text{-Bu})_2\text{Sn}(\text{OCOCH}_3)_2$ was used as a catalyst.

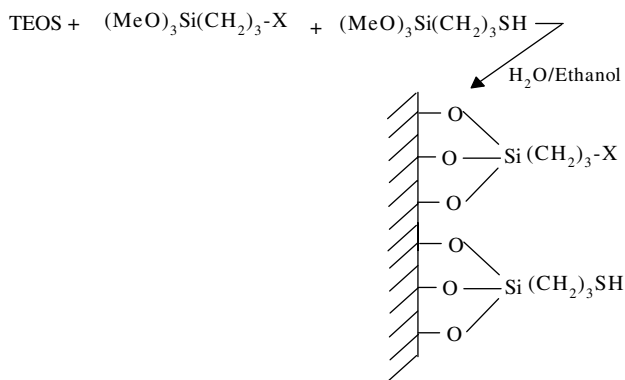
The immobilized thiol-monoamine and thiol-diamine ligand systems form metal(II) complexes when treated with



Scheme 17.



Scheme 18.



Where; X = $-\text{NH}_2$, $-\text{NH}(\text{CH}_2)_2\text{NH}_2$ or $-\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$

Scheme 19.

aqueous metal(II) ion solutions ($\text{M} = \text{Ni}^{2+}$, Cu^{2+} , Cd^{2+} and Hg^{2+}) [104]. Polysiloxane immobilized by hybrid mixture of triamine–thiol ligand as chelating functional groups exhibits high potential for extraction and preconcentration of divalent metal ions such as Co^{2+} , Ni^{2+} and Cu^{2+} at an optimum condition [42]. The optimum uptake results indicate that the triamine–thiol ligand seems to form 1:1 metal to ligand complexes [42].

1.4. Modification method of functionalized polysiloxane xerogels

Since few number of silane coupling agents are available, the modification route was used to prepare new other appropriate polysiloxane ligand systems. Some of the functionalized polysiloxanes can be modified with the appropriate ligand groups. This method was used for the synthesis

of many polysiloxanes ligand system, where the silane coupling agent is not available. The produced polysiloxane immobilized ligand systems exhibit higher density of ligand groups or ligand sites than silica functionalized with the same ligand groups [35].

1.4.1. Immobilized iodopropyl polysiloxane

The iodo-functionalized polysiloxane was prepared using this method by the replacement of the chlorine atom with the iodine on chloropropyl polysiloxane (Scheme 20) [37].

1.4.2. Immobilized amine ligand systems

Polysiloxane immobilized diamine and triamine ligand systems were prepared by the reaction of iodopropyl- or chloropropyl-functionalized polysiloxane with ethylene diamine and diethylene triamine, respectively [45,46,100] (Scheme 21). It is found that the immobilized triamine ligand system prepared by the sol-gel route results in a high amount of complexing ligand (7.3 mmol g^{-1} ligand) than the treatment of iodopolysiloxane with diethylene triamine (4.0 mmol g^{-1}). The immobilized and triamine ligand system exhibit high potential for the extraction of divalent metal ions (Co^{2+} , Ni^{2+} and Cu^{2+}) [45]. The immobilized diamine ligand system forms metal(II) chelate complexes when treated with divalent metal ions (Cu^{+2} , Zn^{+2} and

Cd^{+2}) of aqueous solutions. The metal uptake reaches its maximum at pH 5–6 [45,46]. The uptake results suggest that the immobilized diamine and triamine ligands form nearly 1:1 metal-to-ligand complexes [45,46]. The elemental analysis and FTIR results suggest that all amine ligand systems undergo a substantial leaching of the amine moieties from the siloxane matrix upon treatment with acidic solutions [45,46,100].

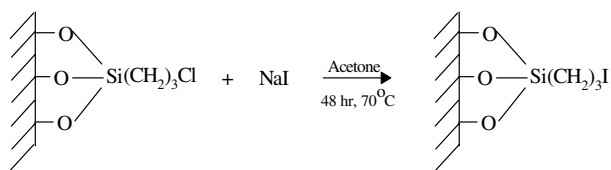
1.4.3. Immobilized iminodiacetate ligand systems

Polysiloxane-immobilized ligand systems with iminodiacetate chelating groups were prepared by the reaction of the halogenofunctionalized polysiloxane with disodium iminodiacetate in dimethylsulphoxide as the solvent [63] (Scheme 22).

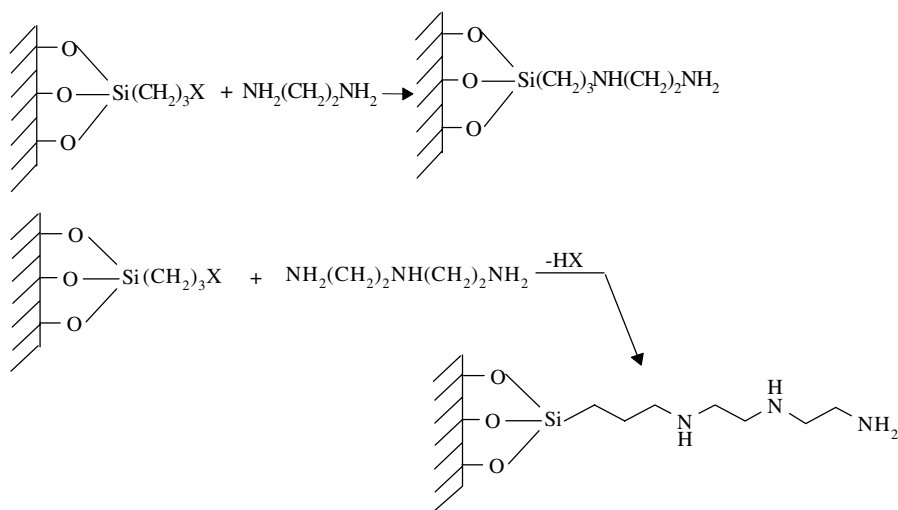
El-Nahhal and co-workers [47,103] used an alternative method to prepare polysiloxane-immobilized system bearing the iminodiacetate groups. The iodopropyl polysiloxane reacted with diethyliminodiacetate, followed by hydrolysis using HCl (Scheme 23). This immobilized ligand system exhibits high potential for the extraction of various divalent and trivalent metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). The analysis reveals that 1:1 metal-to-ligand complexes are accomplished [47].

1.4.4. Immobilized glycinate ligand systems

Polysiloxane-immobilized ligand systems with glycinate chelating groups were prepared by the reaction of the halogeno functionalized polysiloxane with sodium glycinate in dimethylsulphoxide (DMSO) solvent [63] (Scheme 22). It was proven later (^{13}C NMR results discussed later) that the sodium glycinate molecule reacts with halopolysiloxane through the carboxylate end and the chlorine atoms were replaced by the carboxylate group to produce $\text{P-CH}_2)_3\text{-O}_2\text{CH}_2\text{NH}_2$ [41]. An alternative method was used to prepare the immobilized glycinate ligand system by the

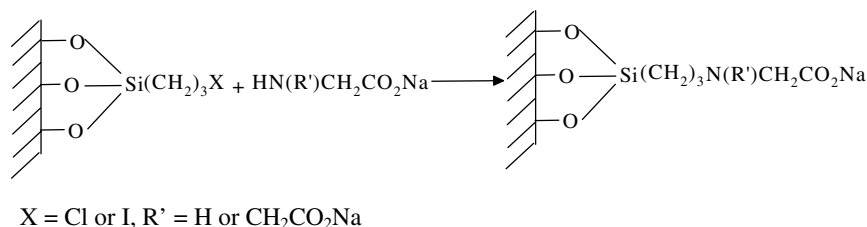


Scheme 20.

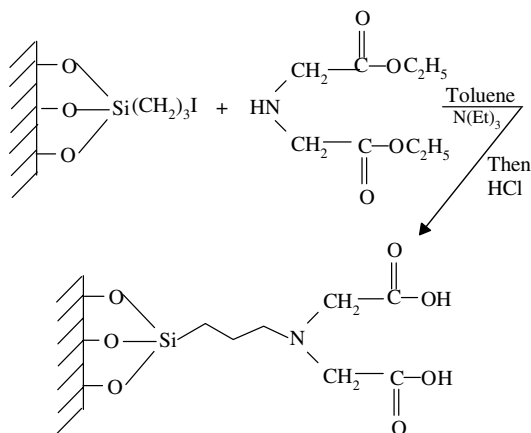


Where X=I or Cl

Scheme 21.



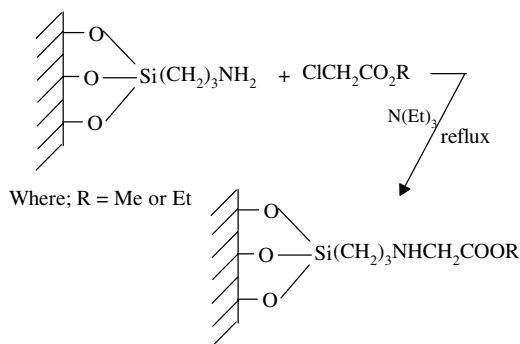
Scheme 22.



Scheme 23.

reaction of polysiloxane-immobilized amine ligand system with methylchloroacetate or ethylchloroacetate (Scheme 24) [102,105]. Treatment of aqueous solutions of divalent metal ions with polysiloxane glycinate ligand system demonstrates that this material exhibits high potential for pre-concentration of divalent metal ions (Cu^{2+} , Zn^{2+} and Cd^{2+}) at optimum conditions [102,105].

It might be expected that the maximum metal loading would correspond to one metal per two glycinate groups. This stoichiometry was not achieved and low metal uptake was found [101]. The low metal uptake may be due to irregularity of the distribution of glycinate groups on the polymer matrix. When used as chromatographic stationary



Scheme 24.

phases, the glycinate immobilized ligand allow clean separation of Cu^{2+} , Ni^{2+} and Co^{2+} metal ions by pH-controlled elution [63]. Co^{2+} and Ni^{2+} can also be cleanly separated by displacement-elution with copper ion.

1.4.5. Immobilized pyrogallol ligand system

This immobilized pyrogallol ligand system was made by two-step reaction by the reaction of the 3-aminopropyl polysiloxane with 1,3-dibromopropane followed by the reaction with the pyrogallol as given in Scheme 25 [108]. The metal ion uptake capacity (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+}) as mmole of M^{n+} per gram of ligand suggests a 1:1 metal-to-ligand ratio complex for the Fe^{3+} and Cu^{2+} . In the case of Co^{2+} and Ni^{2+} the metal-to-ligand ratio is less than 1:1, indicating that less stable complexes are formed [108].

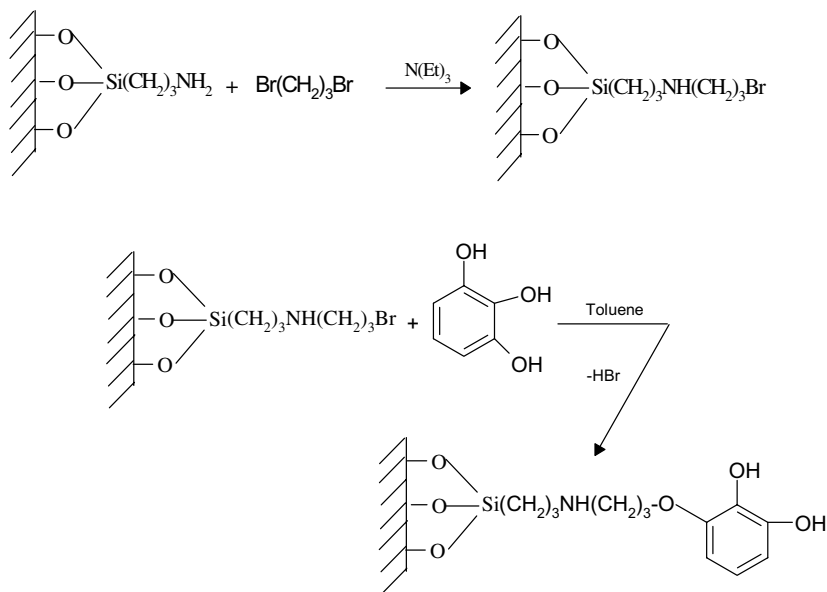
1.4.6. Immobilized ethyl amino benzoate derivatives

The immobilized ethyl amino benzoate ligand systems were prepared by the reaction of 3-iodopolysiloxane with ethyl amino benzoate followed by the reaction with ethylenediamine and diethylenetriamine (Scheme 26). These immobilized ligand systems exhibit high potential for extraction of metal ions (Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with an efficiency of 92–98% after recovery from its primary metal complexes. The uptake results suggest that 1:1 metal-to-ligand ratio complexes are obtained for all metal ions except for the zinc ion [113]. These immobilized ligand systems undergo chemical degradation, the level of which is pH dependent.

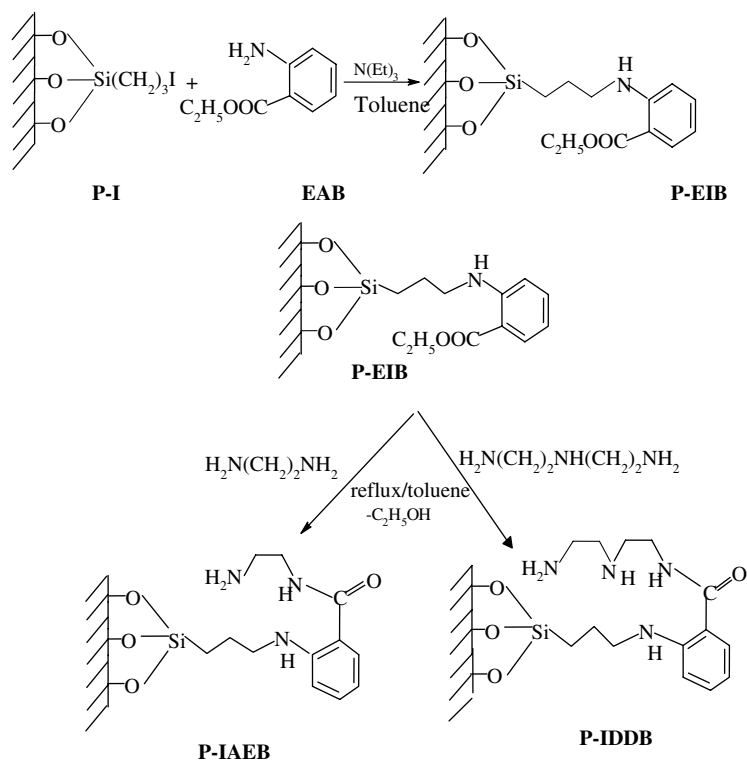
1.4.7. Immobilized polysiloxane iminobis(*N*-2-aminoethylacetamide) and Iminobis(*N*-diethylenetriamineacetamide) ligand systems

The two immobilized ligand systems, iminobis(*N*-2-aminoethylacetamide) and iminobis(*N*-diethylenetriamineacetamide) were prepared by the reaction of the immobilized diethyliminoacetate polysiloxane with ethylenediamine and diethylenetriamine, respectively (Scheme 27) [106,107].

These two immobilized ligand systems exhibit high potential for the extraction of metal ions from aqueous solutions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). The maximum metal uptake capacities suggest 1:1 metal-to-ligand complexes for the iminobis(*N*-2-aminoethylacetamide)



Scheme 25.

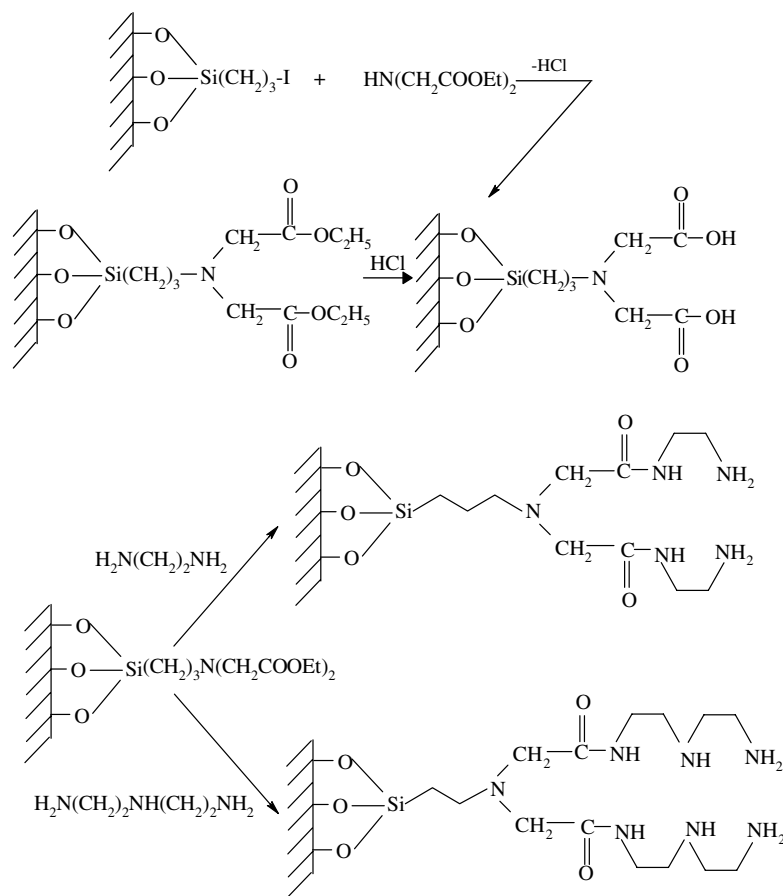


Scheme 26.

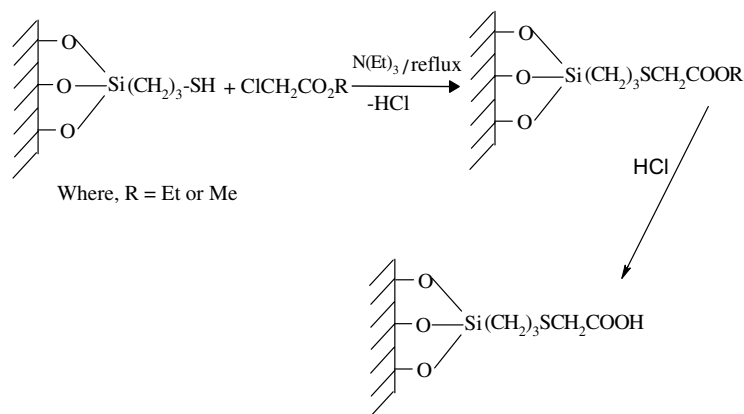
polysiloxane ligand and 2:1 metal-to-ligand complexes for the iminobis(*N*-diethylenetriamineacetamide) ligand systems. The immobilized iminobis(*N*-diethylenetriamineacetamide) ligand system showed a high efficiency of 92–95% after recovery from its primary metal complexes. These immobilized ligand systems were found to be very stable

at pH 6–8, but they undergo substantial leaching upon treatment with acidic and basic solutions [106,107].

This immobilized iminobis(*N*-2-aminoethylacetamide) ligand system exhibits high potential for separation of Cu(II), Ni(II) and Co(II) from aqueous solution containing the three metal ions by pH control [109]. The ligand system



Scheme 27.



Scheme 28.

has been shown to be an effective solid-phase for copper(II) recovery at pH 5.0 [109].

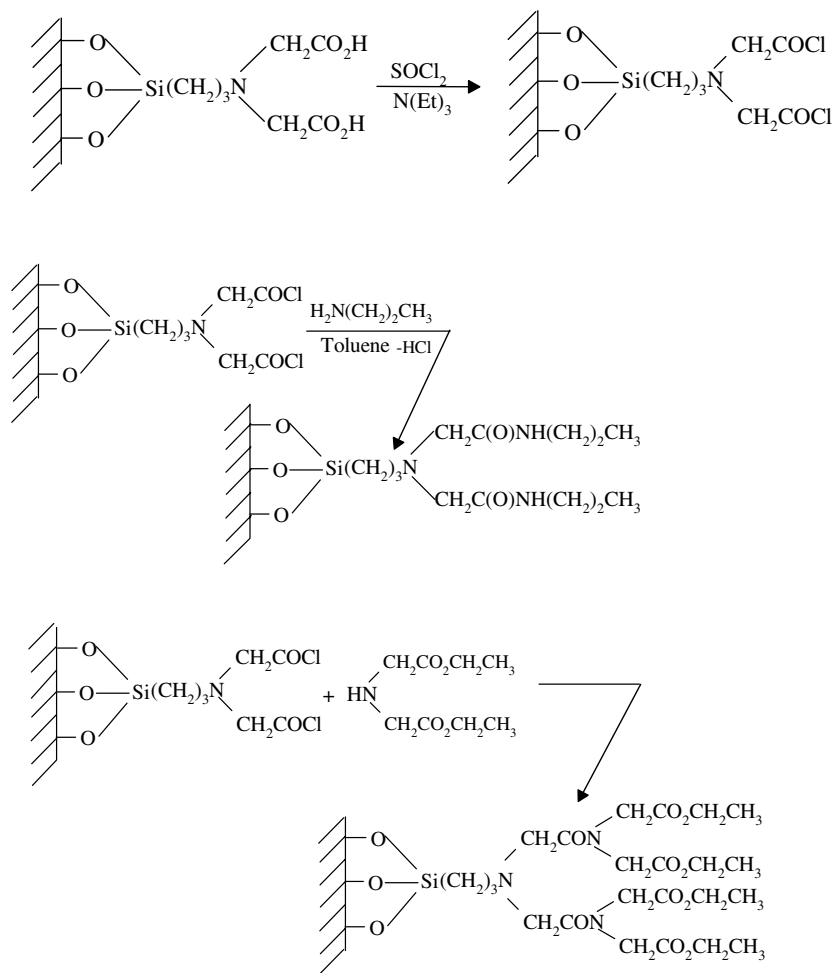
1.4.8. Immobilized thiol-acetate ligand system

Polysiloxanes bearing thiolpropyl ligand system have been modified by the ethylchloroacetate/methylchloroacetate groups [42,44] (Scheme 28). The thiol-acetate ligand system was also prepared by treatment of thiol-acetate silane complexing agent with TEOS [44]. This immobilized

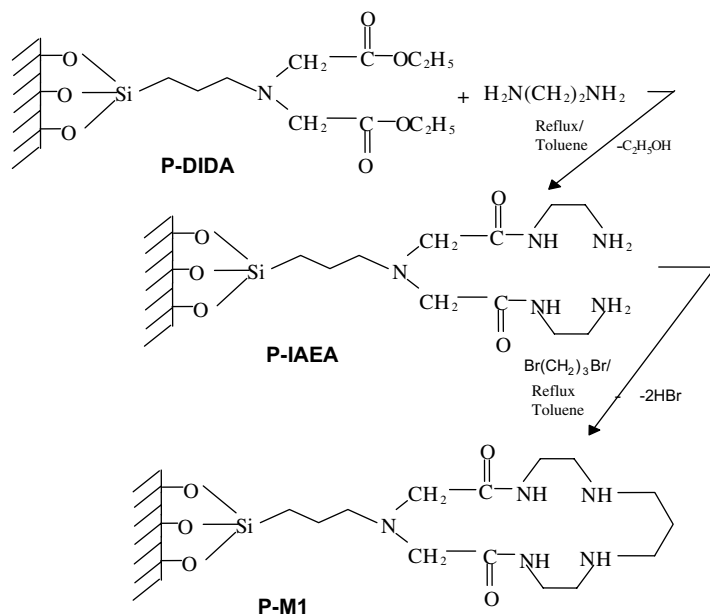
thiol-acetate ligand system shows high uptake capacities of divalent metal ions (Cu^{2+} , Ni^{2+} and Co^{2+}) [42]. The uptake results show no clear stoichiometry structure for complexation with the immobilized thiol-acetate ligand.

1.4.9. Immobilized di(amidomethyl)aminetetraacetic acid ligand system

The iminodiacetate ligand system has been used for the preparation of new ligand systems by modification using



Scheme 29.



Scheme 30.

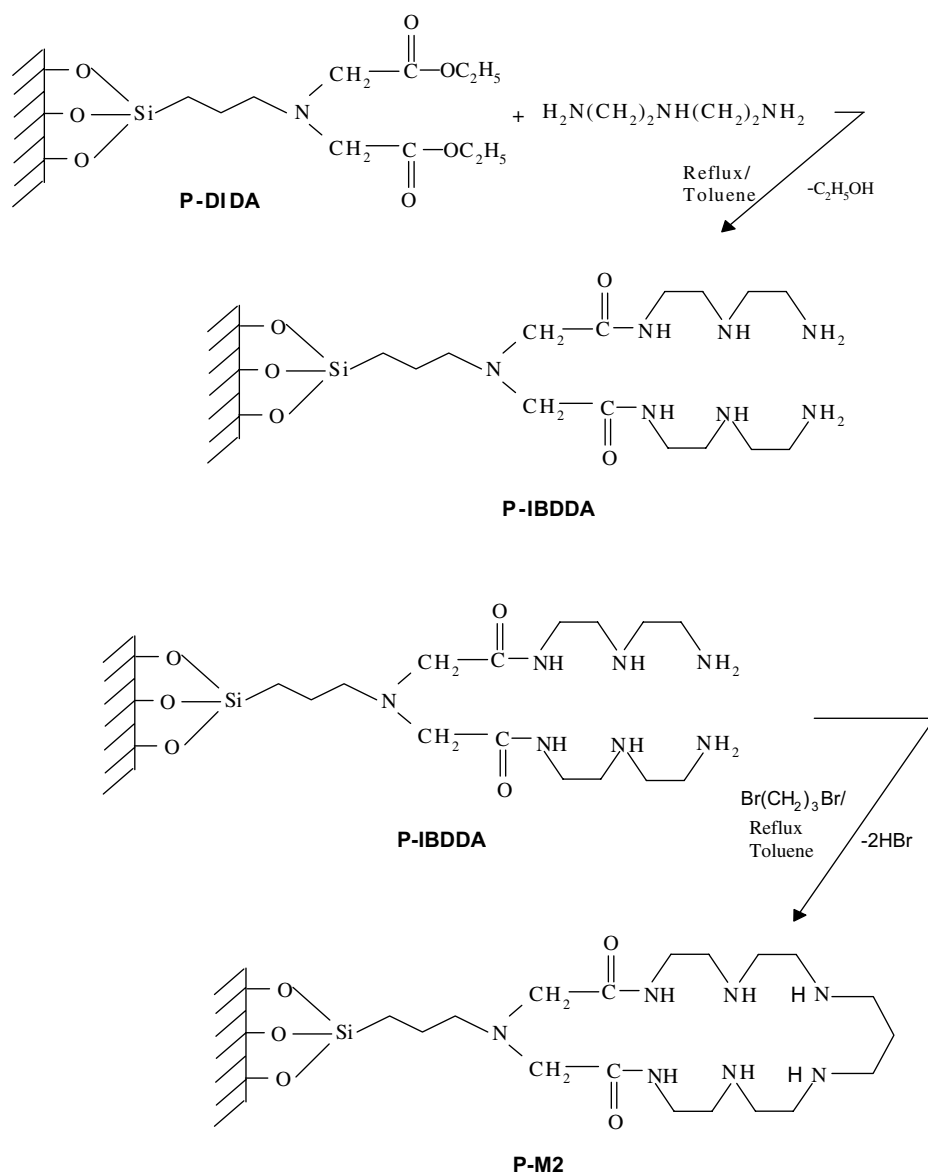
other functional ligand groups, e.g. di(*n*-propylamidomethyl)amine and diethylamidodiacetatedimethylamine (Scheme 29). The immobilized di(amidomethyl)aminetetraacetic acid ligand system showed high potential for extraction of divalent metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) and formed 2:1 metal-to-ligand complexes [110].

1.4.10. Immobilized macrocyclic ligand systems P-M1 and P-M2

Two immobilized macrocyclic ligand systems P-M1 and P-M2 were prepared by treatment of the iminobis(*N*-ethylenediamineacetamide) and iminobis(*N*-diethylenetriamineacetamide) ligand systems with 1,3-dibromopropane, respectively (Schemes 30 and 31, respectively). The polysiloxane-immobilized macrocyclic 1,4,7,11,14-pentaazapentadecane-3,15-dione ligand system (P-M1) was

prepared by treatment of the immobilized diethyliminodiacetate ligand system with ethylene diamine followed by 1,3-dibromopropane [48]. The FTIR and XPS results confirmed the cyclization and formation of the macrocyclic ligand system (P-M1). The immobilized ligand system P-M1 exhibits higher potential for extraction and preconcentration of metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) than its precursor before cyclization [107].

The polysiloxane-immobilized macrocyclic 1,4,7,10,14,17,20-heptaazadocosane-3,21-dione ligand system was prepared by the reaction of the immobilized diethyliminodiacetate ligand system with diethylene triamine followed by 1,3-dibromopropane [114]. The new macrocyclic ligand system P-M2 shows high potential towards metal ions, including Fe^{3+} , Co^{2+} , Ni^{2+} and Zn^{2+} , and it was very selective toward copper ions. Complexation with copper ions



Scheme 31.

involves two copper ions per ligand [114] compared with that of P-M1 ligand system [48].

2. Applications of polysiloxane immobilized ligand systems

Polysiloxanes functionalized chelating ligands have many applications in many fields. Generally, two major applications of such materials have been used. One of these applications was the extraction and separation or isolation of metal ions in batch process or in column chromatography [52,53,101]. On the other hand, these functionalized ligand systems have been used as catalysts in a variety of reactions [31].

Several functionalized groups have been immobilized covalently on the silica surface, such as salicyldiamine, phthalic acid, ethylene diamine and others [118–120]. Silanes with a simple monoamine or diamine functional groups were attached on silica gel surfaces by many co-workers [121]. They have shown that silica gel containing a chemically bonded amine or diamine will quantitatively retain metal ions such as mercury(II), copper(II), zinc(II), manganese(II), cobalt(II) and many other transition metals. They also reported the dithiocarbamates to evaluate their potential for preconcentration of metal ions from solution. Chromatographic behavior of silica immobilized 8-hydroxyquinoline has been investigated [122]. This material had a capacity of about 50 $\mu\text{mol/g}$ and is capable of separating metal ions such as Cu–Ni, Cd–Pb–Zn and La–Gd–Yb at trace levels. It was also used for preconcentration of trace elements from seawater [123,124].

3. Characterization

These materials were characterized by several techniques. These include high-resolution solid-state nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) and X-ray photo electron spectroscopy (XPS) as well as other chemical tools.

3.1. NMR spectra

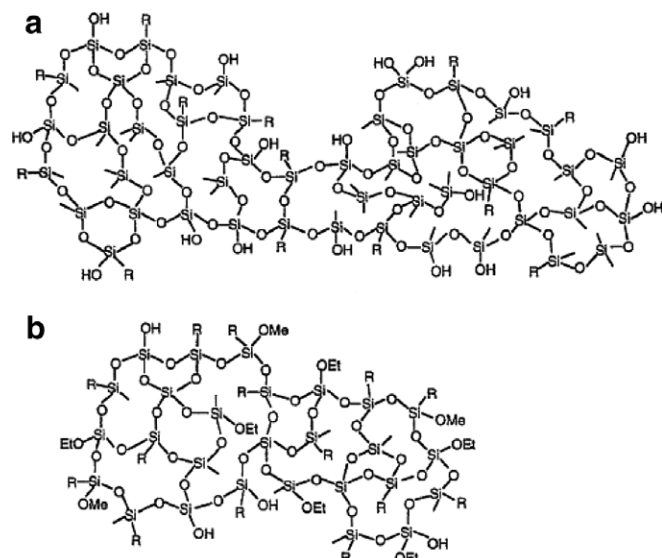
Natural abundance solid-state NMR techniques [125–140] based on cross-polarization and magic angle spinning (CP-MAS) for ^{13}C , ^{29}Si , and ^{15}N as well as corresponding experiments with ^{15}N -enriched samples [141] have served as the basis for structure characterization in this article.

3.1.1. ^{29}Si CP/MAS NMR Results

^{29}Si CP-MAS spectra are expected to provide valuable information on the polysiloxane network such as the extent of attachment of organic moieties to the network, the degree of cross linking of the whole network and especially on any leaching of these materials when treated with acidic solutions. The ^{29}Si NMR spectra of the polysiloxane-immobilized ligand systems show two regions of major intensity centered at about -105 and -60 ppm. These two peak positions correspond to $\text{Si}(\text{O})_4$ and $\text{R}(\text{Si}(\text{O})_3)$, respectively,

where R is an organic containing donor atom [130–138,98,99]. Caravajal et al. [138] used ^{29}Si CP-MAS for structural characterization of 3-aminopropyltrimethoxysilane (APTS) modified silica. A comparison of ^{29}Si CP-MAS NMR spectra of silica modified with 3-chloropropyltriethoxysilane (Cl-MTS) and those of the parent support (MTS) showed that the mechanism of silylation is of nucleophilic attachment at silicon atoms of the hydrophobic part of the surface [137].

^{29}Si CP-MAS and ^{29}Si DP-MAS NMR spectra were used to elucidate the structure of the immobilized monoamine and 3-chloropropyl polysiloxane systems (e.g. determination of the relative amounts of $\text{R}-\text{Si}(\text{O})_3$ and $\text{Si}(\text{O})_4$ moieties of various types). The hypothetical representation structures, i.e. The immobilized amine and the chloropropyl ligand system, are determined [100].



^{29}Si NMR and elemental analysis data for the immobilized monoamine ligand system showed that these materials undergo some leaching when treated with acid or metal ion solutions [100]. The leaching ligand containing species were also identified and characterized [99].

^{29}Si CP-MAS NMR spectra were used to examine silylation of silanols by $(\text{Me}_3\text{Si})_2\text{NH}$. It shows that the silanols attached to ligand $\text{R}(\equiv\text{Si})_2\text{Si}-\text{OH}$ are more reactive towards silylating reagent $(\text{Me}_3\text{Si})_2\text{NH}$ than $(\equiv\text{Si})_3\text{Si}-\text{OH}$. In underivatized silica gel 58% of silanols are not accessible for reaction with $(\text{Me}_3\text{Si})_2\text{NH}$, whereas for polysiloxane amine ligand system, the percentage of silanols that are not accessible is 55%.

3.1.2. ^{13}C CP-MAS NMR Analysis

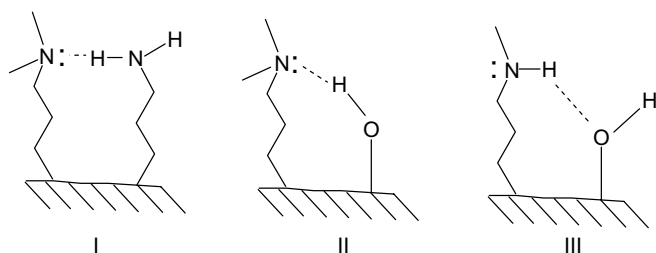
Solid-state ^{13}C CP-MAS NMR provides useful information of surface structure of modified silica or immobilized polysiloxane materials [135–140,99,100]. The ^{13}C NMR spectra of the polysiloxane-immobilized amine ligands show the absence of residual ethoxy or methoxy signals, compared with that of polysiloxane-immobilized 3-chloropropylpolysiloxane system. This probably indicates that a

complete hydrolysis and/or condensation of Si–OEt and Si–OMe groups has occurred for the immobilized amine ligand systems [100].

^{13}C CP-MAS NMR spectra are also used for determination of the number of residual ethoxy groups per silane moiety using the relative intensity of peaks [138]. Samples prepared in aqueous solution, ^{13}C CP-MAS NMR, showed that the reactions with ethoxy group had occurred completely whereas in samples prepared in dry toluene ethoxy reactions were found to increase as the amount of water at silica surface increases [145].

^{13}C CP-MAS NMR spectrum of polysiloxane-immobilized monoamine ligand system prepared by the sol-gel method is similar to that of self polymerized 3-aminopropyltriethoxysilane (APS) polysiloxane system (no $\text{Si}(\text{OEt})_4$ is employed). But it differs from that of APS modified silica [128].

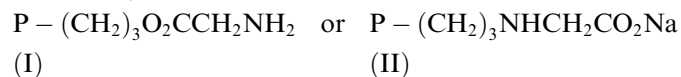
It has been reported that the relatively broad signals of ^{13}C NMR spectra of the immobilized monoamine compared with that of 3-chloro- and 3-(trimethylammonium)propyl polysiloxane in the immobilized monoamine ligand system may involve hydrogen bonding between the amine groups and surface silanols or other ligand groups (structures I, II and III) [41,100] as given below:



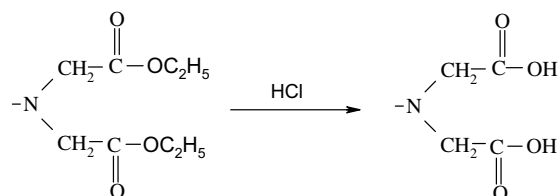
For these systems, the presence of a lot of water molecules on the silica surface may have involved in the hydrogen bonding with the amine and silanol groups. The ^{13}C NMR spectra of immobilized monoamine ligand system after silylation with hexamethyldisilazane (Me_3Si) $_2\text{NH}$ were used to examine the structural changes in the ($-\text{CH}_2\text{CH}_2-\text{NH}_2$) group, after the surface silanols are capped by Me_3Si groups causing an effect in the hydrogen bonding between surface silanols and amine groups. A comparison is made between the ^{13}C NMR spectra of immobilized monoamine ligand system and that of the polysiloxane-immobilized diethylpropyl amine and the polysiloxane-immobilized trimethylpropyl ammonium hydrochloride, where the amine–amine (structure I) and amine–silanols (structures II and III) hydrogen bonding are not possible, respectively [41].

The ^{13}C NMR spectrum of polysiloxane-immobilized glycinate ligand system was prepared by the reaction between the 3-chloropropyl polysiloxane system and sodium glycinate, where two possible products (I and II) ($\text{P}-(\text{CH}_2)_3\text{O}_2\text{CCH}_2\text{NH}_2$ or $\text{P}-(\text{CH}_2)_3\text{NHCH}_2\text{CO}_2\text{Na}$) are expected. The similar ^{13}C spectral pattern of polysilox-

ane-immobilized glycinate ligand system to that of the polysiloxane bearing $-\text{NHCH}_2\text{CO}_2\text{Me}$ emphasized the presence of structure (I) as the chlorine atoms are replaced by the carboxylate groups [41]:



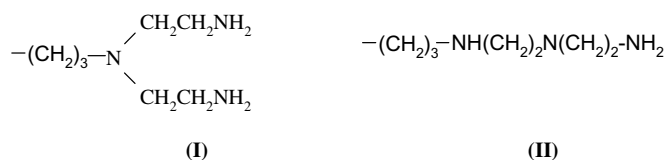
The ^{13}C NMR spectra for the immobilized iminodiacetic acid and for the immobilized diethyliminodiacetate ligand systems are used to examine the extent of hydrolysis of ethoxy groups after treating the immobilized diethyliminodiacetate with hydrochloric acid [47] as given below.



It is found that all ethylacetate groups ($-\text{CO}_2\text{Et}$) were completely hydrolyzed to the acid form ($-\text{CO}_2\text{H}$).

Both ^{13}C and ^{15}N NMR spectra can provide information on the complexation of the immobilized ligands with the metal ions. The observed broadening of carbons in the spectra of $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ complexes of immobilized monoamine ligand system compared with that of the uncomplexed immobilized amine ligands may result from an increase in chemical structure heterogeneity, that not all ligand sites are accessible to metal ion, thereby remaining uncoordinated and therefore having somewhat different chemical shifts from those groups involved in coordination [100].

The ^{13}C NMR spectral data of the immobilized triamine ligand system which prepared by reaction of the 3-chloropropylpolysiloxane with diethylene triamine, where two possible structure forms are present, are consistent with structure (II) [100].



3.1.3. ^{15}N CP-MAS NMR Results

The ^{15}N CP-MAS NMR spectra can be expected to provide useful information about the environment of the amine groups and their interaction with each other or with other proton donors or acceptors, e.g. silanol groups [142–145]. The ^{15}N CP-MAS NMR spectra of primary and secondary amines of samples treated with acid or base solutions have been reported. The spectra of protonated monoamine ligand show that the signals move to lower shielding at

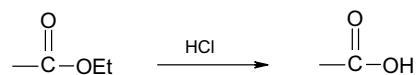
25 ppm whereas in the sample treated by NaOH solution, the signal appear at 45 ppm. The presence of the shoulder at 33 ppm between the free amine peak at 45 ppm indicates the involvement of NH_2 group in hydrogen bonding with the acidic silanols and perhaps with other amine groups. The broad signal observed in the ^{15}N spectrum of the $\text{Cd}(\text{II})$ complex of the immobilized amine ligand system suggests that a substantial fraction of the amine ligand is involved in coordination to the $\text{Cd}(\text{II})$ ions [101].

3.2. FTIR spectra

The FTIR spectra can be used to provide useful information about the presence or absence of functionalized ligand groups during the reaction course [146,147].

The FTIR spectra of the immobilized polysiloxane systems and modified silica gel show three regions of absorptions at $3500\text{--}3000\text{ cm}^{-1}$, $1750\text{--}1600\text{ cm}^{-1}$ and $1200\text{--}900\text{ cm}^{-1}$ due to $\nu(\text{OH})$ or $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{CON})$, $\delta(\text{OH})$ and $\nu(\text{Si-O})$, respectively [99–110,112,112–115].

For example, the FTIR spectrum of the immobilized diethyliminodiacetate ligand system shows strong absorption at 1740 cm^{-1} due to $\nu(\text{C}=\text{O})$, which disappears and shifts to lower frequency (1670 cm^{-1}) upon treatment of the immobilized diethyliminodiacetate with HCl [37] as given below:



The FTIR spectra for the immobilized diethyliminodiacetate show that the $\nu(\text{C}=\text{O})$ at 1740 cm^{-1} disappeared and shifted to 1658 cm^{-1} due to amide group ($-\text{CON}$) upon treatment of the immobilized diethyliminodiacetate with ethylenediamine and/or diethylenetriamine [105,106]. This provides strong evidence that all ethyl acetate groups ($-\text{CO}_2\text{Et}$) were converted into the amide groups ($-\text{N}-\text{C}=\text{O}$). The conversion of the immobilized diamine and triamine derivatives led to the formation of macrocyclic polysiloxanes by the reaction of the derivatives with 1,3-dibromopropane [48,114]. The infra red spectra of the diamine and triamine derivatives before and after treatment with 1,3-dibromopropane showed that the band at 3300 cm^{-1} to primary amine due to $\nu(\text{NH}_2)$ has disappeared and changed into secondary amine $\nu(\text{N-H})$ group and therefore ring closure.

The FTIR spectra were also used to examine the stability of the immobilized monoamine polysiloxane upon treatment with acidic solution. The FTIR spectra of treated samples show an increase of $\nu(\text{OH})$ bands at 3300 cm^{-1} and a decrease of $\nu(\text{Si-O})$ bands at the region $900\text{--}1200\text{ cm}^{-1}$ in comparison with the untreated sample.

3.3. XPS results

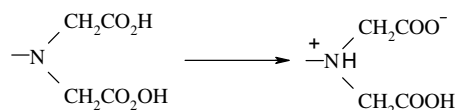
The XPS results give valuable information about the surface chemical composition and chemical environment

of polysiloxane surface ligand groups and their interaction with surface silanols or with other ligand groups [47,99,105,106].

The XPS results of the immobilized primary amine treated with base solutions (0.1 M NaOH) show that most of the amine groups (90%) are in the free form and a small portion (10%) is in the ammonium cation form. When the ligand is treated with 0.1 M HCl, a large contribution of ammonium cation (69%) and only a small portion of free NH_2 (31%) are present [99]. This can be explained that when the monoamine ligand system is treated with base, the protonated amines and/or hydrogen bonding amines by silanol groups have turned into free amine groups [99].

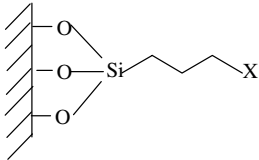
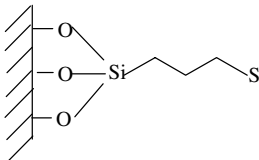
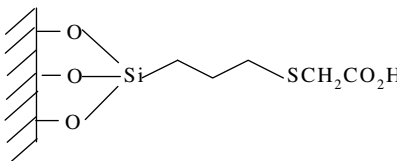
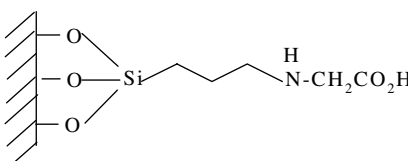
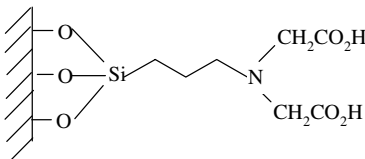
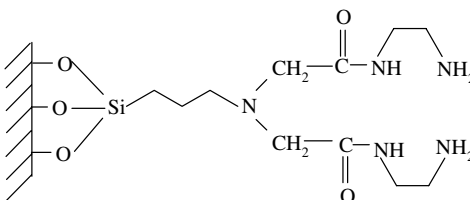
The $\text{NH}_3^+/\text{NH}_2$ ratio has changed, when the ligand system is treated with acid, large portions of amine groups have turned into ammonium cations. The presence of the free amine groups, despite protonation may suggest that some amine groups are buried into the bulk and are not accessible for H^+ [99].

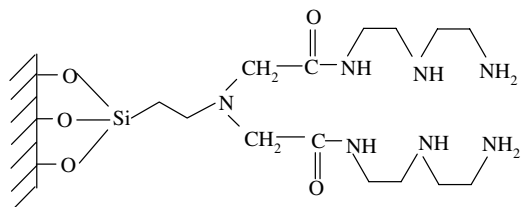
The XPS of silica immobilized ethyliminodiacetate and iminodiacetic acid ligand systems shows a significant difference in the N1s spectra region. The signals are fitted with two components centered at 399.5 and 401.8 eV assigned to free and cation, respectively [47]. It is clearly visible in the acetate form though its extent levels off at 20%. This is due to a strong acid–base interaction with silanol groups resulting in proton transfer towards some amine sites. In the case of the immobilized iminodiacetic acid [47], there is a contribution of 50.7% of protonated form. This may indicate that not all the diethyliminodiacetate groups are hydrolyzed by HCl and the two forms are present.



In the case of the copper complex form, the N1s is similarly fitted with two peaks, with amine cation contribution of 50% for the immobilized ligand to about 25% in the complex [47]. Complexation to the metal has reduced the amine cation from 50% to about 25%. The change in N ratio provides evidence that the N atoms are involved in the coordination to metal ions. The $\text{Cu}(\text{II})$ state is evidenced by the existence of shake-up satellite around 945 eV which is shortly lower than the expected that is consistent with some values reported in the literature for copper complex such as $\text{Cu}(\text{OAc})_2$ [148].

The uptake of copper ions by the immobilized iminodiacetic acid ligand system measured Cu/N ratio suggests a 1:1 metal-to-ligand complexes [26].

Formula	Ref.	Characterization	Method of preparation	Application
 <p>Where X = -NH₂ = -NH(CH₂)₂NH₂ = -NH(CH₂)₂N(CH₂)₂NH₂</p>	[35,36,39,45, 46,99,100]	Elemental analysis, FTIR, CP/MAS NMR and XPS (1) The ligand system suffers from leaching of some ligand containing groups upon treatment with acidic solutions (2) The amine groups mainly exist in the free form with only small protonated amine	Hydrolysis and polycondensation of a mixture of TEOS and the amino silane agent without catalyst Replacement of the halide group (I or Cl) on the pre-halopolysiloxane with the amino functionalized ligand	Metal uptake of divalent metal ions (Co ²⁺ , Ni ⁺ , Cu ²⁺ and Zn ²⁺) Chromatographic separation of Co ²⁺ , Ni ⁺ and Cu ²⁺ using column chromatography
	[115,111,112]	Elemental analysis, FTIR, ¹³ C CP-MAS NMR	Hydrolysis and polycondensation of a mixture of TEOS and the mercapto silane agent with catalyst	Uptake of divalent metal Ions (Cu ²⁺ , Ni ²⁺ and Co ²⁺)
	[41,42,44]	Elemental analysis, FTIR, ¹³ C CP-MAS NMR	Reaction of 3-mercaptopropylpolysiloxane ligand system with ethyl chloroacetate followed by acid hydrolysis	Uptake of divalent metal Ions (Cu ²⁺ , Ni ²⁺ , Co ²⁺ and Zn ²⁺). There is no clear stoichiometry structure
	[41,63,102,105]	Elemental analysis, FTIR and ¹³ C CP-MAS NMR The glycinate groups are attached through the acetate site and not the amine site	Reaction of 3-halopropylpolysiloxane with sodiumglycinate Reaction of monoamine polysiloxane with ethylchloroacetate followed by hydrolysis of the ester group	Metal uptake of Co ²⁺ , Ni ²⁺ and Cu ²⁺ from aqueous solution Chromatographic separation of Co ²⁺ , Ni ²⁺ and Cu ²⁺
	[47,103]	Elemental analysis, solid-state ¹³ C CP-MAS NMR, XPS, FTIR and thermal analysis (TGA)	Replacement of iodide in 3-iodopropyl polysiloxane with diethyliminodiacetate followed by hydrolysis	Extraction and uptake of di- and trivalent metal ions (Mn ²⁺ , Fe ³⁺ Co ²⁺ , Ni ⁺ , Cu ²⁺ and Zn ²⁺) The maximum metal uptake capacities suggest 1:1 complexes
	[106]	Elemental analysis, solid-state ¹³ C CP-MAS NMR, ¹⁵ N CP-MAS NMR XPS, FTIR and thermal analysis (TGA). This system was found to be stable at pH 6–8, but undergoes some leaching upon treatment with acidic solution	Reaction of pre-prepared diethyliminodiacetate polysiloxane with ethylene diamine	Extraction and uptake of di- and trivalent metal ions (Mn ²⁺ , Fe ³⁺ Co ²⁺ , Ni ⁺ , Cu ²⁺ and Zn ²⁺)

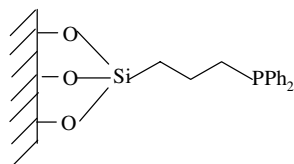


[107]

Elemental analysis, solid-state ^{13}C CP-MAS NMR, ^{15}N CP-MAS NMR XPS, FTIR and thermal analysis (TGA)

Reaction of pre-prepared diethyliminodiacetate polysiloxane with diethylene triamine

The metal uptake capacities suggest 1:1 metal-to-ligand complexes
Chromatographic separation of Co^{2+} , Ni^{2+} and Cu^{2+}
Extraction and uptake of di- and trivalent metal ions (Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+})

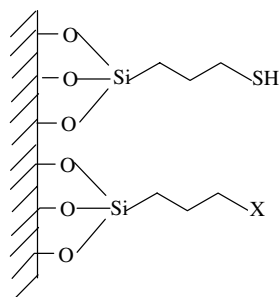


[40]

Solid state ^{13}C CP-MAS NMR, ^1H CP-MAS NMR and ^{31}P CP-MAS NMR

Hydrolysis and polycondensation of TEOS, diphenylphosphonopropyltrimethoxysilane

The metal uptake capacities suggest 2:1 metal-to-ligand complexes
Extraction and uptake of divalent metal ions (Ni^{2+} and Cu^{2+})



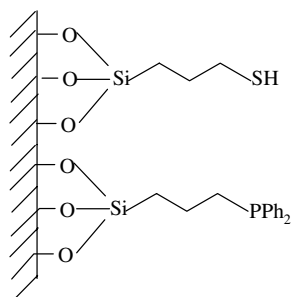
[116,42]

Solid state ^{13}C CP-MAS NMR, ^1H CP-MAS NMR and ^{15}N CP-MAS NMR

Hydrolysis and polycondensation of a mixture of TEOS, 3-mercaptopropyltrimethoxysilane and the amino silane agent in methanol

Extraction and uptake of divalent metal ions (Ni^{2+} , Cu^{2+} , Cd^{2+} and Hg^{2+})

Where X = $-\text{NH}_2$
= $-\text{NH}(\text{CH}_2)_2\text{NH}_2$

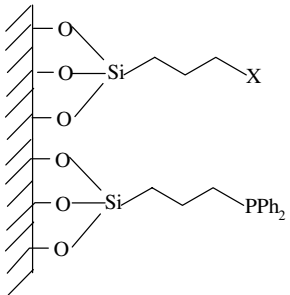
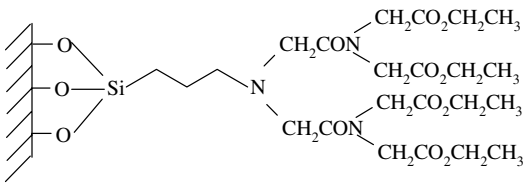
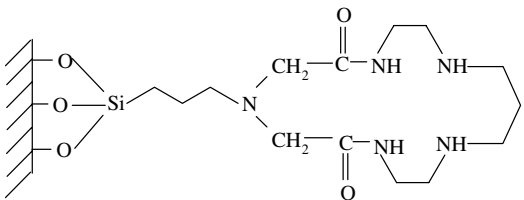
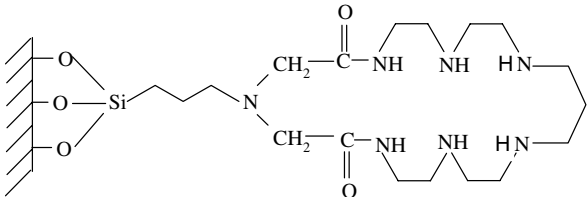


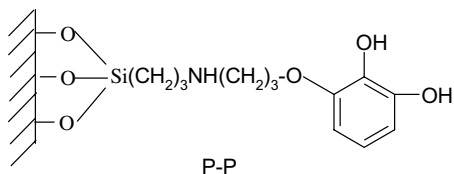
[115]

Solid state ^{13}C CP-MAS NMR, ^1H CP-MAS NMR and ^{31}P CP-MAS NMR

Hydrolytic polycondensation of a mixture of TEOS, 3-mercaptopropyltrimethoxysilane and diphenylphosphonopropyltrimethoxysilane

Extraction and uptake of divalent metal ions (Ni^{2+} and Cu^{2+})

Formula	Ref.	Characterization	Method of preparation	Application
 <p>Where X = -NH₂ or -NH(CH₂)₂NH₂</p>	[115]	<p>Solid state ¹³C CP-MAS NMR, ¹H CP-MAS NMR and ¹⁵N CP-MAS NMR</p> <p>NMR results showed that the hydrolysis was incomplete</p>	Hydrolytic polycondensation of a mixture of TEOS, amino functionalized silane agent and phosphine functionalized silane agent	Extraction and uptake of divalent metal ions (Ni ²⁺ and Cu ²⁺)
	[110]	<p>FTIR and thermal analysis (TGA)</p> <p>The TGA analysis showed that the ligand system is thermally stable</p> <p>FTIR provides that the tetraacetic acid groups are attached onto the polysiloxane matrix</p>	Reaction of pre-prepared diethyliminodiacetate polysiloxane with thionylchloride and diethyliminodiacetate, respectively	Extraction and uptake of divalent metal ions (Co ²⁺ , Ni ²⁺ , Cu ²⁺ and Zn ²⁺). The metal uptake capacities suggest 2:1 metal-to-ligand complexes
	[48]	Elemental analysis, solid-state ¹³ C CP-MAS NMR, XPS, FTIR and thermal analysis (TGA)	Reaction of the pre-prepared polysiloxane immobilized iminobis(<i>N</i> -(2-aminoethyl)acetamide) with 1,3-dibromopropane	2-Extraction and uptake of di- and trivalent metal ions (Fe ³⁺ , Co ²⁺ , Ni ²⁺ and Cu ²⁺). The macrocyclic ligand exhibits higher potential for metal ions than its parent precursor
	[114]	Elemental analysis, solid-state ¹³ C CP-MAS NMR, XPS, FTIR and thermal analysis (TGA)	Reaction of the pre-prepared polysiloxane immobilized iminobis(<i>N</i> -(diethylenediamine)acetamide) with 1,3-dibromopropane	Extraction and uptake of di- and trivalent metal ions (Fe ³⁺ , Co ²⁺ , Ni ²⁺ and Cu ²⁺)

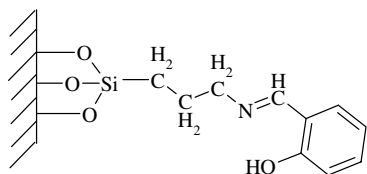


[108]

Elemental analysis, solid-state ^{13}C CP-MAS NMR, XPS, FTIR and Thermal Analysis (TGA)

Reaction of 3-aminopropylpolysiloxane with 1,3-dibromopropane followed by the reaction with pyrogallol

Extraction and uptake of di- and trivalent metal ions (Fe^{3+} , Co^{2+} , Ni^{+} and Cu^{2+}). Complexation with metal ions is in the order of $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{+} > \text{Co}^{2+}$

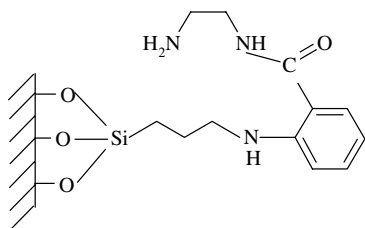


[113]

Elemental analysis, and FTIR

Modification of the immobilized 3-aminopropylpolysiloxane, P- $(\text{CH}_2)_3\text{NH}_2$ with an excess of salicylaldehyde

Extraction and uptake of divalent metal ions (Co^{2+} , Ni^{+} and Cu^{2+})

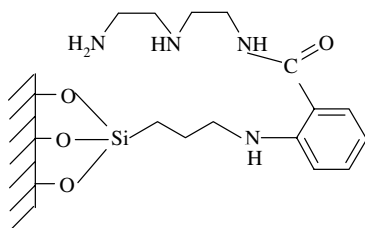


[113]

Elemental analysis, solid-state ^{13}C CP-MAS NMR, XPS, FTIR and thermal analysis (TGA). This system was found to be stable at pH 6–8, but undergoes substantial leaching upon treatment with acidic solution

Reaction of 3-iodopropylpolysiloxane with ethyl-2-aminobenzoate, then with ethylenediamine

Extraction and uptake of di- and trivalent metal ions (Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{+} , Cu^{2+} and Zn^{2+}). This ligand system exhibits high potential for metal ions with an efficiency of 92–98 after recovery



[113]

Elemental analysis, solid-state ^{13}C CP-MAS NMR, XPS, FTIR and thermal analysis (TGA). This system was found to be stable at pH 6–8, but undergoes substantial leaching upon treatment with acidic solution

Reaction of 3-iodopropylpolysiloxane with ethyl-2-aminobenzoate then with diethylenetriamine

Extraction and uptake of di- and trivalent metal ions (Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{+} , Cu^{2+} and Zn^{2+})

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