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REVIEW

Organosilicon Ion-exchange And Complexing Adsorbents

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Literature data concerning research organosilicon ion-exchangers and complexing agents have been summarized and systematized. Data on organophilic organosilicon adsorbents and sorption systems for chromatography are not considered here. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Hydrated silica gels and finely dispersed silica have long been known as efficient adsorbents of organic and inorganic substances.[1] For example, silica is recommended for sorption separation of platinum metals.[2] The idea of increasing the efficiency and selectivity of such sorption materials resulted in their modification with organic and organosilicon surfactants. [3–7] Thus, agents capable of recovering metals forming ammoniates (copper, zinc, cobalt, nickel etc.) were obtained on the basis of silica by this method.[3,5] A series of organosilicon anion-exchangers was synthesized by etherification of silica superficial hydroxyl groups with amino alcohols (mono-, di- and tri-ethanolamine) (Scheme 1).[5]

Sorption materials with acid functions were synthesized by modification of silica and aerosil surfaces with diphenyl(dichloro)silane followed by sulfonation of phenyl groups by oleum (Scheme 2).[8]

The cation-exchangers (sulfosilica and sulfoaerosils) synthesized have a high exchange capacity (200–500 mg g^{-1}) with respect to sodium. Organosilicon cation-exchangers were also obtained by silica modification with hydroxycarboxylic acids, for example, hydroxypropionic acid.[9]

The treatment of silica with 3-aminopropyl(triethoxy)silane and organosilicon disulfonic acid $O[Si(CH_2)_3CH_2C_6H_4SO_3H]_2$ leads to thermostable (290–300 °C) organosilicon cation- and anion-exchangers having an exchange capacity of 6.9–48 mg g^{-1}.[10–12]

To obtain organosilicon ion-exchangers another method was used: copolymerization of siloxanes containing vinyl groups (for example, divinyl(tetrabutoxy)disiloxane) with organic functional monomers (acrylic and metacrylic acids, vinylpyridine, sodium vinylsulfonate, the potassium salt of 4-styrene sulfonic acid, 4-aminostyrene etc.).[13,14] The hydrolytic cleavage of butoxy groups bound to the silicon atom leads to cross-linked structures of copolymers (Scheme 3).

Analogous organosilicon polymers with ion-exchange properties have been synthesized by copolymerization of allyl(triethoxy)silane, vinyl(trichloro)silane, vinyl-organyl siloxanes etc. with various unsaturated organic monomers with subsequent hydrolytic polycondensation of the copolymers obtained.[15–17] Thus, in particular, organosilicon cation sulfo-exchangers possessing a high exchange capacity with respect to NaOH (46–69 mg g^{-1}) and redox properties[18–20] have been synthesized. The redox capacity of one such cation-exchanger with respect to copper is 68.5 mg g^{-1}.[20]

The simplest and most efficient method of preparing organosilicon polymers with ion-exchange properties is based on three-dimensional

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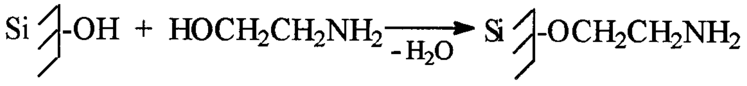
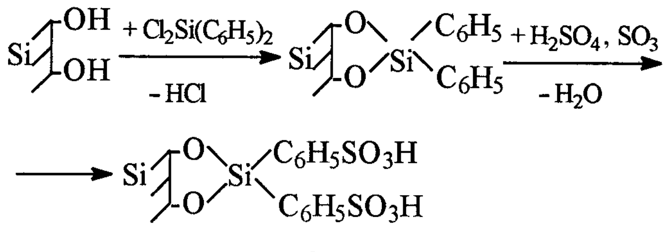
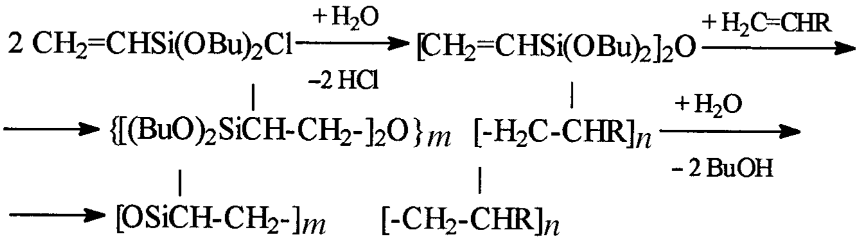


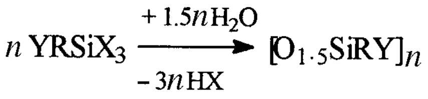
Scheme 1



Scheme 2



Scheme 3



Scheme 4

hydrolytic polycondensation of carbofunctional organosilicon monomers of the $YRSiX_3$ type, where Y is an ion-exchange group, R is a bivalent hydrocarbon radical and X is an easily hydrolyzed substitutent (Cl, OCOR, OR etc.).[21–25] Among such monomers the chloro-anhydrides of trichloro-hydrocarbon acids,[25] dichloro-silyllactones,[22] phenyl(dichloro)silane,[21] trichlorosilyl 'dichloro-phosphinyl' diphenyl[23] and trichlorosilyl(phenyl)-phosphonic acid dichloranhydride[24] have been studied (Scheme 4).

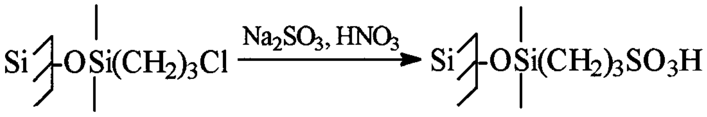
The ion-exchangers obtained by this method show high thermal stability (250 °C).[21–25] However, their ion-exchange properties were not studied intensively and the possibilities for their practical application were not determined.

Thus, all the methods of synthesis of organosilicon ion-exchangers and complexing agents can be divided into three major groups:

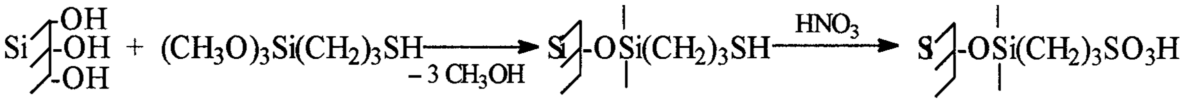
(1) immobilization of organic and organosilicon superficial modifiers on silica
(2) copolymerization and copolycondensation of unsaturated organosilicon and carbofunctional organic monomers
(3) hydrolytic polycondensation of organosilicon monomers of general formula X_3SiRY (the symbols X, R, Y were defined above).

SORPTION MATERIALS BASED ON SILICA WITH GRAFTED ORGANIC AND ORGANOSILICON SUPERFICIAL MODIFIERS

Up to now, grafting of organic or organosilicon superficial modifiers containing ionogenic or complexing groups to silica has been promising method for preparing ion-exchangers and complexing agents. The organosilicon superficial modifiers are connected by strong chemical bonds with free superficial silanol groups of silica at the expense of Si—O—Si bonds. If such modifiers have three reactive substitutents (Cl, OR, OCOR etc.) at the silicon atom, these silicon atoms are bound by oxygen atoms to form superficial siloxane net at the



Scheme 5



Scheme 6

expense of interaction with water absorbed by the modifier surface (for the mechanisms of these superficial reactions, see Ref. 26).

The organic modifiers grafting to silica are bound to its surface at the expense of the formation of hydrolytically unstable Si—O—C groups or by sorption forces. That is why the binding of organic modifiers with the surface of silica is less stable.[26]

A series of chelate-forming adsorbents aimed toward concentration of transition metals from aqueous media has been obtained by modification of silica with organosilicon monomers of general formula $Y(CH_2)_2Si(OR)_3$; $Y = H_2NCH_2CH_2NH—$, $S—C({=}S)N(CH_3)—$, $S—C({=}S)NHCH_2NH—$, $S—C({=}S)NH(CH_2)_2[S—C({=}S)]N—$, etc.[27,28]

An agent for preliminary concentration of oxyanions (AsO_4^{3-}, $Cr_2O_7^{2-}$, SeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, WO_3^{2-}) was prepared by processing glass microspheres with *N*-(2-aminoethyl)-3-aminopropyl(triethoxy)silane.[29] In this case, 90% of the oxyanions of selenium and manganese, dichromate anion and arsenate anions were already extracted after, respectively, 2, 4 and 8 min of contact with solutions. Complete (100%) sorption of selenate anions was observed at pH 2 and the amount of separated SeO_4^{2-} decreased with further increase of pH.

Organosilicon anion-exchange materials were synthesized by radiative chemical grafting of 2-vinyl- and 4-vinyl-pyridine to silica[30] or by radical polymerization of these monomers in the presence of silica.[31]

Agents with carbofunctional ionogenic groups were synthesized by modification of silica with corresponding organosilicon monomers of general formula $YRSi(OR')_3$; $Y = HSO_3^-$, $Cl^-(C_2H_5)_3N^+$; $R = (CH_2)_3$, C_6H_4; $R' = CH_3$, C_2H_5.[32]

A number of efficient adsorbents for gold were obtained by modification of Silichrom-120 with organosilicon amines $H_2N(CH_2CH_2NH)_n\ (CH_2)_3Si(OC_2H_5)_3$ ($n = 0$–2, 4), $Cl^-(CH_3)_3N^+\ (CH_2)_3Si(OC_2H_5)_3$.[33] These agents were also used for the concentration of platinum group metals (platinum and iridium) from chloride, sulfate and nitrate solutions.[34] A sorption–photometric method for the determination of platinum in distillates of alumino-platinum catalysts, and of gold–platinum and gold–platinum–palladium alloys, has been elaborated on the basis of these adsorbents.[34]

Silica modified with 3-chloropropyl(trichloro)-silane was used for the synthesis of a cation sulfo-exchanger (Scheme 5).[35]

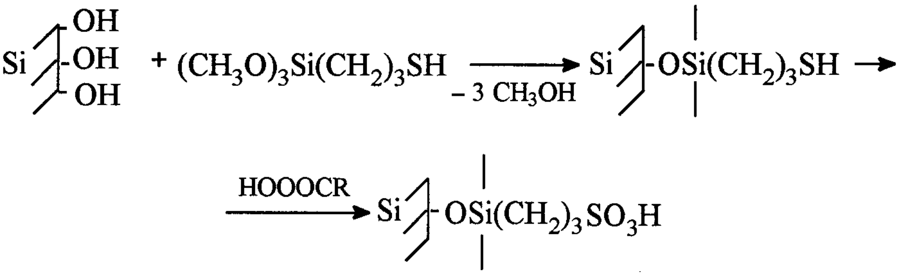
An analogous cation sulfo-exchanger was obtained by modification of silica with 3-trimethoxysilylpropanethiol with further oxidation of mercapto groups to sulfoacidic groups with nitric acid (Scheme 6).[36]

Silica modified with organosilicon monomers of general formula $YCH_2RSiR'R''X$; $Y = HS$, H_2N, C_5H_4N; $R = (—CH_2—)_n$, ($n = 1,2$), C_6H_4; R', $R'' = $ Alk, Ar, AlkO; $X = OR''$; $R''' = $ H, Alk, Ar, Ac[37,38] was recommended as an actinide sorbent, in particular for recovery of uranium from diluted sulfoacid solutions.

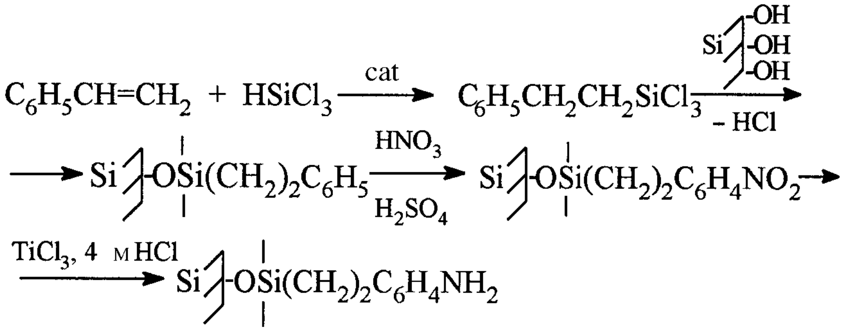
The sorption of ions of radioactive isotopes (americium, plutonium, techetium, europium, cobalt, thorium, uranium, iron, zinc, calcium) by the chelate ion-exchanger Diphosil on the basis of silica containing diphosphonate groups has been investigated.[39] This agent has a high affinity for four-valent actinides but their desorption from its surface is difficult.

Sorption materials efficient with respect to mercury(II), palladium(II) and copper(II) were synthesized by immobilization of amides of 2-thiophenecarboxylic, 2-thienylacetic and 2-furancarboxylic acids on the surface of silica gel.[40]

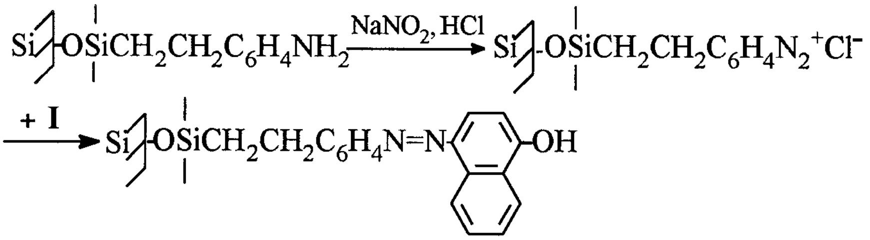
A further attempt was made to obtain on organosilicon cation sulfo-exchanger in an analogous manner, by immobilization of 3-mercaptopro-



Scheme 7



Scheme 8



Scheme 9

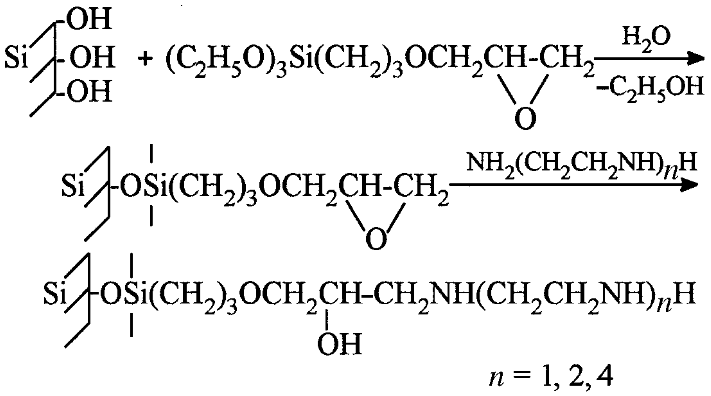
pyl(trimethoxy)silane on the surface of silica with subsequent oxidation of thiol groups to sulfoacidic groups by peracids (Scheme 7).[41]

However, only 50% of the thiol groups were converted into sulfoacid groups. The ion-exchange capacity of these cation sulfo-exchangers with respect to NaOH was not more than 3.5–7.8 mg g^{-1}.

Azo compounds belong to one of the most significant classes of selective analytical reagents,[42] so there is clearly interest in organosilicon adsorbents based on silica with chemically grafted azoreagents on its surface.[42] One of the first and the most complicated stages of preparing such agents is the grafting of the aromatic amine onto the silica surface. A method using grafting includes the use of titanium trichloride in 4M HCl as a reducing agent (Scheme 8).

Amino-phenyl-ethyl groups grafted to silica by this method are diazotized by a standard procedure (by the action of sodium nitrite in an HCl medium). 8-Hydroxyquinoline (**I**), salicylic and salicyhydroxamic acids were used as initial compounds for azo coupling (Scheme 9).

The agents obtained are highly efficient for the recovery of titanium, zirconium and thorium. However, the multistage preparation is a defect. Chemically modified silicas containing superficial groups $\text{—OSi(CH}_2)_n\text{X}$, where $\text{X} = \text{—NH}_2$, $\text{—N}^+(\text{CH}_3)\text{Cl}^-$, $\text{—C}_6\text{H}_4\text{SO}_3\text{H}$, were used for sorp-



Scheme 10

tion of scandium,[43] and analogous agents with $X = —N(CH_2COOH)_2$ were applied for recovery of a titanium peroxide complex[44] and titanium(IV) and europium(III) ions[45] from solution.

The chemically modified silica grafted with hydroxamic groups adsorbs zirconium ions very efficiently over a wide spectrum of medium acidity (0.1–4 M HCl) and in the presence of prevailing amounts of iron(III) and thorium(IV).[46] Modified silica containing sulfonic acid groups also extracts zirconium and titanium, thorium, hafnium and scandium quite effectively At the corresponding pH of medium this agent separates zirconium from titanium quantitatively.[47]

Agents possessing a fairly high sorption capacity with respect to copper (2–3 mm g^{-1})[48] were obtained by immobilization of 8-hydroxyquinoline on porous silica previously modified with aminophenyl(triethoxy)silane.

Silica modified with 3-(1-imidazolyl)propyl groups can be used for the concentration of microquantities of copper, nickel, zinc and cadmium from alcoholic solutions with the aim of determining the content of these impurities in the ethanol used as a fuel in internal combustion engines.[49] Sorption of cobalt(II), nickel(II), mercury(II), silver(I) and gold(III) by silica modified by 3-methyl-1-phenylpyrazol-5-one has been studied. This agent allows determination of the metal selectivity by varying the pH of the medium. Cobalt(II) and nickel(II) were eluted with HCl solutions with $pH < 1$; gold(III) and silver(I) were eluted by solutions with $pH > 5$.[50]

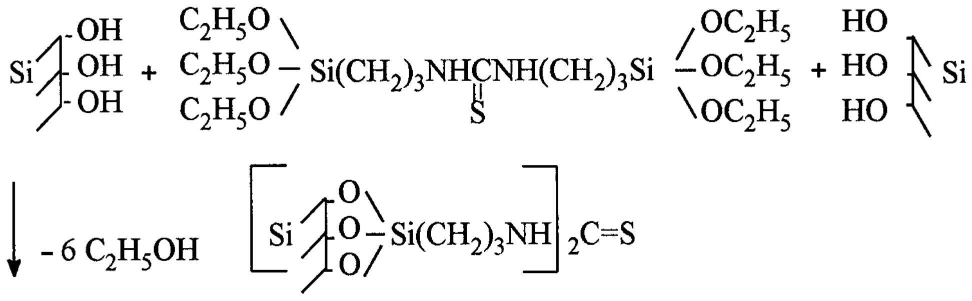
Patent data[51,52] have shown that the adsorbents based on silica modified with 8-hydroxy-7-(trimethoxysilylpropyl)quinoline or with organosilicon amines essentially absorb silver, gold, platinides, actinides, lanthanides and a number of nonferrous metals. At the same time, infused earth or acid clay treated with silanes containing CH_2CH_2SH or $NHCH_2CH_2NH_2$ groups were offered for the treatment of soils polluted with toxic metals such as copper(II), zinc(II), manganese(II), nickel(II), mercury(II), selenium(IV), cadmium(II) etc.[53]

Silica-containing covalently linked semicarbazides, thiosemicarbazides, ethylenediamines, phenylenediamines and phthalic and amber acids were examined as chromium(III), manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), magnesium(II), cadmium(II) and lead(II) adsorbents.[54] Their sorption capacity was higher than that of conventional ion-exchangers.[54]

Adsorbents based on modified silica in which iminodiacetic acid and tetraethyleneamine served as complexing resins were suggested for extensive use in inorganic analysis. The blending of modifiers with the surface of the silica is realized by crosslinking agents such as 3-chloropropyl- and 3-aminopropyl-(trichloro)silanes.[55,56] This approach to the preparation of adsorbents on the basis of silica (involving the use of carbofunctional organosilicon monomers as agents crosslinking the silica matrix with a complexing resin[57,58]) is being widely used at the present time for the synthesis of new sorption materials.[59–62]

An analogous method of preparing sorption materials based on silica modified with (3-glycidoxypropyl)triethoxysilane (to be described as a method of superficial assembly) was used for the preparation of organosilicon sorbents with grafting of ethylenediamine, diethylenetriamine and tetraethylenepentamine groups (Scheme 10).[63]

Characteristics of sorption of copper(II), nickel(II), cobalt(II), zinc(II), manganese(II) and



Scheme 11

tellurium(II) ions by the above materials have S7hy;been studied. The agent with grafting of the —NH(CH_2CH_2NH)$_4$H group was found to be the most efficient.

Silica modified with hexadecyl groups was offered for concentration of copper(II) diethyldithiocarbamate complexes.[64]

Copper(II)-β-diketonate complexes can be extracted from aqueous solutions on the surface of silica modified with octadecyl groups.[65]

Octadecylsilyl silica with a coating of methyl triacrylate–ammonium chloride, deposited in a dynamic regime, is recommended for concentration of trace quantities (2 ng l^{-1}) of zinc from seawater, the concentration factor being 125.[66] Silica modified by ethyldodecyloctadecylammonium nitrate with subsequent sorption of an osmium oxalate complex, was used as an adsorbent in a ^{191}Os/^{191m}Ir generator elaborated for use in nuclear medicine.[67]

Immobilization of pyridinium ions on the surface of silica with the help of chloropropyl(trichloro)silanes resulted in synthesis of agents which effectively extract anionic complexes of zinc(II), cadmium(II) and mercury(II) chlorides from aqueous and alcohol solutions to a high extent and also absorb cobalt(II) and copper(II) ions from acetone and ethanol media.[68,69]

A method of luminescent determination of iridium, involving preliminary concentration by silica with chemically grafted ammonium, guanidinium, triphenylphosphonium and primary amine groups, has been suggested.[70] Such agents perform as anion-exchangers in acid solutions. Silica with grafted iminoacetic groups is recommended as a vanadium(IV), vanadium(V) and molybdenum(VI) adsorbent.

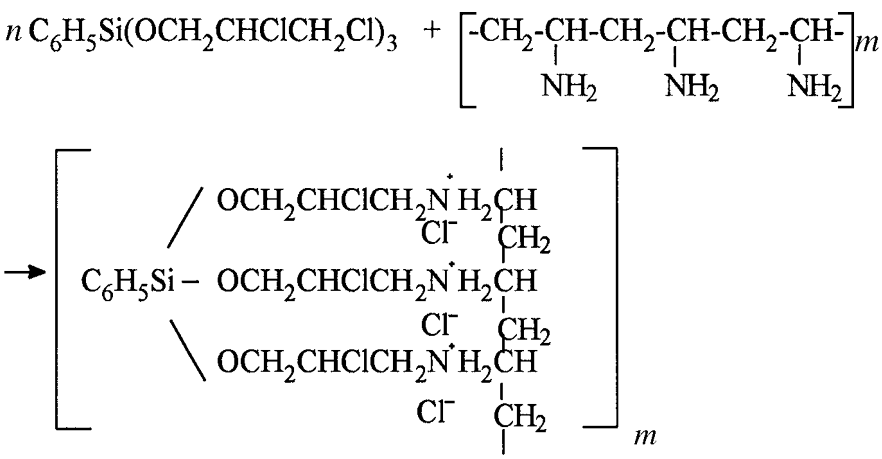
Though the method of superficial assembly (for the preparation of sorption materials based on silica) is widespread, the multistage sequence is considered to be a disadvantage. A more simple and efficient way of chemical modification of silica is based on the use of organosilicon monomers containing ionogenic or complexing groups. 3-Aminopropyl(triethoxy)silane is one such monomer, widely used for obtaining new types of sorption materials.[71,72] Silica modified by 3-aminopropyl(triethoxy)silane is used effectively for selective recovery of gold(III), platinum(IV) and palladium(II) chloride complexes from solutions with pH 2–5.[71] It allows separation of elements from copper(II) and Iron(III).

Agents prepared by superficial condensation of silica with 3-aminopropyl(triethoxy)silane or 3-trimethoxysilylpropanethiol are used for sorption of copper(II), silver(I) and gold(III) ions.[72] Silica modified by $(C_2H_5)_3SiCH_2CH_2CH_2SH$ is a more effective adsorbent of silver(I) and gold(III).[72]

The thiocarbamide and its *N*-organyl derivatives are very interesting complexing agents. The use of organosilicon monomers with carbofunctional thiocarbamide substitutents allows one to obtain effective sorption materials. Thus, agents effective for extracting not only metals such as silver(I), mercury(II), palladium(IV), but also halogen anions (F^-, Br^-) from solutions and complexing thiosulfate and platinum anions of silver, $[Ag(S_2O_3)_2]^{3-}$, were synthesized by immobilization of *N*,*N′*-bis(3-triethoxysilylpropyl)thiocarbamide on the surface of silica.[74] All six ethoxy groups of the modifying agent reacted with superficial hydroxy groups of silica, resulting in the formation of a chemically bonded polymeric coating of this type (Scheme 11).[75]

Natural zeolite, polymethylsilsesquioxane and cellulose acetate fibre modified with *N*,*N′*-bis-(triethoxysilylpropyl)thiocarbamide have been suggested as filter materials to absorb toxic metals (cadmium, cobalt, lead, arsenic, vanadium and others) and carcinogenic components (resins, polynuclear aromatic hydrocarbons, nitrosamines) from tobacco smoke.[76]

The high tendency of thiocarbamide groups



Scheme 12

to form complexes with platinum group metals was used for preparing immobilized rhodium(I) complexes based on silica modified with *N*-phenyl- and *N*-benzoyl-*N*′-(triethoxysilylpropyl)thiocarbamides. These compounds turned out to be very active insoluble and easily regenerated catalysts for styrene hydroformylation.[77,78]

A method of gold determination in samples with a low limit of detection (7–10 wt%) using silica modified with *N*-allyl-*N*′-(triethoxysilylpropyl)-thiocarbamide has been developed.[79] It was also found that gold(III) was reduced to gold(I) with the help of —NH—C(S)—NH groups of the grafted agent to form complexes with a 1:1 structure.

ORGANOSILICON ADSORBENTS BASED ON THE PRODUCTS OF COPOLYMERIZATION AND COPOLYCONDENSATION OF ORGANIC AND ORGANOSILICON MONOMERS

Methods for preparing organosilicon ion-exchangers and complexing agents based on copolymerization and copolycondensation of organosilicon and organic monomers are rather complex.[10] Nevertheless, they have been studied and transferred into practice.

Thus, a number of mechanically durable, thermally and chemically stable anion-exchangers was synthesized by condensation of phenyltris(2,3-dichloropropoxy)silane with polymeric organic amines: polyethylene-polyamine-polyethylenimine, polyxylylene-polyamine and polyvinylpyridine (Scheme 12).[80–82] The copolymers obtained are effective complexing agents, forming 1:1 complexes with transition metals such as copper, nickel and cadmium. The products of interaction of phenyltris(2,3-dichloropropoxy)silane with poly-(vinyl chlorides) have been recommended as ion-exchange membranes.[83]

A method of preparing organosilicon carboxylic cation-exchangers based on copolymerization of methacrylic acid with vinyl(triethoxy)silane in the presence of peroxide initiator has been patented.[84]

A number of anion-exchangers[85] have been synthesized by condensation of oligosiloxanes containing chloromethyl and ethoxy groups with aliphatic and aromatic polyamines. These anion-exchangers extract palladium selectively from aqueous solutions containing gold, platinum and osmium.

$$n\,\mathrm{O(CO)_2R(CO)_2O} + n\,\mathrm{4\text{-}H_2NNH(O)CC_6H_4Si(R_2)C_6H_4C(O)NHNH_2}$$

$$\longrightarrow \mathrm{[\text{-}C(O)C_6H_4Si(R_2)C_6H_4C(O)NHN(OC)_2R(CO)_2NNH\text{-}]}_n$$

Scheme 13

$$[(RO)_3SiCH_2]_2S + 6\,H_2O \xrightarrow[-6\,ROH,\,3\,H_2O]{} \tfrac{1}{x}\,[O_{1.5}SiCH_2SCH_2SiO_{1.5}]_x$$

Scheme 14

Attempts were made to obtain organosilicon agents by heteropolycondensation of compounds with general formula $SiR_{4-n}X_n$ ($R = H$, Alk; $X = OR'$, NR'_2; $n = 1–3$) and $X_nSi(R''Y)_{4-n}$ (R' = alkylen, arylene; Y = Hal, OH, CHO, COOH, SO_3, $PO(OH)_2$; $n = 1–3$) in aqueous solutions of inorganic acids and bases.[86] Polymeric agents were prepared by low-temperature (0–10 °C) polycondensation of aromatic dianhydrides $O(CO)_2R(CO)_2O$ (R = arylene) with organosilicon dihydrazides $[4\text{-}H_2NNHC(O)C_6H_4]_2SiR'_2$ and subsequent cyclization of the adducts obtained (Scheme 13).[87]

Organosilicon polymers forming complexes with copper were obtained by hydrolysis of methyl(2-cyanoethyl)- and methyl(3-cyanopropyl)-dichlorosilanes, with subsequent polymerization of the prepared oligosiloxanes in the presence of tetramethylammonium hydroxide.[88]

Polymeric, highly efficient water-absorbing agents were synthesized by the reaction of organic polymers containing the —COOM group (M = H, alkali metal or NH_4^+, polyacrylic or polymethacrylic acids and their salts, or salts of copolymers of methacrylic acid with starch or vinyl acetate) with organosilicon monomers of general formula $Y(CH_2)_nSiX_{4-n}$ (Y = Cl, OCH_2CH—, H_2N—, SH—, X = OR, $OCOCH_3$, $n = 0, 1, 2$) in the presence of either dibutyltin dilaurate or diacetate[89] or 1,4-dioxane or carbon tetrachlorides and an aqueous solution of sodium hydroxide.[80] The fresh- and salt-water absorbability of the polycondensation product of polyacrylic acid and 3-glycidoxypropyl(trimethoxy)silane in the presence of di(n-butyltin) dilaurate (0.9% salt) is 885.5 g g^{-1} and 105.1 g g^{-1}, respectively.

The method of obtaining ion-exchangers by processing of the composition with 5–10% of a water-soluble sodium or potassium salt of polyorganosiloxanes with general formula $[RSiO_{1.5}]_n$ ($R = C_{1–4}$ alkyl, $C_{2–4}$ alkenyl, phenyl), 30–90% alcohol ROH ($R = C_{1–4}$ alkyl and 5–50% water with the help of strong acid cation-exchangers and a weak base anion-exchanger has been patented.[91]

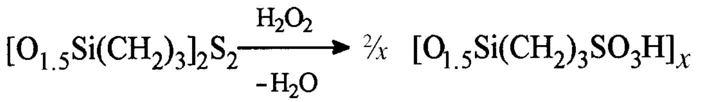
An organosilicon fibrous ion-exchanger, an efficient absorber of ammonium nitrogen from liquid media and also from solutions produced by the food industry (the sorption capacity with respect to NH_4^+ is >50mg g^{-1}), was obtained by processing of polyacrylonitrile fiber previously modified with aluminum(III) chloride at high temperature, with the help of aqueous sodium alkylsiliconate in the presence of hydrazine sulfate.[92]

Organosilicon complexing resins possessing redox-complexing properties with respect to bivalent metal chlorides were prepared by alkylation of oligochloromethyl(methyl)siloxanes with bipyridyl. However, the thermal stability of the prepared metal complexes was higher than that of the initial polymers.[93] The metal complexes obtained with cobalt(II) or zinc(II), for example, were polymeric structures of the π-coordinate type incapable of generating cation radicals.[94] From EPR-spectroscopy data, these complexes differed from the initial polymers, which generated the radical center on the polyquaternized dipyridyl fragment.

TRIMERIC ORGANOSILICON ION-EXCHANGERS AND COMPLEXING RESINS OBTAINED BY HYDROLYTIC POLYCONDENSATION AND COPOLYCONDENSATION OF CARBOFUNCTIONAL ORGANOSILICON MONOMERS

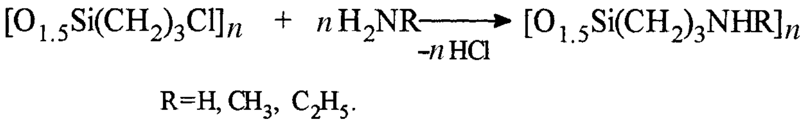
Hydrolytic polycondensation of carbofunctional organosilicon monomers of general formula $YRSiX_3$ or $Y(RSiX_3)_2$ (where Y = ionogenic or complexing group; X = Cl, OR', $OCOR'$, NR'_2, etc.; R = bivalent organic radical; $R' = CH_3$, C_2H_5) is the simplest and most convenient method for the synthesis of organosilicon ion-exchangers and complexing agents. Nevertheless, this approach, in contrast to chemical modification of silica, is very seldom used and data for the agents of this type are limited. Initial investigations[21–25] cited in the introduction have not been developed further.

Data on organosilicon anion-exchangers synthesized by hydrolytic copolycondensation of 3-(ethylenediamine)propyl(triethoxy)silane with tetraethoxysilane[95] are limited. Only those for their sorption capacity with respect to HCl (123 mg g^{-1}) and thermal stability (at 230 °C) are cited. The synthetic polymer was *N*-alkylated with alkyl



$$[O_{1.5}Si(CH_2)_3]_2S_2 \xrightarrow[-H_2O]{H_2O_2} {}^2\!/\!_x\ [O_{1.5}Si(CH_2)_3SO_3H]_x$$

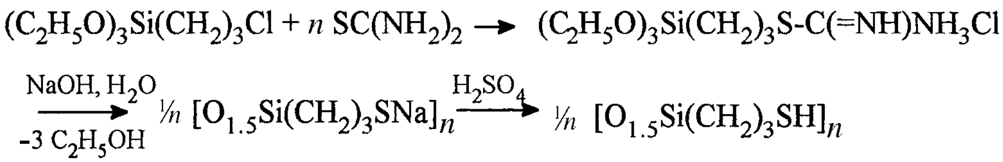
Scheme 15



$$[O_{1.5}Si(CH_2)_3Cl]_n + n\,H_2NR \xrightarrow[-n\,HCl]{} [O_{1.5}Si(CH_2)_3NHR]_n$$

$$R{=}H, CH_3, C_2H_5.$$

Scheme 16



$$(C_2H_5O)_3Si(CH_2)_3Cl + n\ SC(NH_2)_2 \rightarrow (C_2H_5O)_3Si(CH_2)_3S\text{-}C(=NH)NH_3Cl$$

$$\xrightarrow[-3\ C_2H_5OH]{NaOH,\ H_2O} {}^1\!/\!_n\ [O_{1.5}Si(CH_2)_3SNa]_n \xrightarrow{H_2SO_4} {}^1\!/\!_n\ [O_{1.5}Si(CH_2)_3SH]_n$$

Scheme 17

halides and dialkyl sulfates to decrease its basicity. The ion-exchangers obtained by this method have a sorption exchange capacity with respect to 0.1 M HCl lower than that for the initial polymer (93 mg g^{-1}).

Crosslinked polyorganylsiloxanes with elementary R^1SiR^2 units, where R^1 and R^2 were identical or different $O_{1.5}SiR^3$ groups in which R^3 is linear or branched C_1–C_{12} alkylene, $C_{5–6}$ cycloalkylene or $(CH_2)_nR^4(CH_2)_m$, (R^4 is cyclohexlene or phenylene; $n = 1–6$; $m = 0–6$) are recommended as adsorbents of ions or compounds of Group I, II and IV–VIII transition metals, and also of tin and lead. Polyorganylsiloxanes of this kind were obtained by hydrolytic polycondensation of corresponding monomeric organosilicon sulfides and polysulfides.[96] Scheme 14 shows their formation with bis(trialkoxysilylmethyl)sulfides as an example.

Organosilicon cation sulfo-exchangers were prepared by oxidation of polymeric sulfides such as $[(O_{1.5}SiR^3)_2S_k]_x$ (where R^3 is defined as above with hydrogen or sodium peroxide, bromine, peracids or hypochlorous acid salts;[97] Scheme 15 with poly-[bis(*S*,*S*′-silsesquioxanyl-propyl) disulfides] can serve as an example.

The synthetic cation sulfo-exchangers were produced as either as H-forms (A) or in the form of salts $[(O_{1.5}SiCH_2CH_2CH_2SO_3)_yM]_x$ (B), where M is a one- to four-valent ion of the metal and *y* is the metal oxidation state. The exchange capacity of such cation sulfo-exchangers by H^+ is 5 mg g^{-1}. These investigations[96,97] have so for not been developed further.

Polymers synthesized by hydrolytic polycondensation of organosilicon derivatives of thiocarbamide with general formula $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHR$, where R = Ph or C(O)Ph, or $C_6H_4NHC(S)NH(CH_2)_3Si(OC_2H_5)_3$, as well as the products of the modification of silica by these polymers, easily form 1:1 complexes with rhodium.[77,78]

Porous crosslinking polysiloxanes obtained by copolycondensation of three or more silanes $Si(OR)_4$ and $SiR'(OR)_3$, where $R' = H_2NCH_2CH_2CH_2$— in at least one reagent, are good sorption materials.[99]

Organosilicon ion-exchangers were obtained by substitution of the chlorine atom of the C–Cl bond by ionogenic substitutents in the products of hydrolytic polycondensation of phenyl(trichloro)-silane[100] or 3-chloropropyl(trichloro)silane.[101]

A cation sulfo-exchanger with an exchange capacity for NaOH of 29.6 mg g^{-1} and thermally resistant up to 300 °C (analogous to that synthesized earlier[23]) was obtained as a result of sulfonation of polyphenylsilsesquioxane by sulfuric acid.[100]

Ion-exchangers based on poly(3-chloropropylsilsesquioxane) were synthesized by condensation of

$$(RO)_3Si(CH_2)_mSH + 1.5\,H_2O \xrightarrow[-3\,ROH]{} {}^1\!/\!_n\,[O_{1.5}Si(CH_2)_mSH]_n$$

Scheme 18

$$[Ag(S_2O_3)_2]^{3-} \rightleftharpoons Ag^+ + 2S_2O_3{}^{2-}$$

$$[O_{1.5}SiCH_2CH_2SH]_n + nAg^+ \rightarrow [O_{1.5}SiCH_2CH_2SAg]_n + nH^+$$

Scheme 19

the latter with Na_2SO_4, NH_3, $MeNH_2$ or $EtNH_2$ (Scheme 16).[100]

An organosilicon ion-exchanger containing mercapto groups, $[O_{1.5}Si(CH_2)_3SH]_n$, was obtained by the interaction of poly(3-chloropropylsilsesquioxane) with thiacarbamide with subsequent hydrolysis of the reaction product at pH 8.5–9.[102] An analogous ion-exchanger was synthesized by a method reported in Ref. 103 (Scheme 17).

Analogous ion-exchangers were synthesized by the authors using a simple procedure involving hydrolytic polycondensation of ω-mercaptoalkyl-(trialkoxy)silane) $HS(CH_2)_mSi(RO)_3$; $R = CH_3$, C_2H_5; $m = 1–2$ (Scheme 18).[104–106]

The first ion-exchanger of this type (a xerogel of polymercaptomethylsilsesquioxane) was obtained in 1997.[104,105] It is considered to be an efficient adsorbent with respect to mercury(II),[105,107] and quantitatively absorbs mercury(II) even from very dilute solutions (0.01–2 mg l^{-1}) at pH 0.3–12. This ion-exchanger is highly selective with respect to mercury(II) at pH 0.3–3 and absorbs mercury in the presence of metals such as zinc(II), cobalt(II), iron(III) and nickel(II). Such an agent is recommended for the extraction of mercury from sewage water and from chlorine production.[107] It also exhibits high efficiency with respect to tin(II) and lead(II) extraction at $pH > 3$.[108] This provides the basis for developing a method for the determination of tin(II) and lead(II) in mineral waters.[108] The method involves sorption concentration of tin(II) and lead(II) from aqueous samples, followed by atomic-emission (AE) spectral determination of the elements.[109]

The agents containing thiol groups $[O_{1.5}Si(CH_2)_mSH]_n$ ($m = 1, 2$) exhibit high sorption activity with respect to silver(I)[105,106,110,111] at pH 0.3–3 in the presence of prevailing amounts of zin(II), lead(II), iron(III), nickel(II) and cobalt(II). The quantitative extraction of silver(I) from solutions by these agents is possible if their concentration is within the range $3 \times 10^{-6}–8 \times 10^{-1}$ mg ml^{-1}. Poly(2-mercaptoethylsilsesquioxane) ($m = 2$) is suitable for the extraction of silver from thiosulfate solutions, containing the metal as the complex anion $[Ag(S_2O_3)_2]^{3-}$.[111] The sorption ion-exchange mechanism is probably provided by partial dissociation of the complex silver anion, with further recovery of Ag^+ by a cation-exchange mechanism (Scheme 19). The exchange capacities of ion-exchangers are listed in Table 1.

The creation of polymercaptomethylsilsesquioxane xerogel was the beginning of extensive investigations by the present authors in the field of organosilicon ion-exchangers and complexing resins, analogs of organic ion-exchange agents and complexones.[74,104–108,110–128] In all cases the same method of obtaining of such sorption materials was used, that of hydrolytic polycondensation of suitable monomers $X_3Si(CH_2)_mY$, $X_3C_6H_4Y$ or $Z[(CH_2)_mSiX_3]_2$, where $X = Cl$, OCH_3, OC_2H_5; $m = 1–3$; $Y = —SH$, $—SO_2Cl$, $—S(CH_2)_xNH_2$ ($x = 2, 3$); $Z = —NHC(O)NH—$, $—NHC(O)NHC(O)NH—$, 1,4-$NHC(O)C_6H_4C(O)NH—$, $—NHC(S)NH—$, $—NHS(O_2)NH—$, $—NHSSNH—$, $—NHS(O)NH—$, $C_6H_4(CONH—)_2$. Such an approach to the synthesis of organosilicon ion-exchangers and complexing resins became possible due to the production of simple and effective synthetic routes for the corresponding monomers.[106–108,112–116,119–121,128–133]

Hydrolytic polycondensation of most of the synthetic monomers was performed in aqueous or aqueous–dioxane media at pH 7–8 at temperatures of 20 or 60–70 °C (Schemes 20 and 21).[105, 106, 112–114, 116]

In some cases, for example hydrolysis of 2-(triethoxysilylethylthio)ethylamine hydrochloride[131] and of organosilicon monomers based on thioglycolic acid $(C_2H_5O)_3SiCH_2CH_2SCH_2$

Table 1 Organosilicon adsorbents, their properties and sorption activity

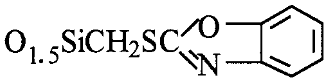
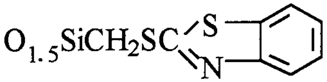
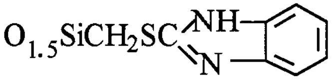
Adsorbent (monomeric unit)	IR data (cm^{-1})	Onset temperature of decomposition (°C)	Adsorbate capacity ($mg\ g^{-1}$)	Static adsorption	Refs
$O_{1.5}SiCH_2SH$	$\nu_{SH} = 2560–2580$	230	Ag(I)	119	108,110
			Hg(II)	20	107
			Se(IV)	2	118
$O_{1.5}Si(CH_2)_2SH$	$\nu_{SH} = 2560–2580$	225	Ag(I)	140	106,111
			Ag(I) (thiosulfate soln)	75	111
$O_{1.5}SiCH_2SO_3Na$	$\nu_{SO_2} = 1070, 1190$	200	Se(IV)	3.4	118
			Te(IV)	12	117
$O_{1.5}Si(CH_2)_2SO_3Na$	$\nu_{SO_2} = 1070, 1190$	270	Se(IV)	6.6	118
			Te(IV)	13	117
$O_{1.5}Si(CH_2)_3SO_3Na$	$\nu_{SO_2} = 1070, 1190$	260	Co(II)	86	74
			Ni(II)	69	74
			Hg(II)	140	74
			Te(IV)	12.6	117
$[O_{1.5}SiCH_3][OSi(CH_3)CH_2SO_3Na]$	$\nu_{SO_2} = 1070, 1200–1210$	240	Pr(III)	13.5	119
			Tb(III)	10.5	119
$O_{1.5}Si(CH_2)_2S(CH_2)_2NH_2$	$\nu_{NH_2} = 3490, 3395$	—	Au(III)	218	113
			Pt(IV)	147	113
			Pd(II)	235	113
$O_{1.5}Si(CH_2)_2S(CH_2)_3NH_2$	$\nu_{NH_2} = 3350, 3390$	—	Au(III)	54	113
			Pt(IV)	41	113
			Pd(II)	45	113
$O_{1.5}Si(CH_2)_3NHC(O)CH_3$	$\nu_{C(O)NH} = 1550, 1010$ $\nu_{CO} = 1630$	210	Au(III)	28	113
			Pt(IV)	25	113
			Pd(II)	21	113
$O_{1.5}Si(CH_2)_3NHC(S)CH_3$	$\nu_{C(S)NH} = 3220, 1530, 1020$	230	Au(III)	230	113
			Pt(IV)	290	113
			Pd(II)	70	113
			Ag(I) (thiosulfate soln)	127	111
$O_{1.5}Si(CH_2)_2SCH_2COONH_4$	$\nu_{CO} = 1740$ $\nu_{NH} = 3300$	—	Au(III)	206	115
			Pt(IV)	14	115
			Pd(II)	44	115
		315	Au(III)	64	120
			Pt(IV)	34	120
			Pd(II)	48	120
		63	Au(III)	140	120
			Pt(IV)	135	120
			Pd(II)	204	120
		153–160	Au(III)	260	120
			Pt(IV)	62	120
			Pd(II)	115	120

Table 1 *continued*

Adsorbent (monomeric unit)	IR data (cm^{-1})	Onset temperature of decomposition (°C)	Adsorbate capacity (mg g^{-1})	Static adsorption	Refs
$[O_{1.5}Si(CH_2)_3NHC(O)]_2C_6H_4$	$\nu_{CO} = 1640$ $\nu_{NH} = 1550, 3280$	—	Au(III)	114	128
			Pt(IV)	19.5	128
			Pd(II)	44.5	128
$O_{1.5}Si(CH_2)_2S(CH_2)_2SiO_{1.5}$		—	Pt(IV)	70	114
			Pd(II)	78	114
$O_{1.5}Si(CH_2)_2SS(CH_2)_2SiO_{1.5}$		230	Au(III)	58	113
			Pt(IV)	50	113
			Pd(II)	53	113
$O_{1.5}Si(CH_2)_3NHC(S)NH(CH_2)_3SiO_{1.5}$	$\nu_{NH} = 3300$ $\delta_{NH} = 1570$ $\nu_{C=S} = 1350$	270	Au(III)	450	127
			Pt(IV)	120	127
			Pd(II)	160	127
			Os(IV)	46	127
			Ir(IV)	48	127
			Rh(IV)	44	127
			Ru(IV)	31	127
			Ag(I)	128	127
			Ag(I) (thiosulfate soln)	170	111
			Hg(II)	210	127
			Cu(II)	137	127
			U(VI)		127
			As(III, V)	145	127
			Sb(III)	110	127
			F(I)	170	127
			Br(I)	156	127
$O_{1.5}Si(CH_2)_3NHC(O)NH(CH_2)_3SiO_{1.5}$	$\nu_{C=O} = 1630$	—	Pr(III)	9	112
			Tb(III)	10.8	112
$[O_{1.5}Si(CH_2)_3NHC(O)]_2NH$	$\nu_{C=O} = 1680$	—	Pr(III)	12	112
			Tb(III)	14.5	112
$O_{1.5}Si(CH_2)_3NHSSNH(CH_2)_3SiO_{1.5}$	$\nu_{NH} = 3260$	—	Au(III)	650	113
			Pt(IV)	55	113
			Pd(II)	380	113
			Ag(I)	396	111
			Ag(I)(thiosulfate soln)	108	111
$O_{1.5}Si(CH_2)_3NHS(O)NH(CH_2)_3SiO_{1.5}$	$\nu_{NH} = 3220$ $\nu_{SC} = 1040–1060$	—	Au(III)	24	113
			Pt(IV)	27	113
		—	Pd(II)	30	113
			Sm(III)	212	125
			Tm(III)	175	125
$O_{1.5}Si(CH_2)_3NHS(O_2)NH(CH_2)_3SiO_{1.5}$	$\nu_{NH} = 3250$ $\delta_{SO_2} = 1300, 1130$		Au(III)	19	113
			Pt(IV)	15	113
			Pd(II)	12	113
			Tm(III)	130	125

$$X_3Si(CH_2)_mY + 1.5\,H_2O \xrightarrow[-3\,HX]{} \frac{1}{n}\,[O_{1.5}Si(CH_2)_mY]_n$$

Scheme 20

$$[X_3Si(CH_2)_m]_2Z + 3\,H_2O \xrightarrow[-6\,HX]{} \frac{1}{n}\,\{[O_{1.5}Si(CH_2)_m]_2Z\}_n$$

Scheme 21

$$(C_2H_5O)_3Si(CH_2)_2S(CH_2)_2NH_2\,HCl + 1.5\,H_2O + NH_3$$
$$\rightarrow \frac{1}{n}\,[O_{1.5}Si(CH_2)_2S(CH_2)_2NH_2]_n + 3C_2H_5OH + NH_4Cl$$

Scheme 22

$$(C_2H_5O)_3Si(CH_2)_2SCH_2COOH + 1.5\,H_2O + NH_3$$
$$\rightarrow \frac{1}{n}\,[O_{1.5}Si(CH_2)_2SCH_2COONH_4]_n + 3C_2H_5OH$$

Scheme 23

COOH,[115] the reaction was performed in 6 M NH_4OH for use either in dehydrochlorination of the polymer obtained[74] (Scheme 22) or in protection of the carboxyl group involved in polycondensation (Scheme 23).

In contrast to other investigations where, for the preparation of organosilicon cation sulfo-exchangers, sulfonation of the crosslinked organosilicon polymers already obtained[25,100] or oxidation of polysilsesquioxanylalkyl sulfides[97] was used, a synthesis of cation sulfo-exchangers of general formula $[O_{1.5}Si(CH_2)_mSO_3H]_n$ was performed by oxidative hydrolytic polycondensation of trialkoxysilylalkanethiols (Scheme 24).[25,97,100]

$$(RO)_3Si(CH_2)_mSH + 3\,H_2O_2 \xrightarrow{H_2O} \frac{1}{n}\,[O_{1.5}Si(CH_2)_mSO_3H]_n + 3ROH$$

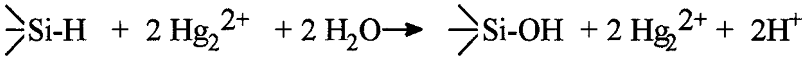
Scheme 24

$$2\,(CH_3)Si(CH_2SO_2Cl)Cl_2 + 7\,H_2O \rightarrow CH_3(HO)_2Si(CH_2SO_2OH)$$
$$+ (HO)_3SiCH_3 + 6\,HCl + CH_3SO_2OH$$

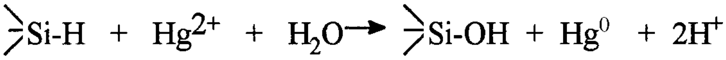
Scheme 25

$$CH_3Si(CH_2SO_2OH)(OH)_2 + (HO)_3SiCH_3 \xrightarrow[-2.5\,H_2O]{}$$
$$\frac{1}{m}\,[OSi(CH_3)CH_2SO_2OH]_m \cdot \frac{1}{n}\,[O_{1.5}SiCH_3]_n$$

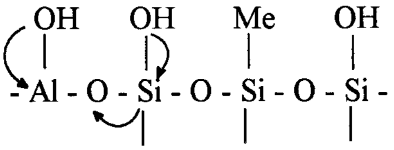
Scheme 26



Scheme 27



Scheme 28



Scheme 29

Polysulfoalkylsilsesquioxanes synthesized by this method were isolated and investigated in the form of salts $[O_{1.5}Si(CH_2)_mSO_3M]$; M = Na, K.[74,118] The organosilicon cation sulfo-exchanger $[O_{1.5}SiCH_3]_m \cdot [OSi(CH_3)CH_2SO_3H]_n$ ($m/n = 3:2$ or 1:1) was obtained by hydrolysis of chlorosulfonylmethyl(methyl)dichlorosilane (Schemes 25,26).[119]

Conditions excluding full cleavage of Si—$ClSO_2CH_2$ have been discovered.[134]

A wide series of carbofunctional polyorganosilsesquioxanes studied as ion-exchangers and complexing agents with respect to silver, gold, platinum group metals, lanthanides, actinides, toxic metals (mercury, copper, tin, lead), chalcogens and halogen anions (F^-, Br^-) etc., has been synthesized. Their physicochemical and sorption characteristics are listed in Table 1.

The ion-exchangers and complexing agents obtained were used for detection and recovery of elements in natural, industrial and synthetic materials. For example, a rapid and effective method for the determination of silver in copper concentrates,[123] or gold in natural objects (auriferous sands and complex ores),[124] and a method for the determination of gold in rocks and ores by combination of chemical and AE spectral analysis[127] with a detection limit of 5×10^{-8}% have been developed based on polymer-containing thiocarbamide groups $[O_{1.5}Si(CH_2)_3NHC(S)NH(CH_2)_3SiO_{1.5}]_n$. An agent with diamino–disulfide groups $[O_{1.5}Si(CH_2)_3NHSSNH(CH_2)_3SiO_{1.5}]_n$ was used for the extraction of silver from nitric acid and thiosulfate solutions from the cinema-production and photographic industry.[111]

In some investigations the products of hydrolytic polycondensations of tetraalkoxy- and trialkoxysilanes containing no carbofunctional substitutents (the sol–gel process) are used as agents. These agents are three-dimensional polysiloxanes containing free hydroxy and alkoxy groups.

A xerogel obtained by hydrolysis of tetraalkoxysilanes $Si(C_nH_{2n+1})_4$, where $n > 4$, has been recommended as an adsorbent for the industrial extraction of uranium from seawater.[98] The product of hydrolytic polycondensation of triethoxysilane — polysilsesquioxane $[HSiO_{1.5}]_n$ — is an efficient adsorbent of mercury(II) with an exchange capacity for mercury of 3–6 g g^{-1}.[135] This agent is suitable for recovery of mercury from industrial solutions. The mechanism of mercury sorption includes the stage of mercury reduction (Schemes 27 and 28). The first stage of the process is physical adsorption of mercury(II) or Mercury(0). The reduction of mercury according to Scheme 27 is performed in strongly acid solutions containing large quantities of mercury and according to Scheme 28, in weak acid solutions with minor quantities of mercury.

The introduction of 1.9–4.9% of aluminum into the products of cohydrolysis of tetraethoxysilane and methyltriethoxysilane (silicopolymethylsiloxanes) leads to quite efficient adsorbents of cesium ions.[136] The mechanism of cesium sorption is thought to be ion-exchange at the expense of superficial hydroxyl groups. The introduction of aluminum into the siloxane matrix increases the acidity of silanol groups owing to displacement of electronic density from oxygen atoms to silicon atoms according to Scheme 29, and thus facilitates the exchange of ions.

Summing up the data of this section, it should be noted that organosilicon ion-exchangers and complexing agents prepared by hydrolytic polycondensation of organosilicon monomers with carbofunctional ionogenic and complexing groups of $X_3Si(CH_2)_mY$, $X_3SiC_6H_4Y$, $Z[(CH_2)_mSiX_3]_2$ types (where the symbols X, Y, Z have been defined above) are most useful. The crosslinked silsesquioxane structure of these polymers is responsible for their high thermal and especially important chemical stability.

CONCLUSIONS

It can be seen that organosilicon ion-exchange and complexing sorbents are effective agents for determining particular elements in natural and industrial media and for recovery of elements from industrial wastes and effluents. Such agents are widely used in present day analytical practice.

However, sorbents prepared by hydrolytic polycondensation of organosilicon monomers with carbofunctional ionic and complexing groups are the most suitable among all the organosilicon sorption materials. The crosslinked silsesquioxane structure of these polymers is responsible for their high thermal and chemical stability.

These agents do not lose their sorption activity, even in a highly aggressive medium such as hot concentrated sulfuric acid (7.5 M and above, at 100 °C).[74]

The silsesquioxane matrix of these polymers does not influence the specific reactivity of the coordination centers of the carbofunctional group. In accordance with this polymers containing sulfhydryl groups are more active with respect to metals of the hydrogen sulfide subgroup, as expected. The organosilicon cation sulfo-exchanger may be used for the recovery of lanthanides, as well as their organic analogs. For example, the specific reactivity of thiocarbamide (formation of isothiuronium salts in acid media, inclination toward thione–thiol tautomerism and the related redox function) is the cause of the wide spectrum of sorption activity of organosilicon agents containing thiocarbamide groups (see Table 1).

The sorption activity of such ion-exchangers and complexing agents is essentially higher than that of silica modified by the corresponding method. These agents can be considered to be new-generation methods.

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