

Synthesis

Spherosiloxanes and Spherometallosiloxanes

Heribert Bürgy^{a)}, Gion Calzaferri^{a)}*, Daniel Herren^{a)}, and Alexandre Zhdanov^{b)}

Abstract. Spherosiloxanes are regularly built spherical silsesquioxanes of the general formula $(\text{RSiO}_{3/2})_n$ ($n = 8, 10, 12, \dots$). A new class of materials is obtained, the spherometallosiloxanes, if some of the Si-atoms in the cage of the polyhedral siloxanes framework are replaced by metal atoms. The synthesis, the structure, and some properties of such molecules are discussed. We have discovered new synthetic routes to spherosiloxanes opening a field of many new interesting molecules. The NMR, IR, and Raman spectra are very simple due to the high symmetry of the molecules. Silanization is a highly successful form of surface modification. Silanes that are able to react with surface OH groups to form silyl-ether bonds can be bound covalently to a surface. We discuss surface-modification experiments based on this principle and report some recent results. Spherosiloxanes attracted our interest as model substances for investigating zeolites because of the resemblance of the framework structure of octasilsesquioxanes to the double four ring of zeolites. We focus on silver and copper zeolites, since they may be useful in an artificial photosynthesis system which is briefly explained.

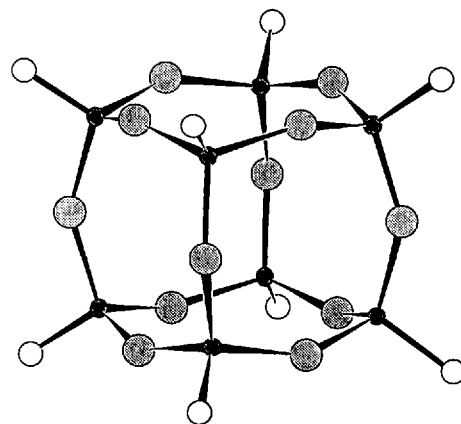
Introduction

The idea of the formation of a polymeric chain from alternating Si- and O-atoms led at the beginning of the 20th century to the discovery of a new class of high-molecular-weight compounds, polymers with inorganic principal molecular chains. A special class of such polymers is represented by the silsesquioxanes: siloxanes consisting of $\text{RSiO}_{3/2}$ units may be considered as the products of the complete hydrolytic condensation of the corresponding trifunctional monomers, XSiY_3 with $\text{Y} = \text{Hal}, \text{OH}, \text{OR}, \text{OCOR}, \text{etc.}$ The first reports on such compounds date back to the second half of the last century, when attempts were undertaken to synthesize the Si-analogues of the carboxylic acids. The compounds obtained by hydrolysis of XSiCl_3 ($\text{X} = \text{H}$ and C_6H_5) were mistaken for anhydrides [1]. The polymer-like character of the so formed siloxanes was discovered in 1914 [2]. Only in 1946, the first volatile so-called spherosiloxane, namely the octa(methylsilsesquioxane), was isolated [3]. Spherosiloxanes are regularly built spherical silsesquioxanes of the general formula $(\text{RSiO}_{3/2})_n$ ($n = 8, 10, 12, \dots$) 1-4 [4]. The first example of an $(-\text{O})_3\text{Si}-\text{X} + \text{Y} \rightarrow (-\text{O})_3\text{Si}-\text{Y} + \text{X}$ substitution in spherosiloxanes $(\text{XSiO}_{3/2})_8$ leading directly to the

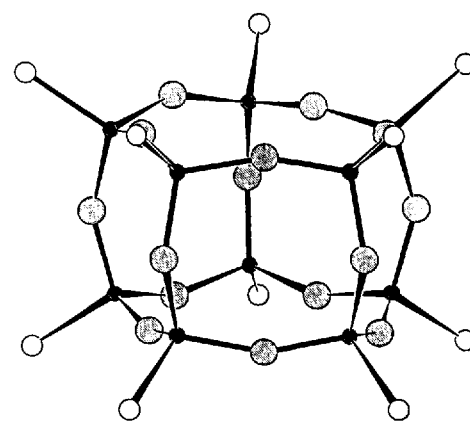
formation of an $(-\text{O})_3\text{Si}-\text{C}$ bond has been found recently [5]. This reaction will lead to a great number of new oligosilsesquioxanes. If a part of the Si-atoms in the cage of the polyhedral siloxane framework of spherosiloxanes is replaced by metal atoms, a new class of materials is obtained, the spherometallosiloxanes [6].

The routes to spherosiloxanes can be divided into three main groups represented in the *Scheme*, depending on the nature of the starting materials.

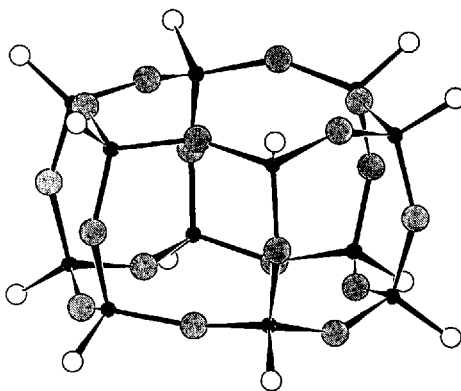
The first group **a** includes reactions that result in the formation of the polyhedral framework. The hydrolytic polycondensation of trifunctional monomers is the most important type of this class. It is a complex, multistep reaction process that leads to polymers and oligomers which may contain the required spherosiloxanes. As an example for this kind of reaction, we comment on the synthesis of octa(hydridosilsesquioxane) $(\text{HSiO}_{3/2})_8$ (**1**, $\text{R} = \text{H}$) as described by *Frye and Collins* [7]: a solution of $(\text{MeO})_3\text{SiH}$ in cyclohexane is added over a 9-h period to a vigorously stirred reaction flask containing AcOH (previously saturated with HCl), cyclohexane, and some conc. HCl. The latter is acting as a catalyst. The organic phase is then washed with H_2O until neutral. After evaporation of the solvent, a white material remains. This is put into a sublimation chamber. Octa(hydridosilsesquioxane) (**1**, $\text{R} = \text{H}$) contaminated with mostly deca(hydridosilsesquioxane) $(\text{HSiO}_{3/2})_{10}$ (**2**, $\text{R} = \text{H}$) can be sublimated at about 100° . Recrystallisation from cyclohexane delivers 13% of pure **1** ($\text{R} = \text{H}$). The synthesis of the higher hydridosilsesquioxanes starts with Cl_3SiH in benzene [7] or toluene [8], containing concentrated H_2SO_4 . The yield of sphero(hydrido-



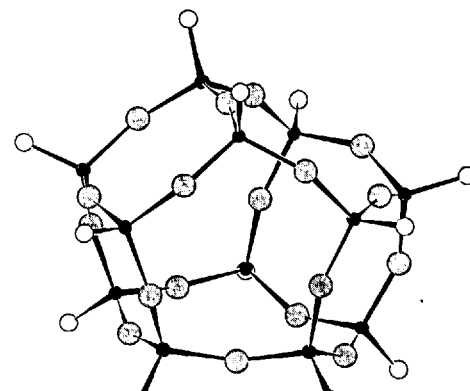
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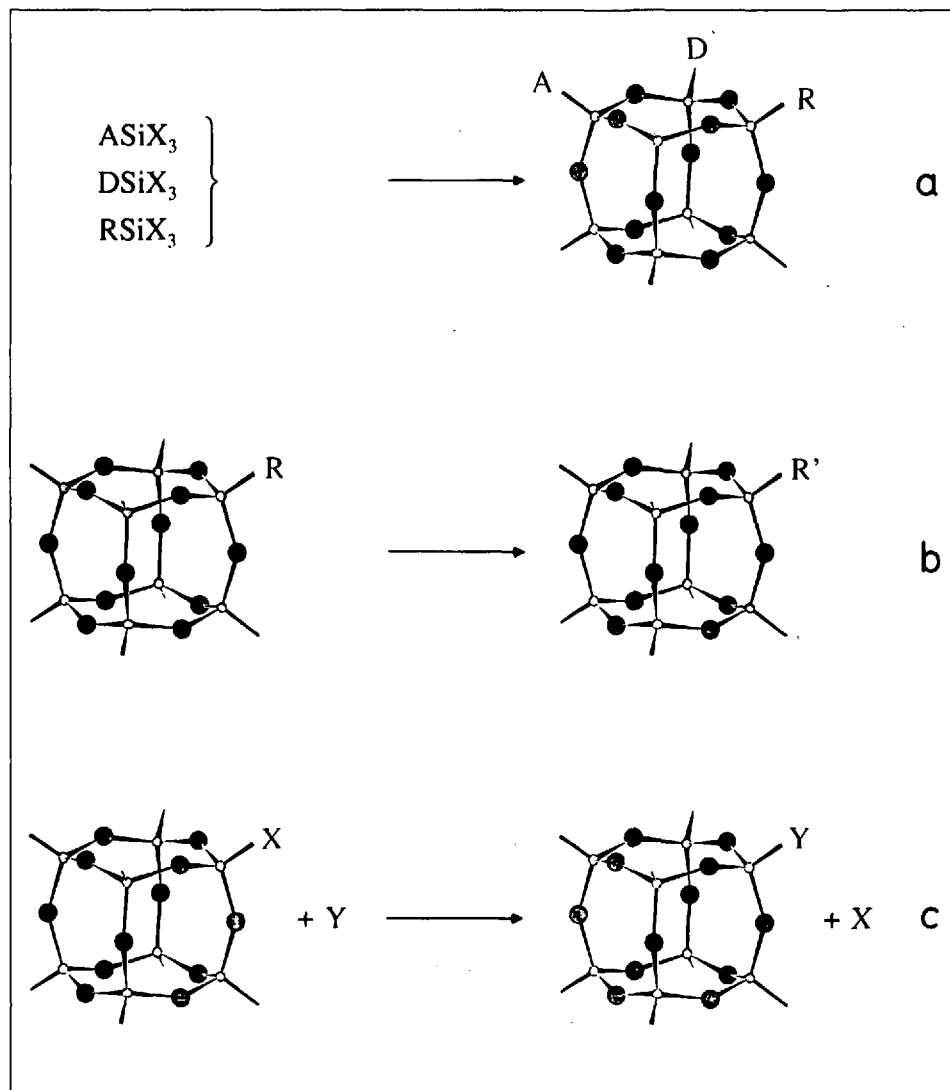
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Scheme



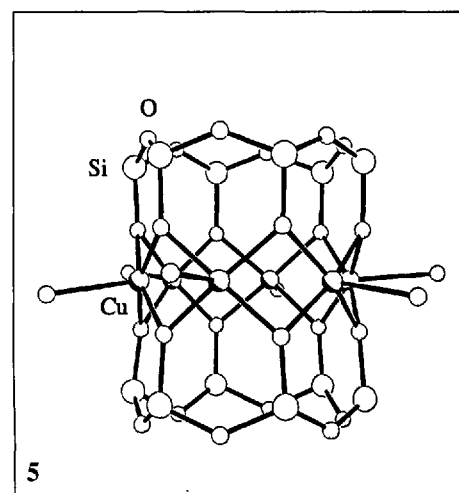
siloxanes) reported by *Frye and Collins* [7] is ca. 10%, thereof 4% $(\text{HSiO}_{3/2})_{10}$, 43% $(\text{HSiO}_{3/2})_{12}$, 39% $(\text{HSiO}_{3/2})_{14}$, 14% $(\text{HSiO}_{3/2})_{16}$, and a small amount of $(\text{HSiO}_{3/2})_{18}$. They can be separated by size-exclusion chromatography, a technique that allows for preparative separation [8]. By means of this polycondensation, it is possible to synthesize spherosiloxanes carrying alkyl, allyl, and aryl substituents. It is also possible to make heterosubstituted products, starting from mixtures of different trifunctional silanes. The reaction rate, the degree of oligomerization, and the yield of the polyhedral compounds formed strongly depend on *i*) the concentration of the initial monomer in the solution, *ii*) the nature of the solvent, *iii*) the character of the substituent(s) in the initial monomer(s), *iv*) the nature of the functional groups in the initial monomer(s), *v*) the type of the catalyst, *vi*) the temperature, *vii*) the addition of H_2O , and *viii*) the solubility of the polyhedral oligomers formed [4]. The influence of these factors, both individually or in combination, has been studied only in general, without any quantitative estimation of their effect on the reaction course. It seems likely that this traditional synthetic route to spherosiloxanes could be optimized to obtain much better yields of specific compounds. Indeed, a new synthetic route that gives a mixture of the hydridosphero-

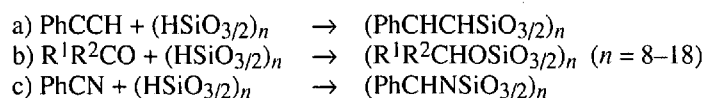
silsesquioxanes **1** and **2** ($\text{R} = \text{H}$) in 27% yield based on the starting material HSiCl_3 has recently been reported by *Agaskar* [9] and successfully been repeated by us. Furthermore, *Feher* and *Weller* have discovered an efficient procedure for the synthesis of polyhedral aluminosilsesquioxanes [10]. Developing this procedure, they have been able to synthesize a number of very interesting molecules, such as $[(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}]$ and $[(\text{Me}_4\text{SbO})_8\text{Si}_2\text{O}_{12}]$ [11], vanadium-containing silsesquioxanes [12] and polyhedral oligometallasilsesquioxanes (POMSS) as models for silica-supported catalysts, Cr on SiO_2 [13]. The latter are used for the coordination polymerization of ethylene. It is expected that a detailed study of the metal-containing POMSS will provide new information on the chemistry of silica-supported metal catalysts.

The second class **b** includes the reactions leading to chemical modifications of the substituents of known spherosiloxanes. Two main problems have to be mastered to make such reactions successful. The silicon-oxygen framework of the spherosiloxanes must not be affected, and the substituent has to have sufficient functionality for the modification reaction. Some effort was undertaken to nitrate octa(phenylsilsesquioxane) and to brominate the latter and

octa(vinylsilsesquioxane) [14]. The authors were, however, not able to control the substitution pattern of the product, and the yield was low. Recently, *Feher* and *Budzichowski* succeeded in hydrogenating aryl-containing spherosiloxanes [15] and in synthesizing functionalised spherosiloxanes of the octa($p\text{-XCH}_2\text{C}_6\text{H}_4\text{SiO}_{3/2}$) type ($\text{X} = \text{I}, \text{OH}, \text{NO}_2\text{O}, \text{AcO}, p\text{-nitrobenzoyl}, \text{methylterephthaloyle}$) [16].

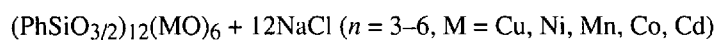
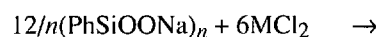
The third group **c** is the $(-\text{O})_3\text{Si-X} + \text{Y} \rightarrow (-\text{O})_3\text{Si-Y} + \text{X}$ substitution of spherosiloxanes $\text{X}_n(\text{SiO}_{3/2})_n$. Until recently, only three reactions of this kind have been known. The first of them is the photochlorination of $(\text{HSiO}_{3/2})_8$ (**1**, $\text{R} = \text{H}$) to $(\text{ClSiO}_{3/2})_8$ reported by *Klemperer* and coworkers as late as 1985 [17]. The methoxylation of $(\text{ClSiO}_{3/2})_8$ by CH_3ONO resulting in $(\text{CH}_3\text{OSiO}_{3/2})_8$ is described in the same paper. It has been further developed by *Agaskar* who was successful to implement a new strategy for the synthesis of organolithic macromolecular materials (OMM's) [18]. OMM's are substances containing both silicate and organic components, with a definite chemical relationship between the two. The trimethylsilylation of various hydridosilsesquioxanes has been published two years later [19]. The fourth reaction of this class is the D exchange of $(\text{HSiO}_{3/2})_8$ to $(\text{DSiO}_{3/2})_8$, recently found by us [20]. It is catalysed by Pd-C. The mechanism of this reaction is dictated by the rigid structure of the $(\text{SiO}_{3/2})_8$ framework, which does neither allow pseudorotation nor an attack from the back. To explain the experimental observation, a new reaction path for tetra-coordinate Si has been postulated [21]. As the latest example of such a reaction, we have shown that platinum-catalysed hydrosilation of $(\text{HSiO}_{3/2})_8$ (**1**, $\text{R} = \text{H}$) can be carried out with high yield [5]. It is likely that this substitution reaction proceeds *via* a radical mechanism. We expect that the hydrosilation reaction is applicable to other sphero(hydridosiloxanes) such as $(\text{HSiO}_{3/2})_n$ with $n = 10, 12, 14, 16, 18$. In view of its broad applicability [22], the following reactions, which lead to the formation of yet unknown spherosiloxanes, should be possible:





Heterosubstituted spherosiloxanes are of great interest, both from an experimental and from a theoretical point of view. Applying hydrosilation, it is easy to obtain pure mono-substituted compounds. For heterosubstituted molecules, a good separation procedure is supposed to be the key step to obtain pure compounds.

Recently, *Zhdanov, Schegolikhina, and Levitsky* (Nesmejanov Institute of Organoelement Compounds of the Academy of Sciences of the U.S.S.R.) have been able to synthesize a new class of materials in which a part of the Si-atoms in the cage of the polyhedral siloxane framework of spherosiloxanes is replaced by metal atoms [6]. These coloured crystalline substances are obtained in an exchange reaction between equivalent amounts of the Na salts of phenylsilsesquioxanes and a divalent metal chloride:

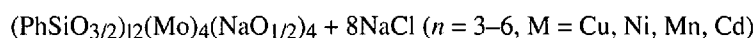
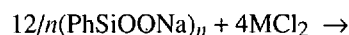


The compounds are of identical, three layered structure and are received in excellent yields (up to 70% after recrystallisation). The middle layer, formed by six metal atoms, is connected *via* O-atoms to the Si-atoms of the two outer layering six membered siloxane rings as shown for the copper compound 5.

It is interesting to see that the metal atoms are coordinated by four O-atoms of the siloxane 'crowns' and with one O-atom of a solvent molecule (*e.g.* alcohol). If the typical coordination number of the metal in such a compound exceeds five (*e.g.* six in an octahedral structure) the centre of the cage is occupied by an element which coordinates to each of the six metal atoms. An example of such a coordinating centre for the Co, Ni, Mn, and Cd derivatives is the chlorine ion, see 6. The negative charge of the Cl^- ion is

compensated by a Na^+ ion laying not in the cage but near the silsesquioxane 'crown'.

Formula 5 shows the structure of the Cu^{2+} derivate, the coordination number of copper being five. If more than an equivalent amount of the Na salt of the phenylsilsesquioxane compared to the metal chloride is used, the Na salts of the metallosiloxanes are formed:



The best known representative of these compounds is $(\text{PhSiO}_{3/2})_{12}(\text{CuO})_4(\text{NaO}_{1/2})_4$ (7). This fine crystalline product can be dissolved in many polar solvents (*e.g.* alcohols, ketones, and esters) showing a deep blue colour. It possesses interesting substructures. In one of them, each of the

four O-atoms is connected to two Cu and one Si-atom. The Ni, the Mn, and the Cd analogues can also be synthesized, but their detailed structure is still in question. The mechanism of formation of these metallosiloxanes is yet unknown. The structure of $(\text{PhSiOONa})_3$ in the crystalline state is trimeric. How and when the dimerisation reaction leading to the formation of the six-membered rings of the metallosiloxanes proceeds, is not yet understood. It is well known, that such six-membered rings, carrying O-atoms in the *cis*-positions, are very stable and are frequently found in siloxanes. Furthermore, the structure of 7 is not built by two six-membered silsesquioxane rings but by a deformed twelve-membered one, defined by the numbering.

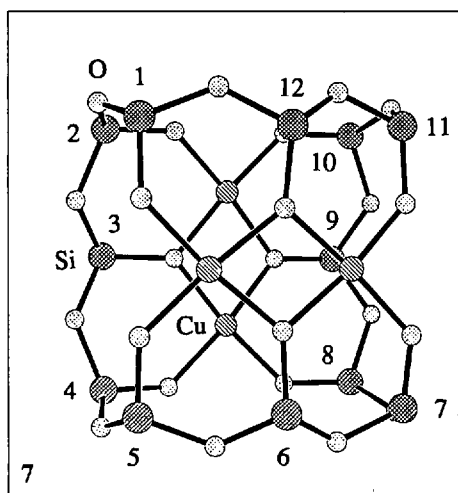
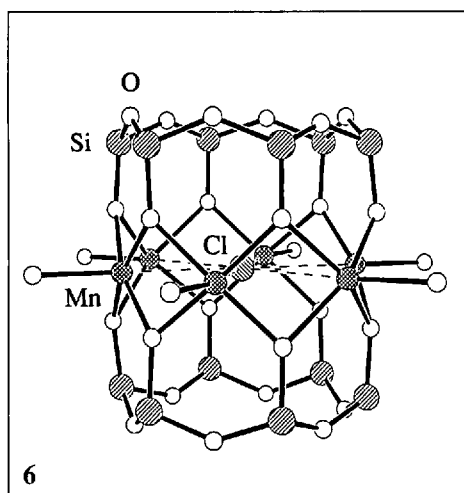
Properties

Most of the known spherosiloxanes are colourless crystalline substances. Those bearing long alkyl substituents (starting from heptyl) are transparent, viscous liquids. With growing chain length of the substituents, the solubility, and volatility of the organyl-silsesquioxanes increase, while the melting point decreases. Spherosiloxanes bearing alkyl substituents have a high thermal stability and a high resistance to moisture.

They are chemically inert, and resist the action of sunlight, O_2 and O_3 . These are reasons for some of their valuable technical properties [4]. The most powerful tool for the determination of the structure of the spherosiloxanes is still single crystal X-ray diffraction. The structure of most of the accessible spherosiloxanes has been determined by means of this method. MS is an informative method for the investigation of spherosiloxanes. In case of octa(hexyl-silsesquioxane), the most intense peak is due to the $[\text{M-hexyl}]^+$ ion, the second intense origins from $[\text{M-(hexyl)}_2]^{2+}$. Intense isotope ion peaks are detected an] their distribution corresponds to the natural abundance.

The high symmetry of the nearly spherical spherosiloxanes makes it very attractive to study their IR and Raman spectra and to interpret them in terms of normal coordinates. The symmetrical octasilsesquioxane $(\text{HSiO}_{3/2})_8$ (1, R = H) is especially simple. It possesses O_h symmetry and 78 vibrational degrees of freedom. Its IR spectrum consists of six fundamental absorptions, as shown in Fig. 1a. The spectrum has been measured in a CCl_4 solution in a 0.2-mm thin CsI liquid cell [23]. The Raman spectrum which is slightly more complicated consists of 13 fundamental vibrations. Normal coordinate analysis and analysis of the resulting potential energy distribution shows that the fundamental modes of this molecule can be described within a good approximation in terms of the internal vibrations $\nu(\text{Si-H})$, $\nu(\text{Si-O})$, $\delta(\text{O-Si-H})$, $\delta(\text{O-Si-O})$, and $\delta(\text{Si-O-Si})$ [24]. ν is the abbreviation for stretching modes and δ is used for bending modes. The interpretation of the absorptions is as follows: $2276 \text{ cm}^{-1} = \nu(\text{Si-H})$, $1141 \text{ cm}^{-1} = \nu(\text{Si-O})$, $880 \text{ cm}^{-1} = \delta(\text{O-Si-H})$, $566 \text{ cm}^{-1} = \delta(\text{O-Si-O})$, $465 \text{ cm}^{-1} = \nu(\text{Si-O})$, and $399 \text{ cm}^{-1} = \delta(\text{O-Si-O})$. A more detailed analysis is in progress [25].

Vibrational spectra analysis of octa-(methylsilsesquioxane) in terms of normal modes has been carried out to some extent by *Kolesov et al.* [26]. These authors describe anomalously high values for the non-diagonal second order force constants, *i.e.*, the interaction constant of bonds having no common atom. They attribute their finding



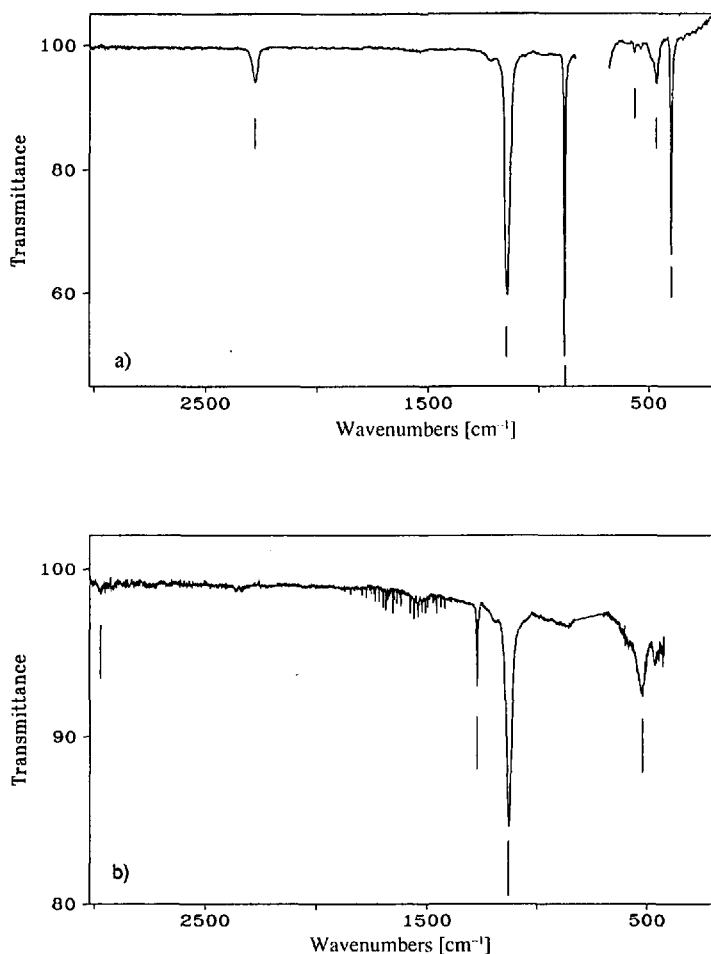


Fig. 1. a) FTIR spectra of $(\text{HSiO}_{3/2})_8$ in CCl_4 at RT. b) FTIR spectra of $(\text{CH}_3\text{SiO}_{3/2})_8$ in CCl_4 at RT. Water $\delta(\text{HOH})$ ro-vibrational structure is also on this spectrum; see text.

to the existence of delocalized molecular orbitals. How hyperconjugation plays a role in the molecular orbitals of $(-\text{O})_3\text{Si}-\text{CH}_3$ has been discussed recently [21], and it will be interesting to carry out a more detailed analysis of the forcefield of octa(methylsilsesquioxane). The IR spectrum of $(\text{CH}_3\text{SiO}_{3/2})_8$ is shown in Fig. 1b. For illustrative purposes, this spectrum was measured in purged mode of our FTIR spectrometer. The ro-vibrational structure belonging to the bending mode of the few remaining water molecules in the sample compartment are, therefore, clearly visible. Usually, these contributions are subtracted from the FTIR spectra reported in the literature. If measured in vacuum mode, there are no such additional absorptions, see Fig. 1a. In Fig. 1b only the lines indicated do belong to the $(\text{CH}_3\text{SiO}_{3/2})_8$ molecules. The framework modes are only slightly shifted with respect to $(\text{HSiO}_{3/2})_8$. Due to the low solubility of octa(methylsilsesquioxane) in CCl_4 the weak symmetrical and asymmetrical $\nu(\text{C}-\text{H})$ absorption at about 2900 cm^{-1} is difficult to observe in this spectrum. The absorption at 1270 cm^{-1} corresponds to a $\delta(\text{Si}-\text{C}-\text{H})$ mode. The ^1H -NMR spectrum and the ^{29}Si -NMR spectrum of $(\text{HSiO}_{3/2})_8$ (I , $\text{R} = \text{H}$) are amazingly simple, see Fig. 2. They have been measured in a $\text{CDCl}_3/\text{CCl}_4$ solution. The ^1H -NMR spectrum consists of a single peak and some weak satellites. The satellites are due to the

coupling of ^1H with ^{29}Si . In the ^{29}Si -NMR spectrum, which has been measured under proton decoupling, only a single peak is observed [23].

Discussion

Many applications of spherosiloxanes have been proposed so far, based on their structural, chemical, and physical properties. Klemperer and coworkers have used $(\text{CH}_3\text{OSiO}_{3/2})_8$ as molecular building blocks for the synthesis of ceramic materials [17]. The rigid cube $(\text{SiO}_{3/2})_8$ core offers the possibility of generating porous yet rigid materials due to geometric factors limiting the density with which corner-linked cubes can fill space. The authors have some evidence, that the framework structure of the starting material does not degrade during the hydrolysis procedure. The hydridosilsesquioxanes $(\text{HSiO}_{3/2})_n$ ($n = 8, 10, 12, 14,$

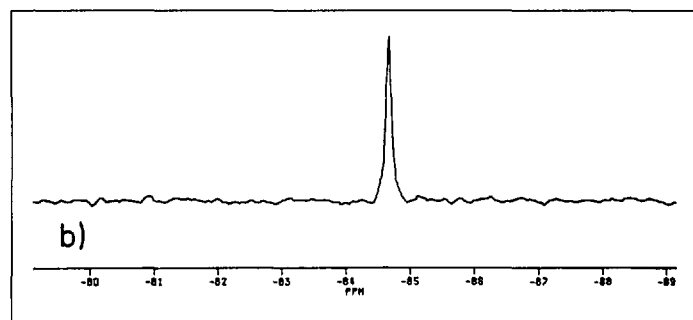
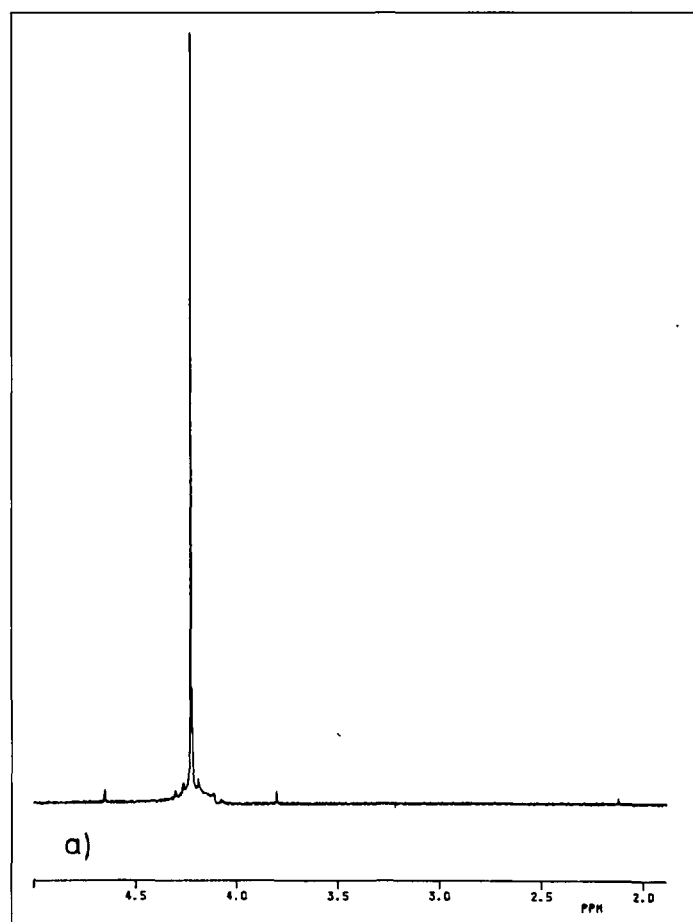
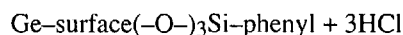
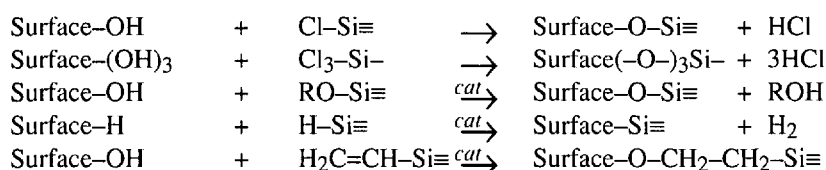


Fig. 2. a) ^1H -NMR spectrum of $(\text{HSiO}_{3/2})_8$ (I , $\text{R} = \text{H}$). Due to the octahedral structure of the compound, it shows only one single main peak. The satellites are due to the coupling of the ^1H with ^{29}Si . b) ^{29}Si -NMR spectrum of $(\text{HSiO}_{3/2})_8$.

16, 18) are very interesting molecules for generating extremely thin SiO_2 layers under well controlled conditions. Well defined SiO_2 layers are needed for example in microelectronics, in micro-sensor technologies and in solar cells.

Others regard spherosiloxanes as models for silica surfaces [27], as precursors for studying zeolite synthesis pathways [28], as interesting candidates for photo-resist materials [15] and so on. Note that Fourier transform attenuated total internal reflectance spectroscopy (ATR-FTIR) studies have allowed to characterize double-four-ring silicates under synthesis conditions for silicon-rich zeolites [29]. We have applied this technique in surface modification experiments [23][30][31]. Silanization is a highly successful form of surface modification. Silanes that are able to react with surface OH groups to form silyl-ether bonds can be bound covalently to the surface. Reactions that have been discussed for this



purpose are:

The last three reactions are attractive because no corrosive HCl is formed. They are, however, difficult to study, since a catalyst is needed. The reactions with the chlorosilanes are easy to carry out and the HCl formed during the reaction can be neutralized by adding a small amount of an appropriate base. For these molecules, it is relatively easy to follow the deposition kinetics out of a solution by means of ATR-FTIR spectroscopy, if the substrate is sufficiently transparent in the IR. Many semiconducting crystals are sufficiently

The reaction conditions were as described above. We have observed a *Langmuir* isotherm behaviour with the typical clear saturation at approximately monomolecular coverage. As already described for the reaction with 4-[(trichlorosilyl)methyl]benzotrile on Ge, the reaction is slower than expected and is only completed after 4–10 h, depending on the conditions [23][30]. We believe that the ATR-FTIR technique and also the FTIR transmission technique developed by us for studying IR transmission of very thin zeolite pellets [33] can be applied

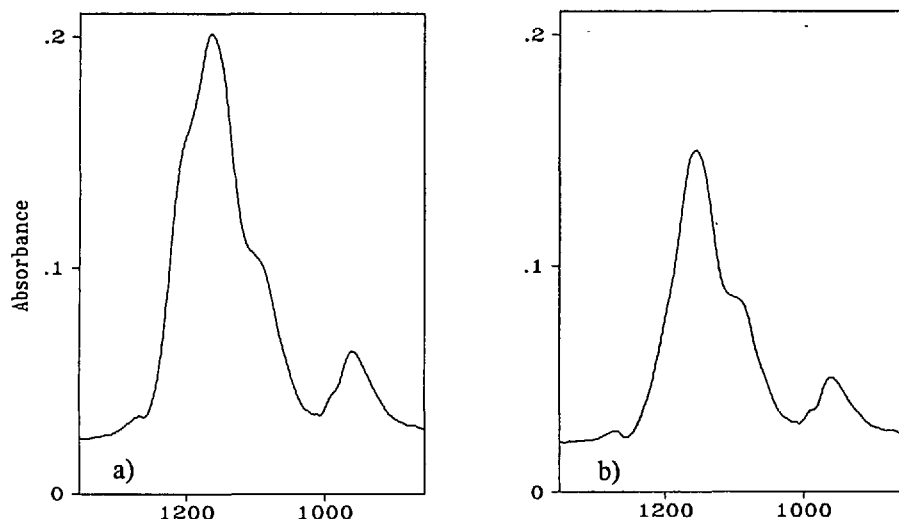


Fig. 3. In situ FTIR-ATR spectra of a surface modification with $(\text{ClSiO}_{3/2})_8$ on a Ge crystal. a) Light polarized parallel to the surface, b) light polarized perpendicular to the surface.

transparent in the IR for this technique which has been described in detail by *Harrick* [32]. A very convenient material to use is Ge. We, therefore, represent as an example two spectra obtained by reacting the surface of a Ge crystal with $(\text{ClSiO}_{3/2})_8$, see Fig. 3. To measure these spectra, a Ge crystal of $1\text{ cm} \times 0.5\text{ cm} \times 0.1\text{ cm}$ size was placed in a reaction chamber filled with CCl_4 . Then, a very diluted solution of $(\text{ClSiO}_{3/2})_8$ in CCl_4 was allowed in a continuous flow experiment to react for 20 h. The spectra were measured with polarized light in the range of the siloxane framework vibrations. Measurements with polarized IR light give information about optical constants and the geometry of the surface substrate. It is, therefore, interesting that the shoulder at 1200 cm^{-1} shows a significant dependence on the polarization of the light.

In another experiment we have measured the kinetics of the reaction $\text{Ge-surface-(OH)}_3 + \text{Cl}_3\text{-Si-phenyl} \rightarrow$

successfully to the spherometallosiloxanes and to the monograin surface modification with zeolites.

While the electronic structure of symmetrical octa(silsesquioxanes) $(\text{XSiO}_{3/2})_8$ ($\text{X}=\text{H, Cl, OH, CH}_3$) is now very well understood [21], little is known with respect to the new spherometallosiloxanes, and an investigation seems worthwhile. The intense colour, the chemical stability, and the inorganic nature of the metallosiloxanes make them efficient colouring materials for transparent plastics. Some polymetallo-organosiloxanes can be used as catalysts in the hardening procedure of epoxy or siloxane resins and composites. The use of polyferro-organosiloxanes as catalysts can raise the yield and the selectivity of the chlorination reaction in organic chemistry. They are effective thermo stabilizers for some siloxane varnishes [34].

Spherosiloxanes have attracted our interest as model substances for investigating

zeolites due to the resemblance of the framework structure of octasilsesquioxanes to the double four ring in zeolites A and CoAPO-50 [35]. We focus on Ag and Cu zeolites because of their possible usefulness in an artificial photosynthesis system. The bottle neck in chemical approaches to artificial photosynthesis on a molecular level has always been the O_2 production from H_2O

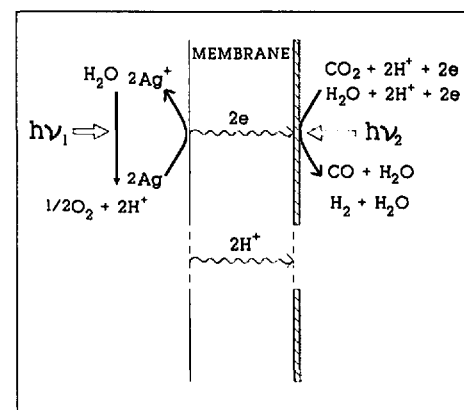


Fig. 4. Artificial photosynthesis system for the H_2O splitting and/or the CO_2 reduction in which two photons are involved.

Electrons are moving through a modified zeolite, while protons are transported through an ion permeable membrane.

[36]. We have successfully worked on this reaction [37][38], so that it has become interesting to try and realize water splitting or CO_2 reduction. Our research approach is explained in Fig. 4 [39]. For the reductive part, in which for example H_2 is produced by reducing H_2O , we rely on systems described by other research groups [40–42], while the oxidative part needed for the O_2 production by oxidizing H_2O is designed according to a system developed in our laboratory. The attractive aspect of this approach is that the reductive, the oxidative, and the electron conductive parts can be studied separately. The problem to be solved is to connect the oxidative part which delivers the two electrons and the two protons to the reductive part. By covalently linking $1\text{-}\mu\text{m}$ sized zeolite A particles as a dense quasi monograin layer onto an electrode, we have succeeded in preparing an Ag zeolite electrode which shows that the reduction and oxidation steps in the zeolite are reversible [43]. This means that we have now a single, well defined step to go in order to completely realize the process explained in Fig. 4 and with more details in [39][44][45].

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Bestimmung von Selen in Lebensmitteln und in Mineralien mittels Neutronenaktivierungsanalysen

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Abstract. The determination of Se became important, since it was recognized that this trace element is essential for the human and animal diet. Lately, it was found that most patients suffering from a cancer disease manifest very low values of Se in their blood plasma. Activation analysis is a well suited technique to measure the concentrations of Se in a vast range of materials with very different concentrations. At the lower end of concentrations, a radiochemical separation of Se following the irradiation is mandatory to obtain reliable results in the determination.

Einleitung

Selen galt seit langem als äusserst toxisches Element. Erst 1957 wurde seine essentielle Bedeutung für den Menschen erkannt

[1]. Durch Abgabe von Selentabletten an die Bevölkerung der Keshan-Region in China konnte die *Kashin-Becksche* Krankheit, eine rheumatisch-athritische Erkrankung, fast vollständig eliminiert werden. Heute ist be-

kannt, dass bei vielen weiteren Krankheiten wie Krebs, Leukämie oder AIDS der Se-Gehalt im Blut einen Mangel aufzeigt. Es ist daher wichtig, dass die Bevölkerung genügend mit Se versorgt wird. Dieses Spurenelement kommt in Fleisch, Fisch und Getreideprodukten angereichert vor [2][3], wogegen es in Gemüse, Früchten und Milchprodukten verarmt ist [3]. Der tägliche Mindestbedarf des Menschen beträgt 1 µg Se/kg Körpergewicht [2]. Im allgemeinen sind die Böden der Schweiz recht arm an Se [4]. Importiertes Getreide aus den USA oder Kanada weist einen 10 bis 100mal höheren Gehalt an diesem essentiellen Element auf als Weizen, der in der Schweiz geerntet wurde. Eine ausreichende Versorgung der Schweiz mit Se ist Dank der Getreideimporte gewährleistet. Die Entwicklung einer

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