The Dynamic Status Quo of Polyhedral Silsesquioxane Coordination Chemistry

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The chemistry of polyhedral oligomeric silsesquioxanes (POSS) has taken a tremendous leap over the past decade. New synthetic approaches have been developed, and new complexes based on elements throughout the periodic table have been synthesized and applied in catalytic processes such as alkene epoxidation, Oppenauer oxidation, alkene polymerization, Diels–Alders reactions and alkene metathesis. The use of silsesquioxane ligands as models for silica surface has provided an intimate knowledge of the reactions on the surface of this much-used support. New methods have been developed to incorporate silsesquioxanes into new materials. Encapsulation in siloxane polymers has provided precision supports for catalysts and controlled calcination has produced materials with well-defined metal oxide particles. This paper reviews the history and the latest developments of silsesquioxane chemistry.

Silsesquioxanes: Introduction and History

Polyhedral oligomeric silsesquioxanes (POSS), or simply silasesquioxanes or silsesquioxanes is the general IUPAC name for a family of polycyclic compounds consisting of silicon and oxygen (See Figure 1). The name sil(a)sesquioxane is derived from *sil-oxane* (compounds of silicon and oxygen) and *sesqui* (Latin, meaning one and a half), and the general name reflects the ratio of silicon and oxygen in the completely condensed silsesquioxanes $[RSiO_{3/2}]_{2n}$ (vide infra).

Silsesquioxanes are part of a larger family of silicon-oxygen compounds, called spherosilicates. The main feature of

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In 1992, Erik Abbenhuis obtained his PhD thesis at Utrecht University having worked in the group of Prof. Dr. G. van Koten on "Intramolecular Coordination in Tantalum Alkylidene Chemistry". He continued with academic research as a postdoc, first in Strasbourg, then at the ETH Zürich, following his appointment as a fellow of the Royal Dutch Academy of Arts and Sciences in 1994. He now has his own research group at Eindhoven University of Technology, coached by Prof. Dr. D. Vogt, in which emphasis is put on molecular aspects of heterogeneous catalysis.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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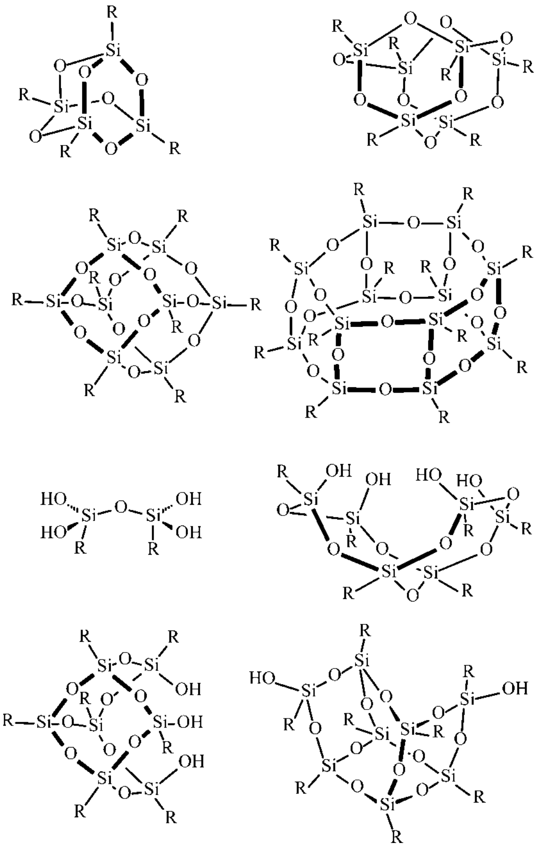
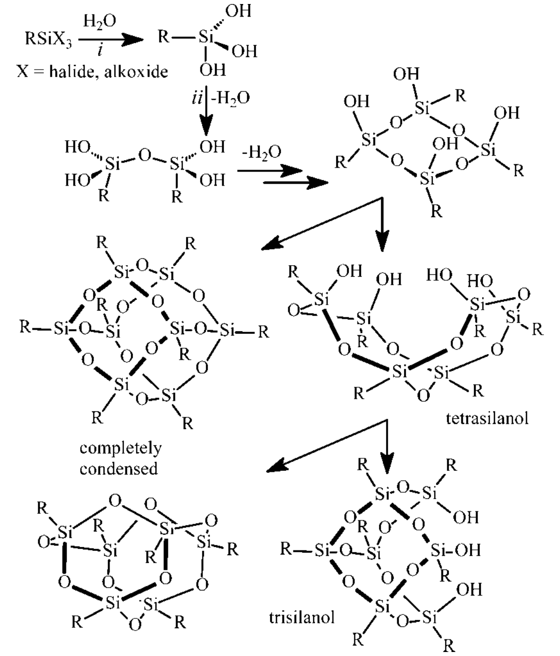


Figure 1. Overview of incompletely and completely condensed silsesquioxanes in the literature (typical R groups include: Me, Et, *i*Pr, *i*Bu, *i*Oc (isooctyl), Ph, *c*-C_5H_9, *c*-C_6H_{11}, *c*-C_7H_{13}, norbornyl)

silsesquioxanes is the presence of one non-silicate, organic group on the silicon atoms. The initial discovery of silsesquioxanes dates back to 1946, when Scott[1] described completely condensed methyl-substituted silsesquioxanes. Although he was not able to assign their exact structure, he was able to determine that the general formula was $[(CH_3)SiO_{3/2}]_{2n}$, in which *n* was an integer. Nine years later, the molecular structure of a series of organosilsesquioxanes was determined by single-crystal X-ray diffraction by Barry et al.[2] They first showed the cubic or hexagonal prismatic shape of the completely condensed molecules.

A major contribution to the synthesis of silsesquioxanes (completely and incompletely condensed) was published by Brown and Vogt in 1965.[3] They described the polycondensation of cyclohexyltrichlorosilane in an acetone/water mixture. The main products that were formed at the beginning of the reaction were incompletely condensed dimers $[RSi(OH)_2ORSi(OH)_2$, R = cyclohexyl] and higher oligomers, that still contained silanol groups. After some time (days to months), the cubic, incompletely condensed silsesquioxane trisilanol $(R_7Si_7O_9)(OH)_3$ was formed to a greater extent together with the completely condensed $R_6Si_6O_9$ with no residual silanol groups. In the 1990s, Feher described the same procedure for cyclopentyl- and cycloheptyltrichlorosilane. In this case no completely condensed products were isolated. The hydrolytic polycondensation of cyclopentyltrichlorosilane led exclusively to the formation of the trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, while polycondensation of cycloheptyltrichlorosilane led to a mixture of the trisilanol $(c\text{-}C_7H_{13})_7Si_7O_9(OH)_3$ and the tetrasilanol $(c\text{-}C_7H_{13})_6Si_6O_7(OH)_4$. The application of norbornyl as the organic side-group was explored by Hambley et al. A mixture of trisilanol and tetrasilanol was formed.[4]

The process of formation of the silsesquioxane compounds is thought to be a multi-step hydrolysis-condensation reaction (see Scheme 1). The first step is the hydrolysis of an alkylsilane precursor with water, forming organopolysilanol compounds (step *i*). In the right environment, depending on the concentration of water and solvent, and the pH, these precursors can condense with each other, leading to the formation of oligosiloxanes (step *ii*). The thermodynamics,[5−7] kinetics and solubility of the products will determine the resulting product mixture, ranging from lower oligosiloxane dimers or tetramers, to polyhedral oligomeric silsesquioxanes like the tetra- and trisilanol silsesquioxanes.



Scheme 1. Generalized formation scheme for siloxanes and silsesquioxane-type compounds

For a long time the major hurdle in the use of silsesquioxanes was the long preparation time (ranging from a few weeks to 36 months) and the limitation of the organic side-groups on the silicon atoms. New developments and ideas have shortened the preparation times considerably. The use of high-throughput experimentation and synthesis robots may accelerate the optimization of synthesis conditions.[8] Recently, base-catalyzed polycondensation reactions have proven to be an excellent way to prepare large quantities of silsesquioxanes. Lichtenhan and Abbenhuis have applied for patents on the preparation of completely condensed and incompletely condensed silsesquioxanes with isobutyl and isooctyl side-groups that can be prepared on large scales in a short time.

Until recently, functionalization of silsesquioxane silanols has been limited to either corner-capping of trisilanols with a trihaloorganosilane moiety, leaving no further reactive silanol group (*a*), or reaction of the trisilanol with mono- or dihaloorganosilane reactants, leaving two or one silanol groups, respectively (*b*). In the first case, a large number of possible side groups can be introduced, ranging from simple alkyl groups to reactive alcohols, amines and alkenyl groups. These groups allow the silsesquioxane cores to be included in polymeric materials. Furthermore, there is a substantial interest in octafunctional silsesquioxanes where all the side groups on the silicon atoms are identical and reactive. In these cases the functionality ranges from alkyls, alcohols, amides and carboxylates to halides, nitrates and phosphanes.[9−24] These can even be used as building blocks for dendrimers, as shown by Cole-Hamilton et al. for use in catalytic hydroformylation reactions (vide infra).[25−28] In the second case, the introduction of reactive functional groups besides the silsesquioxane's silanols has proved to be more complex. To date, the groups in the added functionality are limited to trialkyl- and triarylsilicon and -tin groups, and these groups are more often used for protection of one or more of the silanol groups than for functionalization. Selectivity in these reactions either arises from the different acidities of the silanols of the starting material or from steric hindrance of the silylating agent.

Metal Silsesquioxanes

Feher et al. initiated the research towards the use of silsesquioxane molecules as ligands for main group and transition metals at the end of the 1980s,[29] considering silsesquioxanes as models for industrially used silica supports. The resemblance of silsesquioxanes to silica supports is not only apparent from the molecular structure, but the electronic properties of silsesquioxane silanol groups mimic the behavior of silica as well.

In Figure 2, a few important structural similarities between silsesquioxanes and schematized silica surfaces are depicted. First of all, the defined orientation of the silanol groups, which is also present in silsesquioxanes, may ensure a strong multi-dentate bonding to metals. Furthermore, silsesquioxanes have enough residual siloxane bridges to resemble the silica surface and these residual siloxane bridges can interact with the metal.

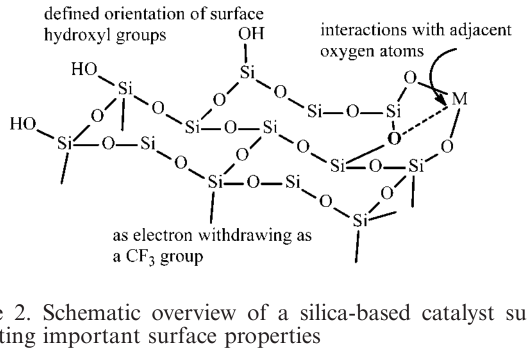


Figure 2. Schematic overview of a silica-based catalyst support, indicating important surface properties

Silsesquioxane silanols can be modified by silylation to resemble the different silanol sites that can be present on a silica surface. Dijkstra et al. performed an in-depth study on the synthesis and characterization of silsesquioxane models for silica silanol sites (see Figure 3).[30] By comparison of the relative ion-pair acidities in THF for the different silanol sites, they found that the geminal silanols are among the least acidic, and hence least reactive, silanol groups, closely followed by isolated silanol groups. Due to their ability for extensive hydrogen bonding, the Brønsted acidity of vicinal disilanol and trisilanol groups is orders of magnitude larger. These findings provide insight into the relative reactivity of species on a silica surface.

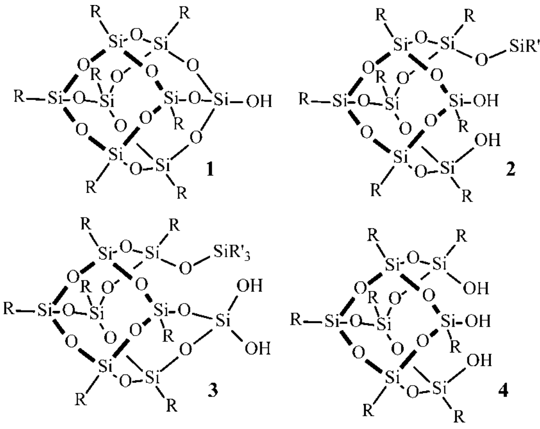


Figure 3. Silsesquioxane representations of silanol sites on silica surfaces: **1** isolated silanol; **2** vicinal disilanol; **3** geminal disilanol; **4** vicinal trisilanol

Since the discovery of silsesquioxanes, a rich coordination chemistry has been developed with elements throughout the periodic table; at present, these involve: Li, Na, K, Be, Mg, Sc, Y, La, U, Ti, Zr, Hf, V, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Pt, Cu, Au, Zn, B, Al, Ga, Tl, Ge, Sn, Pb, N, P, As, Sb, Bi, S, F, Cl.

Group 1 (Li, Na, K)

Feher et al. have reported sodium complexes as intermediates in the synthesis of transition metal complexes.[31] These intermediates were either not isolated or found to be unstable out of solution. The groups of Aspinall, Edelmann and Abbenhuis have used lithium silsesquioxanes extensively as a transmetallation agent to prepare transition metal complexes.[32−34] In some cases the lithium ions remain present in the transition or main group metal complex.[32,34−36] Duchateau et al. reported a mixed boron-lithium silsesquioxane.[37] The group of Edelmann also reported a potassium silsesquioxane complex and gave a crystal structure, although no experimental details were provided.[34]

Group 2 (Be, Mg)

The chemistry of Group 2 elements has not been explored much in the past. Edelmann et al. published a crystal structure of a mixed beryllium-lithium silsesquioxane.[35]

Smet et al. reported the use of a magnesium-substituted silsesquioxane as an intermediate in the reaction with epoxides.[38] Lichtenhan reported a polymeric material based on a silsesquioxane disilanol and dialkylmagnesium.[39] Liu and Feher reported the application of magnesium-substituted silsesquioxanes as model supports for titanium-based alkene polymerization catalysts.[40,41] Hanssen described the synthesis and reactivity studies of a tetranuclear magnesium complex, and Maxim subsequently used this complex to prepare microporous magnesium-containing silica materials.[42,43]

Group 3 (Sc, Y, La, Lanthanides and Actinides)

Hermann et al. first mentioned the synthesis and crystal structures of Nd and Y silsesquioxanes complexes.[44] Due to the high solubility of Group 3 silsesquioxanes they were not able to isolate a “naked’ Y silsesquioxane, but addition of coordinating triphenylphosphane oxide yielded crystals suitable for X-ray crystal-structure analysis. The large ion-size and high electrophilicity of the ion induced a high degree of coordination of siloxide and siloxane groups from the ligand to the metal showing, for the first time, an interaction of a siloxane bridge with a metal ion. Aspinall et al. isolated a PMDTA adduct of an yttrium silsesquioxane.[45] By applying the method of lithium transmetallation they also synthesized a mixed lithium-ytterbium complex.[32] Edelmann et al. displayed a great interest in the synthesis of Group 3 and lanthanide complexes. They reported samarium and scandium complexes of the isolated silanol silsesquioxane **1** (Figure 3),[36] a seven-coordinate cerium(IV) silsesquioxane (starting from a Ce^{III} precursor),[46] and various mixed-metal lithium-lanthanide complexes.[34] They also reported the synthesis of the first known actinide silsesquioxane complex: a six-coordinate uranium(VI) complex that was formed regardless of the uranium precursor.[34] Although most of the papers deal with models for catalysts on silica surfaces, no catalytic experiments were performed.

Group 4 (Ti, Zr, Hf)

Much work has been done on Group 4 silsesquioxane complexes and the application of these complexes in catalytic processes such as ethylene polymerization,[40,41,47−54] alkene epoxidation[8,38,55−68] and Oppenhauer oxidations.[69] Most of the work in this area has been the topic of several excellent review articles.[34,52][65] A specific interest in the group of Abbenhuis is the heterogenization of active and selective epoxidation catalysts (Figure 4). Krijnen et al. reported the heterogenization of titanium silsesquioxane complexes in mesoporous MCM-41 type materials.[60][62][64][70] No leaching was observed for all-silica MCM-41 materials, while aluminum-containing MCM-41 had to be silylated after impregnation of the titanium silsesquioxane complex.

Skowronska-Ptasinski et al. described the copolymerization and cross-linking of vinyl-substituted silsesquioxane titanium complexes with siloxane oligomers.[58] The resulting materials proved to be active and selective catalysts for the epoxidation of alkenes with the cheap oxidant hydrogen peroxide. A material obtained by physical encapsulation of a non-vinyl-functionalized titanium silsesquioxane complex was also active as a catalyst, while the titanium complex in solution could not activate hydrogen peroxide. This emphasies the importance of the physical surrounding of the catalytic center in epoxidation reactions, where one should avoid high concentrations of water and peroxide near the active metal center. More about Group 4 silsesquioxane complexes can be found in the literature.[29,31,39][71−76]

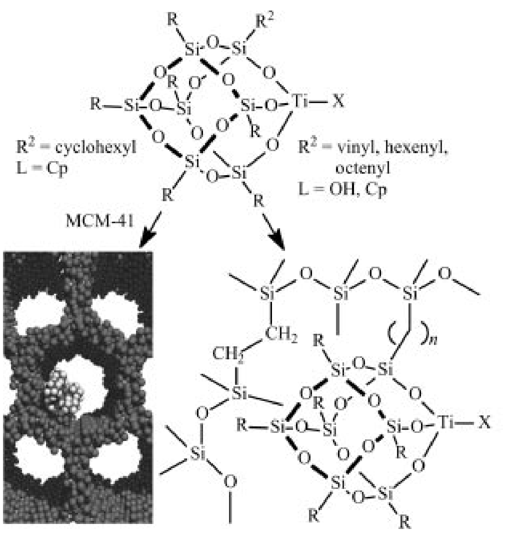


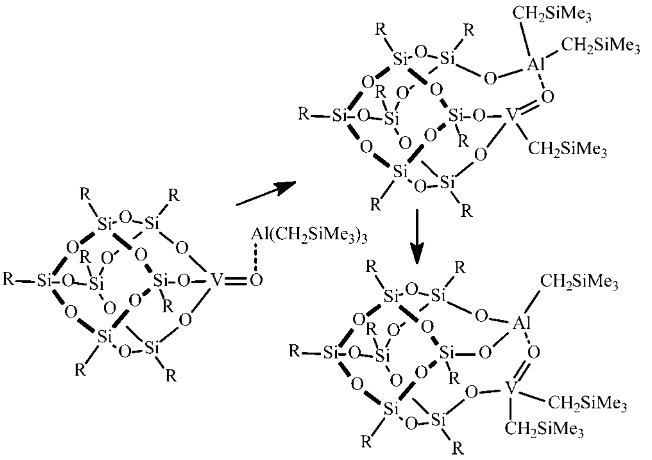
Figure 4. Immobilization of a titanium silsesquioxane complex by physisorption in a mesoporous MCM-41 host (left) or tethering to a 3D-netted siloxane polymer (right)

Group 5 (V, Ta)

Feher et al. explored the use of Group 5 metals ligated by silsesquioxanes by reacting vanadium(III) and vanadium(V) precursors with silsesquioxane trisilanol compounds.[76−79] The magnetic properties of the paramagnetic vanadium(III) silsesquioxanes were studied. The application of the diamagnetic vanadium(V) silsesquioxane complexes as precursors for ethylene polymerization was studied in-depth. Based on in situ NMR studies they were able to propose a catalytic model for the interaction of the vanadium systems with aluminium activators. One of the most important steps for the activation of the system was the breaking of metal-siloxy bonds in order for the metal to gain its catalytic activity, as shown in Scheme 2.

Wada et al. used the vanadium(V) complexes to prepare microporous vanadium silicates by controlled calcination of the complex in air at 723 K. The materials proved to be efficient catalysts for the photocatalytic oxidation of methane,[81] benzene and cyclohexane.[82]

The other metal in Group 5 that was investigated was tantalum. Basset et al. used a tantalum silsesquioxane complex as a model compound to explain the formation of tantalum alkylidene species on a silica surface.[83]



Scheme 2. Activation of a vanadium(v) silsesquioxane complex with an alkylaluminum compound

Group 6 (Cr, Mo, W)

Reaction of chromium oxide with a mono-protected trisilanol led to the formation of a bis-oxo chromium silsesquioxide ester (see Figure 5). Feher et al. tested this compound in the polymerization of ethylene as a surface model for the chromium-based Phillips catalyst.[80,84] It produced medium molecular weight polyethylene with a high polydispersity, indicating multiple active sites. Vorstenbosch et al. employed this type of chromium silsesquioxane ester for the catalytic epoxidation of alkenes with *tert*-butyl hydroperoxide. Although the respective epoxide was formed in high yield, it was found that the active species in the reaction was a non-silsesquioxane chromium species, an indication of metal leaching.[59] Maxim et al. used the chromium silsesquioxane for the synthesis of microporous-silica-supported chromium that was found to be active in the low-temperature catalytic oxidation of ammonia.[85,86]

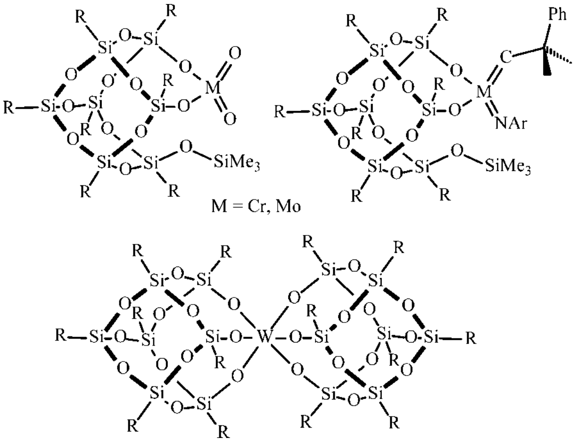


Figure 5. Examples of silsesquioxane group 6 metal complexes

Feher et al. also synthesized the corresponding molybdenum bis-oxo silsesquioxide ester by a thallium transmetallation route (vide infra).[87] A variant of the well-known molybdenum-based Schrock carbene complex showed high activity in olefin metathesis reactions (see Figure 5).[31] The high activity was attributed to the highly electron-withdrawing character of the silsesquioxane framework. Cross-metathesis of vinyl-substituted silsesquioxanes with the Schrock carbene complex [$Mo(CHCMe_2Ph)(NAr)\{OCMe(CF_3)_2\}_2$] yielded a silsesquioxane with an alkylidene-metal fragment attached to the former vinyl side-group.[88] In an attempt to synthesize a model for silica-supported tungsten catalysts, Smet et al. synthesized a bis(silsesquioxane)-tungsten complex (Figure 5), for which the synthesis is atypical as no base is required to trap the HCl formed.[89] More reports of Group 6 metal silsesquioxanes can be found in the literature.[9,29,87,90–92]

Group 7

To date, no one has reported the synthesis of Group 7 metal silsesquioxanes where the metal is directly linked to the silanol groups. Attempts to synthesize rhenium silsesquioxane complexes resulted in either dehydration reactions of the silsesquioxane, or yielded complicated product mixtures.[93] Lücke et al. reported the synthesis of a octafunctionalized phosphorous silsesquioxane that was used a ligand for [$MnCp(CO)_2$].[9]

Group 8 (Fe, Ru, Os)

Although the introduction of iron, in the form of ferrocene, as a side-group on the silicon was reported in 1993,[94–96] Ott et al.[97] and Edelmann et al.[98] have only recently reported the synthesis and application of iron silsesquioxanes where the iron atom is attached to the silanolate groups (Figure 6).

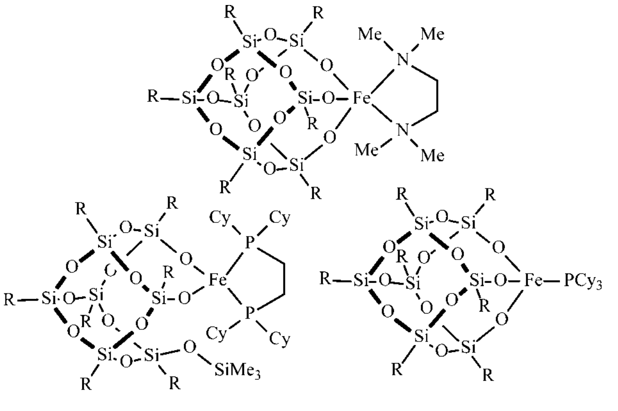


Figure 6. Iron silsesquioxanes reported by Ott et al. and Edelmann et al.

Ott et al. used monophosphanes and diphosphanes as stabilizing agents for the unfilled coordination space on the metal. Addition of small amounts of water to these compounds led to the loss of the phosphane ligand and the formation of anionic oxygen-bridged bis(iron-silsesquioxane) species. Because of structural similarities to the active center of iron found in zeolites, they applied the iron silsesquioxane complexes in the catalytic oxidation of benzene with N_2O to phenol. No conversion into phenol was observed, possibly due to the low temperature. Edelmann et al. used TMEDA instead of diphosphanes. The complex of Edelmann was used by Maxim et al. to prepare iron on microporous silica by controlled calcination of the complex.[33] The iron was well dispersed in the material and was present as nanosized metal oxide particles of about 2−8 nm. The addition of extra silsesquioxane trisilanol to the mixture before calcination enabled them to vary the iron content in the material, while keeping the material properties unchanged. Mixing a third component into the pre-calcination mixture — the chromium silsesquioxide ester (vide supra) — allowed Maxim et al. to synthesize silica-supported mixed-metal materials.[99] These materials were tested in catalytic decomposition of N_2O to N_2 and O_2, and were found to be more active than the iron-only systems, and more selective than the chromium-only systems. A mixed metal-oxide phase (Fe−Cr−Si−O) was identified by Raman spectroscopy.

Four examples of ruthenium attached to a silsesquioxane core have been reported. Feher et al. synthesized one complex by a cross-metathesis route as described for molybdenum.[88] Wada et al. used a phosphorus-functionalized silsesquioxane as a ligand for ruthenium.[100] Marsmann et al. used thiol-functionalized silsesquioxanes to bind to ruthenium and osmium carbonyl clusters.[101] Hong et al. published Ru(terpy)$_3$ complexes covalently linked to a silsesquioxane dendrimer.[102]

Liu et al. reported the crystal structure of a silsesquioxane-substituted osmium cluster in 1990 (Figure 7).[103]

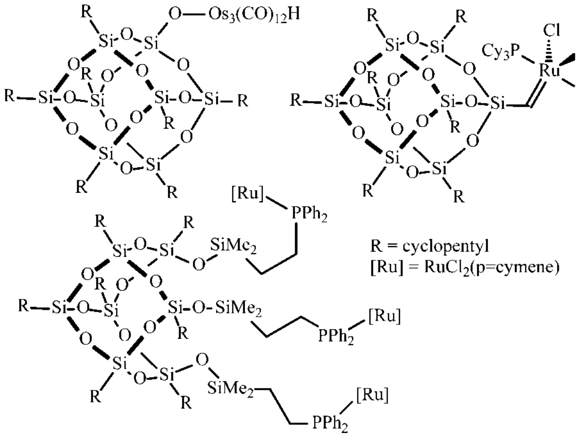


Figure 7. Examples of silsesquioxane complexes of osmium and ruthenium

Group 9−10 (Co, Rh, Pt)

The direct coupling of metals in this group to the silanol functionality of silsesquioxanes has been limited to platinum (see Figure 8). Abbenhuis et al. described the reaction of Pt(CO$_3$)(dppe) with trisilanol and mono-silylated disilanol silsesquioxane ligands.[104] Johnson et al.,[105] and Feher et al.[31] used mono-silylated thallium silsesquioxide complexes as a transmetallating agent to make silsesquioxane platinum compounds, although in some cases the use of thallium silsesquioxide complexes frustrated the synthesis of the complex due to residual thallium ions in the isolated materials.[105]

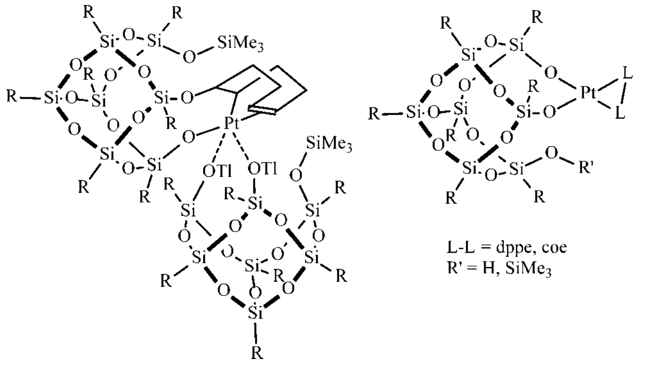


Figure 8. Pt silsesquioxane complexes by Abbenhuis, Feher and Johnson

Other reported ways of attaching Group 9−10 metals to silsesquioxanes are coordination of a donor group to the metal (S,[101][106] P[9,25,28,100,106−108]) and oxidative addition of a metal to Si−H (Co,[95,109] Rh[110]). Cole-Hamilton et al. used phosphorous-functionalized silsesquioxane-based dendrimers as ligands for rhodium to perform hydroformylation reactions.[25,28] They found a positive dendritic effect towards the linear product. Nowotny et al. used a phosphorous-functionalized silsesquioxane to chelate a Rh cluster to function as a model for a P-functionalized silica surface.[107] No catalytic tests were reported for the silsesquioxane compound.

Group 11−12 (Cu, Au, Zn)

Silsesquioxane complex chemistry has not been developed to a large extent for metals in these groups. Edelmann et al. treated (CuO*t*Bu)$_4$ with monosilylated disilanol and obtained a product with a crystal structure in which the tetrameric core of the copper alkoxide was maintained (see Figure 9). Pugin et al. used sulfur-functionalized silsesquioxanes as ligands for Au$_{55}$ clusters and were able to correlate the increased Coulomb gap to the increased size of the cluster going from PPh$_3$ to the silsesquioxane-based ligand.[111] Abis et al. prepared di- and trisubstituted gold silsesquioxanes as a model for the interaction of gold carbamate precursors with silica surfaces (see Figure 9).[112]

Group 13 (B, Al, Ga, Tl)

Due to the high reactivity of the precursors from this group, particularly the alkyl complexes, with silanol groups, the silanolate coordination chemistry is well developed. Duchateau et al.,[113−115] Edelmann et al.,[116] and Feher et al.[117−119] prepared aluminum silsesquioxane complexes as models for aluminum sites in zeolites and on silica, and as models for methyl alumoxane compounds. Abbenhuis et al. applied aluminum-containing silsesquioxane polymers as heterogeneous catalysts for the acceleration of Diels−Alder reactions of enones.[120] Maxim et al. used aluminum silses-

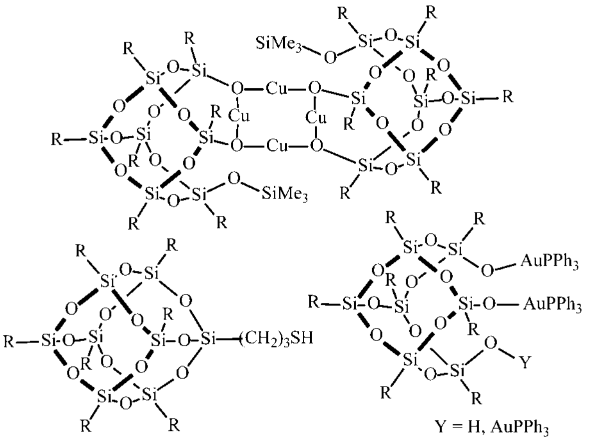


Figure 9. Examples of complexes of copper and gold and a thiol-functionalized ligand for gold clusters

quioxanes as precursors for microporous aluminosilicates by controlled calcination.[43]

Feher et al.[121] and Duchateau et al.[37] investigated the interaction of gallium precursors ($GaMe_3$ and $GaCl_3$).[122] Wada et al. used gallium silsesquioxane precursors to synthesize microporous gallium silicate materials with acidic sites by controlled calcination of the complexes in air.[123]

The interaction of boron with silsesquioxanes was the topic of research of Feher, Collins and Duchateau. Feher et al.[124] and Duchateau et al.[37] investigated the possible geometries that can be adopted by boron in a strained silsesquioxane environment. They found that boron can assume both trigonal-square and tetrahedral geometries. Collins[125] and Duchateau[50] synthesized silsesquioxane organoboranes and organoborates that could be used as models for silica-supported borane activators for Group 4 olefin polymerization catalysts (Figure 10). Reaction with bisalkylzirconocene complexes showed that both boranes and borates were susceptible to borane-zirconium exchange reactions, rendering the catalyst inactive. They concluded that the grafting of boranes on silica is not a useful method for subsequent immobilization of polymerization catalysts.

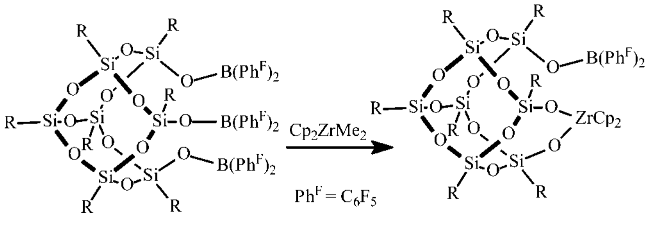


Figure 10. Interaction of dimethylzirconocene with a tris(organobora)silsesquioxane leading to borane-zirconocene exchange (Collins et al.)

Thallium silsesquioxane complexes have been mainly applied for transmetallation reactions where the thallium is replaced by high-valent transition metals.[31][87] Their ability to withstand dehydration reactions of the silsesquioxane framework, a common occurrence when using high-valent transition metals in combination with amine bases, make these complexes suitable for the synthesis of middle and late transition metal complexes, although the high toxicity is a serious disadvantage.

Outlook of Silsesquioxane Complex Chemistry

Besides extending the range of metals that can form complexes with silsesquioxane ligands, there are many challenges for the future of silsesquioxane chemistry. The introduction of functional groups besides the silanol groups could give new insights in the coordination chemistry of silsesquioxanes, and the introduction of coordinating groups like amines, thiols and phosphanes could have interesting effects on the catalytic performance of metal complexes. The introduction of silsesquioxane ligands and complexes in an approach as proposed by Skowronska-Ptasinski can revolutionize the way supported catalysts are made, due to the precise environment in which the metal center is incorporated. Controlled calcination of mixtures of silsesquioxane ligands and metal complexes yields highly dispersed, small metal oxide particles or even molecularly dispersed metal ions on a silica surface, with controllable multi-metallic content. Finally, the knowledge gained from the silsesquioxane model work should be transferred more to actual silica-supported systems or the ideas should be used to synthesize active and selective homogeneous catalysts, appropriate for industrial use.

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