CHEMISTRY OF SILICATES AND ALUMINOSILICATES

JIŘÍ PINKAS

Department of Inorganic Chemistry, Masaryk University in Brno, Kotlářská 2, 611 37 Brno, Czech Republic

E-mail: jpinkas@chemi.muni.cz

The review briefly summarizes the most exciting current trends in a broad area of inorganic and organometallic chemistry of silicates and aluminosilicates. The coverage of subjects is not exhaustive but rather selective due to the great extent of this field. Chosen topics illustrate current achievements and possible directions of future development that include silicon compounds with coordination numbers five and six, silicon with unusual N and S ligand environments, improved characterization techniques for oligomeric silicate species in solution and the gas phase, synthesis and structure of polysilanols and their derivatives, such as metallasilicates and silsesquioxanes, and their application in homogeneous and heterogeneous polymerization catalysis. Relevant advances in surface organometallic chemistry of silica, new sol-gel routes to oxide and hybrid materials based on hydrolytic and non-hydrolytic reactions, synthesis of mesoporous silica and chemical modifications of its intrapore surface, and synthesis of molecular models of zeolite building units are also highlighted. Developments in mass spectrometry (SIMS) with heavy projectiles and advanced NMR spectroscopic characterization methods that allow better characterization of silicates finish this overview. References cover the most pertinent reports and review articles past 1993.

INTRODUCTION

The modern chemistry of silicates (Si–O) and metallasilicates (Si–O–M) is very broad and diverse, ranging from minerals to organometallic siloxanes and catalysts to microporous zeolites to mesoporous silica and hybrid materials [1, 2]. Silicon and aluminum are the second and the third most abundant elements in the Earth crust [3] and yet they are never encountered in the nature in their elemental form. Instead they combine with oxygen and form a multitude of aluminosilicate minerals, such as garnets, topaz, beryl, pyroxenes, amphiboles, kaolinite, muskovite, pyrophyllite, mullite, zeolites, feldspars, and many others. From this long list of materials one can glimpse the immense importance of silicates for the mankind. Silicate dust particles containing Mg, Fe, Al, Ca, and Na are present also in the interstellar and circumstellar medium [4]. Their detection is based on analysis of the silicate bands in the IR spectra [5]. In this review, we tried to briefly summarize the most exciting current trends starting from silicon compounds with unusual coordination numbers five and six, studies of oligomeric silicate species in solution and the gas phase, synthesis, chemical reactivity and structural characterization of silanols and their derivatives, such as metallasilicates and silsesquioxanes, and their application in homogeneous and heterogeneous catalysis, surface organometallic chemistry of silica directed toward the rational fabrication of active sites,

sol-gel routes to silica-based oxide and hybrid materials, non-hydrolytic sol-gel reactions, synthesis and modification of mesoporous silica, synthesis of molecular models of zeolite building units, and developments in mass spectrometric and NMR spectroscopic methods applied to silicates and aluminosilicates. References cover the most relevant review articles and accounts past 1993 and aim the reader at vast numbers of original reports in many areas of the silicate and aluminosilicate research.

Unusual coordination environments

Both in minerals and synthetic compounds, silicon prefers coordination number four with a tetrahedral atomic environment. At normal conditions, high coordination numbers five and six are rare. However, the octahedral coordination is stabilized by high pressure in phases, such as stishovite and the perovskite-analog $(Mg,Fe)SiO_3$ in the upper mantle of the Earth. Consequently, most of the silicon atoms in our planet are present as six-coordinate SiO_6 moieties. Furthermore, silicon phosphates, such as SiP_2O_7, have been obtained at ambient pressure that contain polymeric network structures of SiO_6 octahedra and PO_4 tetrahedra [6] and ^{29}Si NMR studies revealed the presence of five-coordinate centers in alkali metal glasses [7]. Good examples of molecular compounds with five-coordinate silicon cen-

ters are silatranes, R-Si(OCH$_2$CH$_2$)$_3$N [8, 9]. A molecular organometallic compound containing a SiO$_6$ central unit was formed by the reaction of the aqueous solution of the Kläui acid [(C$_5$H$_5$)Co{P(O)(OH)$_2$}$_3$H] with glass container walls [10]. A number of coordination complex anions possessing hypervalent penta- and hexacoordinate silicon centers [11] are also known with multifunctional carboxylic acids [12] and o-dihydroxybenzene [13]. Also a large group of zwitterionic pentacoordinate silicates was structurally characterized [14]. Silica dissolves in ethylene glycol at elevated temperatures in the presence of alkali bases or triethanolamine catalyst yielding a variety of five- and six-coordinate species [15]. These reactions may become significant direct routes to organosilicones a organosilanes with exploitation of sand and silicate mineral resources. In general, the five-coordinate Si species serve as precursors for the transformations to alkoxides, ceramics, or organosiloxanes and silanes. They also act as intermediates in the complex reaction mixtures in the hydrothermal synthesis of zeolites, [16] sol-gel one-pot synthesis of mullite and cordierite [17], or synthesis of tetramethoxysilane from a variety of silicate minerals and dimethyl carbonate [18]. The five- and six-coordinate silicates were observed even in aqueous solutions at high concentrations by ^{29}Si NMR spectroscopy [19].

Aluminium prefers octahedral coordination in hydrated cations, oxides, hydroxides and coordination complexes. On the other hand, four-coordinate aluminium is found in the central tetrahedron in the Keggin-type polycation [AlO$_4$A1$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ and in the basic aluminate solutions as [Al(OH)$_4$]$^-$ [20]. In aluminosilicates and particularly in zeolites, aluminium replaces silicon at the tetrahedral coordination sites. A multitude of minerals and synthetic materials is composed of chains, rings, layers and three-dimensional arrays formed by corner-sharing of SiO$_4$ and AlO$_4$ tetrahedral units. The isoelectronic relationship between (SiO$_2$)$_2$ and [AlSiO$_4$]$^-$ is the foundation of vast aluminosilicate chemistry [21]. Pentacoordinate AlO$_5$ moieties are less common but not rare.

Nitridosilicates and nitridoaluminosilicates are families of compounds derived from silicates and aluminosilicates by replacing oxygens with nitrogens. The synthesis is not trivial as they are prepared at high temperatures from Si(NH)$_2$ or Si$_3$N$_4$ and metals or metal azides under nitrogen atmosphere. They usually contain three-dimensional networks of [SiN$_4$]$^{8-}$ tetrahedra connected through their vertices or edges. Nitridosilicates display more structural variability in comparison to their oxoanalogs. Besides zeolite-analogous networks and a discrete nitrido-*cyclo*-trisilicate anion [22] they feature SiN$_6$ octahedral units and triply and quadruply bridging nitrogen atoms. The interest of materials scientists in these compounds and also in a related group

of sialons (Si–Al–O–N) and sions (Si–O–N) was stimulated by their outstanding thermal, chemical, and mechanical stability [23, 24]. Compounds containing SiS$_4$ tetrahedra in their structures are sulfur analogs of orthooxosilicates. They were prepared either from elements by halogen assisted vapor phase transport reactions or from a particular metal and SiS$_2$ in a CsCl flux [25, 26].

Solution and gas phase clusters

Hydrolysis of Al^{3+} in aqueous solution upon raising pH leads to condensation and the formation of polycations. This complicated behavior is traditionally described by two models. One is based on cyclic hexameric fragments composed of edge-sharing octahedra that are related to gibbsite. Their subsequent coalescence and condensation leads to solid Al(OH)$_3$. The other mechanism is supported by the experimental observation of the Keggin Al$_{13}$ ion in ^{27}Al NMR spectra. A unified model was proposed, that considers both types of intermediates in the time dependent and dynamic process of polymerization and aging which is also influenced by the rate of neutralization [27]. Silicic acid forms a large number of oligomeric polysilicates by condensation in aqueous solutions (figure 1). The distribution of linear, branched, cyclic, and polyhedral anions depends on concentration, temperature, pH, ionic strength, and the nature of cations present. Silicic acid or silicate anions react with aluminium to form hydroxyaluminosilicate species of similar cage-like structures [28, 29].
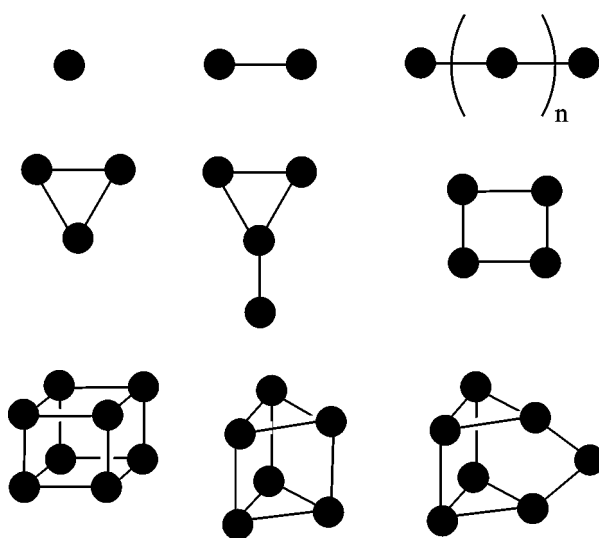

Figure 1. Examples of structural units of oligomeric silicates and aluminosilicates. Points represent Al/SiO$_4$ tetrahedral units, connecting lines are the oxygen bridges.

Volatile compounds of silicon and aluminium, such as hydrides, alkyls, halides, and alkoxides, serve as precursors to oxides in chemical vapor deposition (CVD) processes. Thin films of SiO_2 are applied as passivating and insulating layers in the fabrication of microelectronic circuits. A constantly decreasing size of devices requires certain stability and permeability characteristics that silica cannot meet. A replacement was found in alumina and aluminosilicates that display negligible ion migration effects and possess a high chemical stability, thermal conductivity and radiation resistance. Aluminosilicates have an advantage of remaining amorphous even upon heating and can be prepared either from a mixture of silicon and aluminium precursor compounds or from a single source precursor containing both elements in a desired ratio. However, the stoichiometry control is still a problem in both methods [30]. The complexity of the formation of solid products from small molecular precursors in the CVD processes was demonstrated for the reaction of $SiCl_4$ with oxygen, which leads to amorphous SiO_2 above 1000°C. At slightly lower temperatures, a vast number of intermediate chlorosiloxane clusters $Si_nO_{n+x}Cl_{2(n-x)}$ with up to 70 silicon atoms were characterized by analytical, mass spectrometric, NMR spectroscopic and structural techniques. These clusters represent structural fragments of solids and their stepwise growth manifests a continuous transition from molecular to solid state materials [31]. In a related process, fumed silica (AEROSIL) is produced by the combustion of $SiCl_4$ in the hot H_2/O_2 flame. Here the hydrolysis reaction is an important initial step that proceeds through assumed intermediate silafosgene $SiOCl_2$ and molecular SiO_2 to finally provide SiO_2 nanopowders with an extremely fine particle size [32].

Silanols

Organosilanols are reactive precursors for many metallasilicates and hybrid materials discussed here (figure 2). Simple organosilanols $R_nSi(OH)_{4-n}$ can be derived from silicic acid by progressively replacing hydroxyls with organyl groups. Two major synthetic methods are hydrolysis of Si–X bonds (X = H, halogen, alkoxide, carboxylate) and oxidation of Si–H groups. In contrast to their carbon kins, silanols easily undergo self-condensation to siloxanes resulting in the formation of linear, cyclic and polyhedral oligomers with Si–O–Si bridges. Sterically demanding R groups may be used as protection to increase their stability. In the solid state, organosilanols form extensive networks of hydrogen bonds and thus display a rich variety of cyclic, chain, tape, sheet, cage, and 3D framework structures [33-35].

Silica and aluminosilicates play a crucial role in catalysis which is traditionally divided into homogeneous and heterogeneous. Even though the heterogeneous systems are industrially much more important, they are usually used in a black box manner because the knowledge about the precise nature of active sites is limited due to their low concentration on an active catalyst and difficult experimental detection. On the other hand, the homogeneous catalysts are molecular and thus easily amenable to structural and mechanistic studies and details are known on many catalytic mechanisms [36]. Organometallic surface chemistry on amorphous and periodically organized SiO_2 and molecular models of the active sites built from silanols and silsesquioxanes are gradually bridging the gap between these two areas [37-39]. Two types of reactive sites are present on the supporting silica surface: strained siloxane bridges Si–O–Si and silanols Si–OH (figure 3). The protic character of the silanols is exploited in the reactions with organometallic compounds, such as metal alkyls, amides, silylamides, and alkoxides, that lead to well
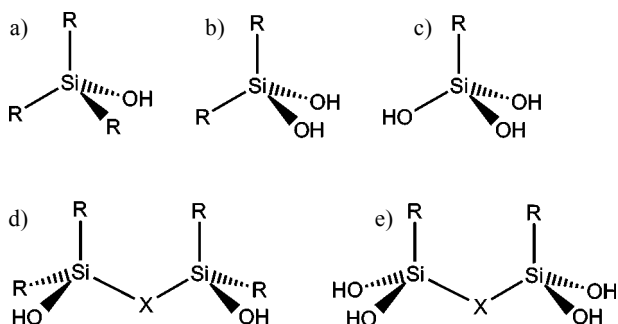

Figure 2. a) Monosilanols, b) silanediols, c) silanetriols, d) disilanols, and e) bis-silanediols; R = organyls, X = O or other spacer groups.
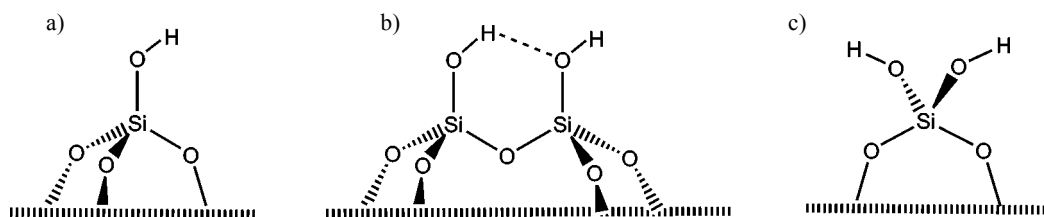

Figure 3. a) Isolated, b) vicinal, and c) geminal silanol groups at the silica surface.

defined and highly catalytically active models mimicking the active sites of the heterogeneous system. A large variety of methods, such as solid state NMR spectroscopy, IR spectroscopy, EXAFS, XANES, SEM, TEM, and ESR, have been employed to investigate these systems [40].

Silicas with a wide variety of surface-immobilized inorganic and organic reagents are applied as catalysts with improved selectivity and hold promise for more environmentally friendly technology [41]. Furthermore, organometallics are employed also in the modification of reactivity and selectivity of zeolitic molecular sieves by the reactions of the surface OH groups [42, 43]. The same reactivity mode is also exploited in the fabrication of self-assembled monolayers (SAM) that are produced on atomically flat surfaces of silicon wafers with native SiO_2 or on mica sheets. Long chain aliphatic trichlorosilanes ($RSiCl_3$), such as octadecyltrichlorosilane (OTS), are hydrolyzed by surface-adsorbed water and undergo condensation with the surface OH groups. The extended aliphatic chains are thus covalently anchored through the silanetriol head-groups and form a tightly packed two-dimensional film [44, 45]. SAM can be manipulated by scanning probe lithography with promising applications in nanotechnology [46, 47].

Silsesquioxanes

Silsesquioxanes form a diverse group of polyhedral compounds and polymers that are derived formally from silanetriols $RSi(OH)_3$ by condensation of the Si–OH groups. Their structure is based on trifunctional building units $RSiO_3$ where each silicon possesses an organic R group and three bridging oxygens which interconnect these units. The silsesquioxane moieties assemble in a variety of ways. A complete condensation of a limited number of units leads to polyhedral oligomeric silsesquioxanes (POSS) or spherosiloxanes. They form cages of different sizes and shapes,

$(RSiO_{3/2})_{2n}$ ($n = 3, 4, 5, ...$), trigonal-prismatic ($n = 3$, D3R, figure 4a), cubic ($n = 4$, D4R, figure 4b), pentagonal-prismatic ($n = 5$). An incomplete condensation provides a variety of cyclic, polycyclic, and polyhedral molecules with several remaining reactive Si–OH groups (figure 4c) [48]. On the other hand, amorphous polymeric networks result from irregular connection of an infinite number of units. Highly controlled synthetic reactions lead to the ladder-type oligosilsesquioxanes with different number of rungs [49].

Four most common methods used to prepare functionalized silsesquioxanes are a direct hydrolytic condensation of $RSiX_3$, hydrosilylation of hydridosilsesquioxanes, silylation of spherosilicates, and synthetic modification of organic substituents on readily available silsesquioxane molecules. The octasilsesquioxane cubic cage has an inner void of dimensions suitable for encapsulating small species, such as H and D atoms [50] or a fluoride ion [51].

Besides self-condensation, silanols react with a variety of metal hydrides, alkyls, amides, alkoxides, and halides and form metal-siloxide complexes. In these structures, silanolate anions serve as terminal, bridging, and chelating groups and form a multitude of cyclic, polycyclic, and polyhedral structures [52-55]. One of the workhorses of anaerobic synthetic chemistry - silicone grease - can become, accidentally or deliberately, a reagent in the reactions with highly polar metal compounds that lead to organometallasiloxanes [56]. For example, aluminium halides and hydrides cleave linear and cyclic polydimethylsiloxanes and provide cyclic products (figure 5).

Silanetriols offer three functional OH groups at a single nodal point that are used for building a variety of cyclic and polyhedral metallasiloxane molecules. These compounds are soluble in organic solvents and thus are amenable to investigation by NMR spectroscopy and other solution techniques [57-60]. Among the multitude of structurally characterized metallasilicate pohyhedral molecules, cubic aluminosilicate cages are most closely

a)

b)

c)

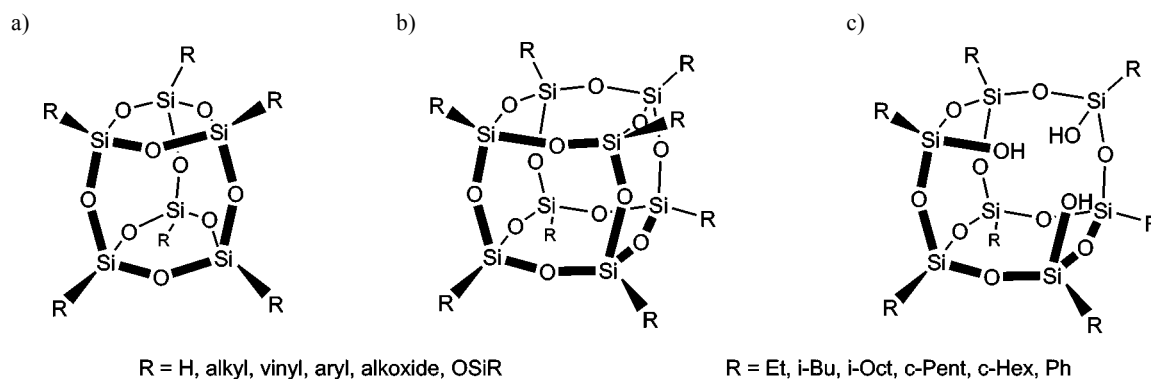R = H, alkyl, vinyl, aryl, alkoxide, OSiR   R = Et, i-Bu, i-Oct, c-Pent, c-Hex, Ph

Figure 4. a, b) Fully and c) partially condensed silsesquioxane cage molecules.

related to a structural motif of zeolites, the so-called double-four-ring (D4R) secondary building unit [61]. Amino-analogs of silanetriols are triaminosilanes $RSi(NH_2)_3$ that similarly provide access to iminosilicate cages and rings [62].

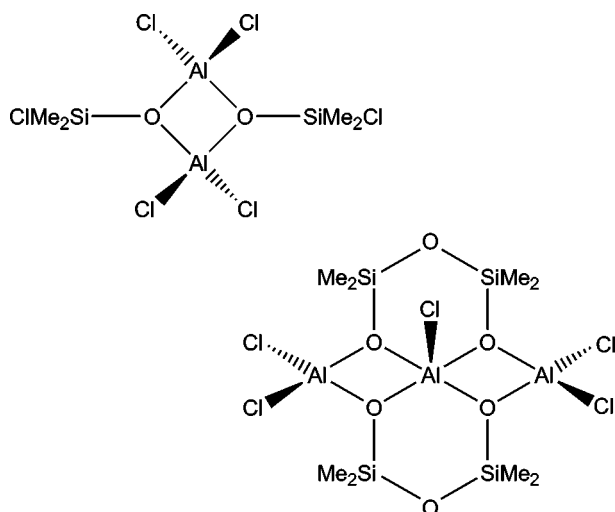Derivatives of $R_7Si_7O_9(OH)_3$ (R = cyclopentyl, cyclohexyl, figure 4c) hold a special position among the incompletely condensed silsesquioxanes. They feature a cubic skeleton with one missing silicon corner and three remaining reactive Si–OH groups. This moiety bears a close resemblance to structural features of silica surface [63]. Reactivity of the protic groups of $R_7Si_7O_9(OH)_3$ was utilized in reactions with a variety of organo-metallics to build monomeric or dimeric compounds (Scheme 1) as models for species present at the silica surface in heterogeneous silica-supported catalysts of olefin polymerization and epoxidation [64-66]. Most of the elements of the periodic table were incorporated in the polyhedral silsesquioxane structures [67]. These discrete organic-soluble molecules are easily studied by solution techniques [68, 69] and act as homogeneous catalysts in their own right [70].

Compounds $R_7Si_7O_9(OH)_3$ were also used in the reactions with functionalized trichlorosilanes, $P–SiCl_3$ (P = polymerizable group), to prepare cubic molecules containing seven inert organic groups for solubility purposes and one reactive functional group (ester, epoxy, olefin, nitrile) that serves for linking the octasilsesquioxane units to polymer chains. Polymers of different types (pendant, bead, and star, Scheme 2) were prepared by copolymerization with organic monomers,

Figure 5. Aluminodimethylsiloxanes.
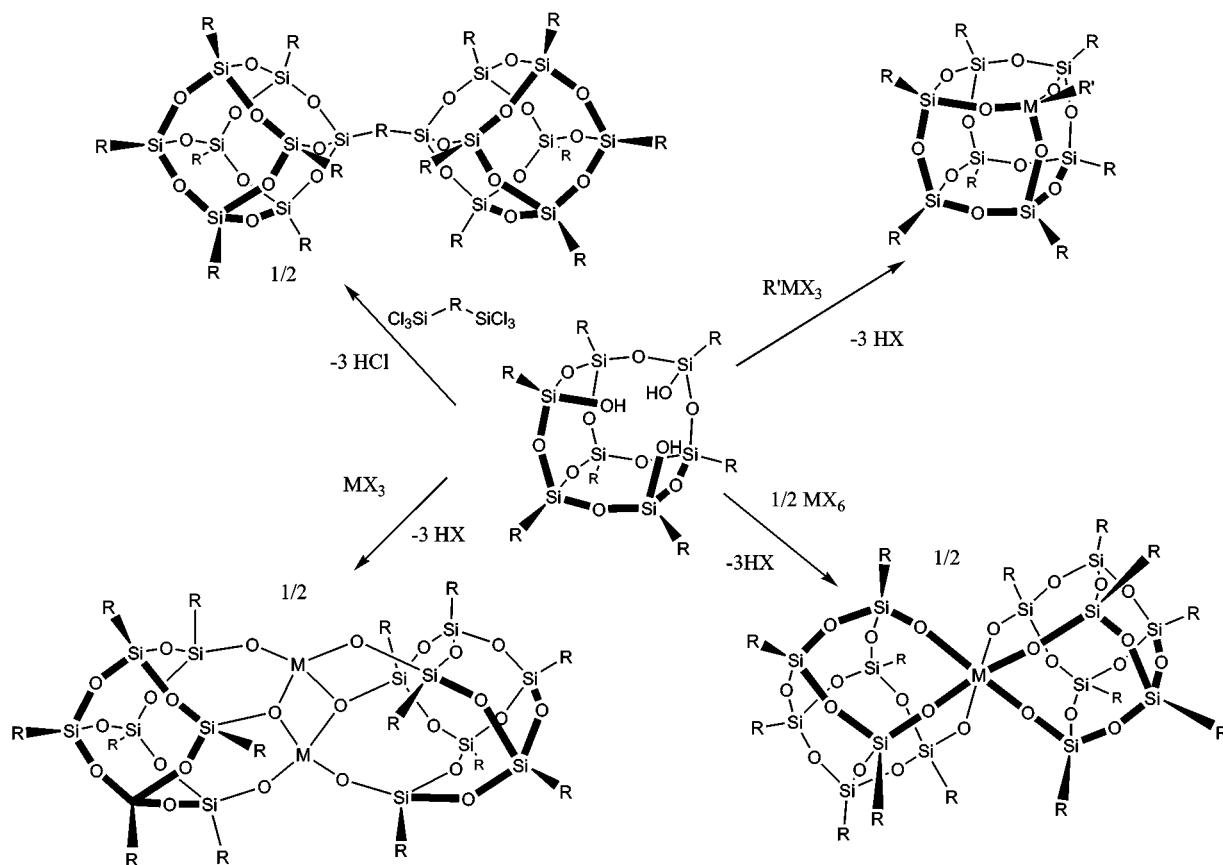
Scheme 1

such as acrylates, urethanes, and styrenes [71-73]. Cubic $R_8Si_8O_{12}$ silsesquioxanes were used as octafunctional cores in the divergent or convergent syntheses of dendrimers. The high functionality of these molecules provides an advantage over other types of core, e.g. tetrahedral, in a reduced number of reaction steps required to obtain globular molecules with a large array of terminal surface groups [74]. The silsesquioxane molecules with multiple reactive functional groups have been synthesized for the purpose of integration into polymer networks and serve as monomeric units for the preparation of crosslinked polymeric resins. Major chemical routes to crosslinking silsesquioxane cages are hydrosilylation, hydrolysis-condensation, silylation, hydride oxidation, and olefin radical polymerization [75, 76]. Resulting porous networks (Scheme 2) constitute a class of new silicate inorganic-organic hybrid materials and possess a large specific surface area and a high thermal stability [77].
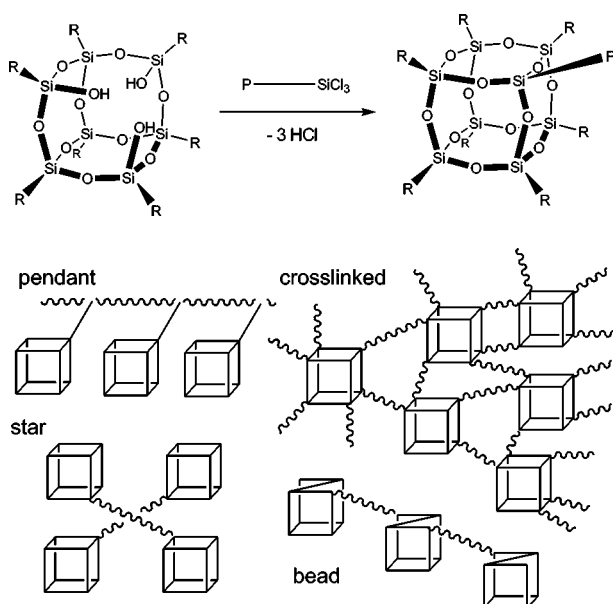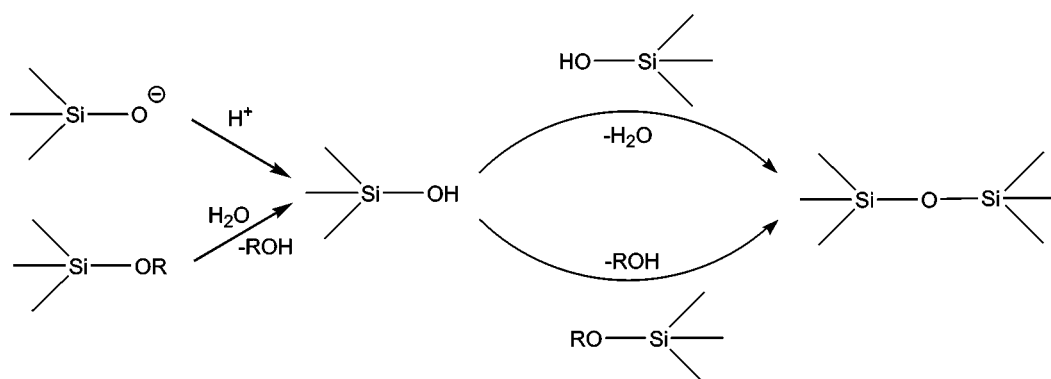

Scheme 2

Sol-gel synthesis and hybrid materials

One of the major areas in the chemistry of silica is the sol-gel processing. There are two classes of starting materials, basic aqueous solutions of inorganic silicates and alcoholic solutions of silicon alkoxides. The first step in both routes is the formation of silanol functionalities, either by acidifying and protonation of the silicate, or by hydrolysis of silicon alkoxides by water. The next step is the condensation of the silanol and siloxide groups and the formation of Si–O–Si bonds that constitute the skeletal framework of all silica materials discussed here (Scheme 3) [78].

The condensation-polymerization reactions lead to large polymeric molecules that form a colloidal solution - a sol. A gel is formed by an extensive polymerization of reactive moieties on the polysilicate molecules giving rise to a three dimensional crosslinked network. Further treatment of the gel leads, depending on the conditions, to dense oxides or glasses, xerogel powders, microporous zeolites, mesostructured and mesoporous silica materials, or aerogels. An example of a dense oxide prepared by the sol-gel route is mullite, $2Al_2O_3.SiO_2$. It is one of the aluminosilicate minerals that contain only aluminium and silicon and is relatively rare in nature. Because of its wide industrial applications, many synthetic routes were studied to prepare mullite powders and bodies [79]. A novel route to mixed-metal silicates is based on the facile thermolysis of metal siloxide precursors containing the $(tBuO)_3SiO$-substituents that easily undergo the isobutane elimination followed by the condensation of the resulting OH groups [80]. Aluminosilicate materials were obtained by solid-state and solution thermolysis of the $\{Me_2Al[OSi(OtBu)_3]\}_2$ single source precursors. Upon calcination, materials partially crystallized to mullite. The formation of gels in refluxing toluene constitutes an alternative to the classical hydrolytic sol-gel methods [81].
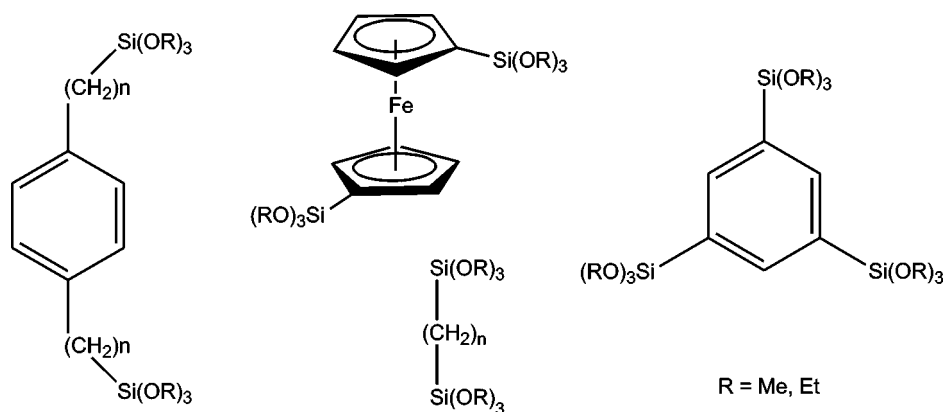

Scheme 3

Figure 6. Examples of bridged polyfunctional silicon alkoxides.

A partial replacement of TEOS in the sol-gel reaction mixtures by organically substituted alkoxides $RSi(OEt)_3$ or bridged polyfunctional alkoxides (figure 6) and subsequent hydrolysis and condensation leads to organosilicas, hybrid organic-inorganic materials that possess improved mechanical and optical properties and chemical stability. The silicate linkages provide structural rigidity, while the terminal or bridging organic groups allow extensive tailoring of the material properties [82-86].

The intricate structure of a gel can be preserved by special drying techniques that avoid a collapse of the network to powder (xerogel). Supercritical drying provides silica aerogels with extremely low densities and excellent thermal insulation properties [87, 88].
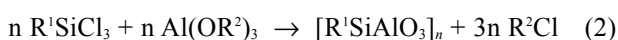
Mesoporous silica

A major breakthrough in the nanoscopic organization of silica occurred with the discovery of supramolecular templating. In contrast to the structure-directing action in the synthesis of zeolites, where small molecules serve as templating agents for microporous frameworks, supramolecular templating involves organization of amphiphilic surfactant molecules and silicate/aluminosilicate building blocks into larger aggregates - micelles or liquid crystalline phases. The amphiphilic molecules used for this purpose are cationic [89], anionic, or nonionic [90-92]. A silica source, such as sodium silicate or silicon alkoxides, and a template are mixed in an aqueous solution and heated or aged to produce a solid precipitate. This mesostructured product is then separated, washed, and carefully calcined to burn off organics from the pores. Mesoporous silica with a hexagonally close-packed array of pores with diameters 20-100 Å and a narrow pore size distribution is obtained. A commonly used acronym for these materials is MCM-41 [93]. Other morphologies, such as lamellar, cubic, worm-hole, and sponge-like, were obtained by controlling the synthesis conditions (pH, temperature, concentration) and the nature of templates. A variable surfactant chain length gives a control of the pore diameter. Even though the walls are amorphous, the long-range order in the pore arrangement leads to observable diffractions in the powder X-ray patterns at very low angles [94-96]. The self-organization of inorganic silica precursors and the organic templates in the mesoporous materials involve processes such as an assembly of surfactant molecules to rod-like micelles, different types of interaction of negatively or positively (below the isoelectric point of silica at pH = 2) multiply-charged silica oligomers with the hydrophilic headgroups of the surfactant, condensation of silica network, interactions with cosurfactants and counterions, and hydrogen bonding in the systems with nonionic surfactants. These are the key factors in the control of the evolution of these materials, however, their importance may vary depending on the particular system and actual conditions. None of the proposed reaction mechanisms provides an exclusive and definitive answer [97].

The mesoporous aluminosilicates are promising acid catalysts and increasing aluminium content changes hydrophobic silica to mildly hydrophilic. However, well-ordered structures are obtained with more difficulties than pure silica materials. A direct addition of aluminium sources, such as alkoxides, sodium aluminate, or Al_{13} polycation, into the reaction mixture lead to low incorporation levels of Al and less ordered structures. The improved synthetic strategies include recrystallization of amorphous walls to nanosized zeolite crystallites, an assembly of thick-wall silica structures with a subsequent post-synthesis treatment for introducing AlO_4 units into the framework, or directly assembling zeolitic seeds to the aluminosilicate mesostructures [98]. Many other metal cations (Ti, V, Fe, Cr) can be isomorphously substituted for Si^{4+} in the amorphous walls of mesoporous silicas and function as redoxactive catalytic centers [99]. An extensive intrapore chemistry based on sorption, ion exchange, reduction of

the inserted species, inclusion of complexes, grafting on the internal walls, and polymerization in the channels was developed inside the highly regular MCM materials [100-103]. One method of introducing organic groups onto the internal surface is the one pot synthesis based on co-condensation of a mixture of organotrialkoxosilanes with TEOS in the presence of surfactants as described above for the sol-gel synthesis of hybrid materials. The other postsynthesis procedure is direct grafting, the reaction of surface silanol OH groups with functionalized trialkoxosilanes, such as $(MeO)_3Si(CH_2)_3NH_2$. Furthermore, reactive centers can be tethered to the pore walls by secondary modifications of the anchored functional silanes by organometallics or coordination complexes [104]. Ordered mesoporous organosilicas display an improved activity in redox and acid/base catalysis, and find applications in environmental remediations by adsorption removal of toxic heavy metals and organic pollutants. Mesoporous silica films appear to have a large potential as low-k materials in electronic industry [105].

Besides an extensive and well developed area of aqueous sol-gel chemistry of silica and aluminosilicates, new nonaqueous methods are being developed that can complement the traditional hydrolytic processes. These routes are also called nonhydrolytic because they are based on the reactions that do not employ water as a source of oxygen for the formation of Si–O–Si and Al–O–Si bonds. In the absence of water, hydrolytic reactions of alkoxide precursors are retarded. Instead, other condensation mechanisms are put into action and alternative oxygen donors are used (alkoxides, alcohols, ethers, ketones). The reactions of silicon and aluminium alkoxides and halides are accompanied by the release of alkylhalides and lead to the condensation to a network of bonds (equation (1), (2)).

$$X_3Si\text{-}OR + Cl\text{-}SiY_3 \rightarrow RCl + X_3Si\text{–}O\text{–}SiY_3 \qquad (1)$$

$$n\ R^1SiCl_3 + n\ Al(OR^2)_3 \rightarrow [R^1SiAlO_3]_n + 3n\ R^2Cl \qquad (2)$$

The major advantages of the nonhydrolytic over hydrolytic approach are the irreversibility of the bond forming reactions, compatibility of the precursors with polymeric systems forming inorganic-organic hybrid materials, and the possibility to use water-sensitive or insoluble precursors [106-108].

Zeolites

One of the industrially most important family of aluminosilicate compounds are zeolites. These microporous solids - molecular sieves - are widely used as desiccating agents, ion exchangers, and as solid, shape-selective Lewis-acid or redox catalysts. They form three-dimensional frameworks of tetrahedral SiO_4 and AlO_4 primary building units. A more detailed treatment of this wide topic is beyond the scope of this article and can be found elsewhere [109]. Here we only want to highlight the relation of the so-called secondary building units (SBU) to the molecular silsesquioxanes because it has bearing on the most crucial questions in the zeolite chemistry, i.e. what is the nucleation and framework growth mechanism.

The formation of a crystalline phase is a very complicated process taking place in a multicomponent heterogeneous reaction mixture that evolves with time and its conditions depend on a multitude of variables. While our understanding of the zeolite crystallization is only in the beginning, three mechanistic models were proposed [110]. The solution-mediated mechanism relies on dissolution of solid reagents, followed by the diffusion transport of the silicate species to the nucleation sites and the crystal growth in the final step. The nature of the diffusing molecules is still a matter of debate. Single and double four-rings (D4R) were identified by spectroscopic methods, however it is not completely clear whether they are the nucleating species or they form larger structures evolving into the nucleation centers. The solid-to-solid transformations of amorphous aluminosilicate gels to crystalline zeolite structures without the need for the presence of small soluble silicate or aluminate molecules were also observed in some experiments. An aggregation, densification and crystallization of nanometer-size particles lead to zeolite crystals [111]. Finally, it was shown that zeolites can be synthesized by a topotactic reaction of layered silicates where precursors can be transformed by condensation reactions into three-dimensional porous silicate frameworks by simple calcination procedures [112]. HF is known to act as a mineralizing agent that improves the solubility of the silicate anions and catalyses the condensation reactions involved in the formation of the Si–O–Si bonds. Fluoride is then bound as SiO_4F in the resulting structure [113] or it is only encapsulated within the silicate cages, such as D4R.

Analysis methods of aluminosilicates

The frameworks of aluminosilicates contain three magnetically active nuclei, ^{27}Al, ^{29}Si, and ^{17}O, that are amenable to the spectral investigation by solid-state NMR techniques and can provide information about the composition, element ordering, geometrical parameters, and chemical properties, such as acidity. A correlation of ^{29}Si isotropic chemical shifts with the $SiO_x(OSi)_{4-x}$ and $Si(OAl)_x(OSi)_{4-x}$ structural motifs is well understood. Quadrupolar ^{27}Al and ^{17}O nuclei allow extraction of other useful parameters, such as quadrupolar coupling and asymmetry. The ^{27}Al NMR spectra of zeolites

and other aluminosilicates are, in general, much simpler than their ^{29}Si NMR counterparts since, according to Loewenstein's rule (which forbids Al–O–Al pairs), only one tetrahedral Al(OSi)$_4$ environment exists in the frameworks. The ^{27}Al NMR chemical shifts are the best tool for distinguishing the coordination environments of aluminium. Specific regions can be assigned to signals of AlO$_4$, AlO$_5$, or AlO$_6$ polyhedra [114, 115]. The solution NMR studies on silicates enriched to 95% in ^{29}Si lead to identification of many oligomeric species [116].

Mass spectrometric (MS) studies find applications in the molecular systems, such as alkoxides, molecular silsesquioxanes and silicone complexes [117]. A combination of gas chromatography with mass spectrometry (EI and CI) allowed the separation and characterization of a vast number of hydrolysis intermediates and products in the reaction mixture of one of the most important silicon alkoxide Si(OEt)$_4$ (TEOS). Linear, cyclic and polycyclic ethoxysilanes and ethoxysilanols with up to eight silicon atoms in the molecule were identified in the reaction mixture. Chemical ionization by methane (CH$_5^+$) proceeds by a proton transfer to siloxane oxygen and allows better identification of higher oligomers. The distribution of oligomeric silicate species in an aqueous solution was successfully studied by the electrospray ionization (ESI) mass spectrometry [118].

Much more difficult situation is in MS of silicates, zeolites and silicate-containing hybrid polymers. Their refractory and involatile nature restricts the routine use of common techniques, such as electron impact ionization, for study of these systems. The formation of ions is prevented by a three-dimensional network of strong polar bonds. Energetic ionization techniques were employed to generate gaseous silicate and aluminosilicate ions. Laser desorption FT MS was used to generate large silicate oligomers [119, 120]. Also secondary ion MS (SIMS) with ionization by a beam of energetic ions, such as Ga$^+$ or ReO$_4^-$, was used to eject ions from the surface of solid zeolite samples on impact. The bombardment with Ga$^+$ lead mostly to small ions and thus only atomic information was obtained. Polyatomic ReO$_4^-$ projectiles are capable of ejecting larger fragments [121, 122]. Ion mobility measurements provide information about the conformation of the ions. Different shaped ions have distinct collisional cross-sections and hence different drift times when moving through a buffer gas [123].

CONCLUSION

Silicates and aluminosilicates will undoubtedly continue to play the central role in many areas of basic and applied research, such as chemical catalysis, classical and advanced materials production, theoretical chemistry, and geochemistry. Their importance stems not only from the vast natural abundance but also from their immense compositional variability and structural diversity, not unlike the organic compounds. The five- and six-coordinate silicon species will attract even more interest from the point of view of their chemical behavior [124-125], catalytic activity, NMR spectroscopic properties, stereochemistry and also as a probe of fundamental bonding concepts [126]. A major research effort will be aimed at understanding of the mechanism and gaining control over the molecule-to-solid transformations, both in the gas phase and solution. This area is so far the least understood and most controversial. The mechanism of the zeolite framework formation is just one important example where an intense debate continues [127-129]. The goal is to understand the whole reaction sequence from the precursor molecules to the intermediate oligomeric cluster units to nucleation species and nanoparticles and finally to growing crystalline framework. In order to tackle such complex problems, a multitude of powerful analytical, physico-chemical, spectroscopic, and microscopic techniques with abilities to probe the systems at various length scales, will have to be employed in a mutual concert. The key to the success will be to assure the representativeness of a studied model system which has to correspond to the composition and speciation of a real reaction mixture. Advances in computational schemes will bring new views on possible reaction pathways that could be compared with the experimental data [130]. Further progress in the synthetic techniques is to be expected from the application of nonaqueous fluoride-activated reactions leading to new zeolite structures. Also new metallasilicate and hybrid materials will result from the exploitation of nonhydrolytic sol-gel reactions. Mesoporous silica and organosilicas will remain in the center of attention in the heterogeneous catalyst development. An improved control over the chemical composition, pore size, surface functionalization, and hydrothermal stability will be sought. Ordered arrays of pores will serve as molds for the fabrication of nanostructured metallic, semiconducting, and carbon materials [131, 132]. Combinatorial techniques will be able to probe the multidimensional space of reaction parameters and variables in the syntheses of new oxidic, zeolitic, and hybrid materials [133, 134]. However, in this effort a judicious choice of a starting parameter subset will have to be guided by chemical intuition and knowledge or by the optimization results obtained by the application of artificial neural networks on experimental data [135].

References

1. Jutzi P., Schubert U., Ed.: *Silicon Chemistry. From the Atom to Extended Systems*, Wiley-VCH, Weinheim 2003.
2. Corriu R. J. P., Jutzi P., Ed.: *Tailor-Made Silicon-Oxygen Compounds*, Vieweg, Braunscheweig 1996.
3. Favero G., Jobstraibizer P.: Coord.Chem.Rev. *149*, 367 (1996).
4. Demyk K., Jones A. P., Dartois E., Cox P., d'Hendecourt L.: Astron.Astrophys. *349*, 267 (1999).
5. Gaidos E., Koresko C.: New Astronomy *9*, 33 (2003).
6. Poojary D. M., Borade R. B., Campbell III F. L., Clearfield A.: J. Solid State Chem. *112*, 106 (1994).
7. Stebbins J. F., McMillan P.: J. Non-Crystalline Solids *160*, 116 (1993).
8. Gevorgyan V., Borisova L., Vyater A., Ryabova V., Lukevics E.: J.Organomet.Chem. *548*, 149 (1997).
9. Verkade J. G.: Coord.Chem.Rev. *137*, 233 (1994).
10. Kläui W., Mocigemba N., Weber-Schuster A., Bell R., Frank W., Mootz D., Poll W., Wunderlich H.: Chem.Eur.J. *8*, 2335 (2002).
11. Holmes R. R.: Chem.Rev. *96*, 927 (1996).
12. Balkus Jr. K. J., Gabrielova I. S., Bott S. G.: Inorg. Chem. *34*, 5776 (1995).
13. Hahn F. E., Keck M., Raymond K. N.: Inorg.Chem. *34*, 1402 (1995).
14. Tacke R., Pülm M., Wagner B.: Adv. Organomet. Chem. *44*, 221 (1999).
15. Cheng H., Tamaki R., Laine R. M., Babonneau F., Chujo Y., Treadwell D. R.: J.Am.Chem.Soc. *122*, 10063 (2000).
16. Herreros B., Carr S. W., Klinowski J.: Science *263*, 1585 (1994).
17. Laine R. M., Treadwell D. R., Mueller B. L., Bickmore C. R., Waldner K. F., Hinklin T. R.: J.Mater. Chem. *6*, 1441 (1996).
18. Lewis L. N., Schattenmann F. J., Jordan T. M., Carnahan J. C., Flanagan W. P., Wroczynski R. J., Lemmon J. P., Anostario J. M., Othon M. A.: Inorg.Chem. *41*, 2608 (2002).
19. Kinrade S. D., Del Nin J. W., Schach A. S., Sloan T. A., Wilson K. L., Knight C. T. G.: Science *285*, 1542 (1999).
20. Powell A. K., Heath S. L.: Coord.Chem.Rev. *149*, 59 (1996).
21. Downs A. J., Ed.: *Chemistry of Aluminium, Gallium, Indium and Thallium*, Chapman & Hall, London 1993.
22. Lissner F., Schleid T.: Z.Anorg.Allg.Chem. *630*, 2226 (2004).
23. Schnick W., Bettenhausen R., Götze B., Höppe H. A., Huppertz H., Irran E., Köllisch K., Lauterbach R., Orth M., Rannabauer S., Schlieper T., Schwarze B., Wester F.: Z.Anorg. Allg.Chem. *629*, 902 (2003).
24. Schnick W., Huppertz H.: Chem.Eur.J. *3*, 679 (1997).
25. Hatscher S. T., Urland W.: Z. Anorg.Allg.Chem. *628*, 1673 (2002).
26. Hartenbach I., Schleid T.: Z. Anorg.Allg.Chem. *629*, 394 (2003).
27. Bi S., Wang C., Cao Q., Zhang C.: Coord.Chem.Rev. *248*, 441 (2004).
28. Swaddle T. W.: Coord. Chem.Rev. *219-221*, 665 (2001).
29. Rowatt E., Williams R. J. P.: Coord.Chem.Rev. *149*, 167 (1996).
30. Barron A. R. in: *CVD of Nonmetals*, p. 262-319, Ed. Rees Jr. W.S., VCH, Weinheim 1996.
31. Binnewies M., Jug K.: Eur.J.Inorg.Chem. *6*, 1127 (2000).
32. Hannebauer B., Menzel F.: Z.Anorg.Allg.Chem. *629*, 1485 (2003).
33. Chandrasekhar V., Boomishankar R., Nagendran S.: Chem.Rev. *104*, 5847 (2004).
34. Lickiss P.D.: Adv. Inorg.Chem. 42, 147 (1995).
35. Haiduc I., Edelmann F. T.: *Supramolecular Organometallic Chemistry*, VCH, Weinheim 1999.
36. Thomas J. M.: Angew.Chem.Intl.Ed.Engl. *33*, 913 (1994).
37. Coperet C., Basset J.-M., Chabanas M., Saint-Arroman R. P.: Angew.Chem.Intl.Ed. *42*, 156 (2003).
38. Schwartz J., Bernasek S. L.: Catal.Today *66*, 3 (2001).
39. Anwander R.: Chem.Mater. *13*, 4419 (2001).
40. Thomas J. M.: Faraday Discuss. *105*, 1 (1996).
41. Price P. M., Clark J. H., Macquarrie D. J.: J.Chem. Soc., Dalton Trans. *101* (2000).
42. Lefebvre F., de Mallmann A., Basset J.-M.: Eur.J. Inorg.Chem. *361* (1999).
43. Guzman J., Gates B. C.: Dalton Trans. 3303 (2003).
44. Ulman A.: Chem.Rev. *96*, 1533 (1996).
45. Schreiber F.: Prog.Surf.Sci. *65*, 151 (2000).
46. Liu G.-Y., Xu S., Qian Y.: Acc.Chem.Res. *33*, 457 (2000).
47. Kraemer S., Fuierer R. R., Gorman C. B.: Chem.Rev. *103*, 4367 (2003).
48. Harrison P. G.: J.Organometal.Chem. *542*, 141 (1997).
49. Unno M., Suto A., Matsumoto H.: J.Am.Chem.Soc. *124*, 1574 (2002).
50. Hayashino Y., Isobe T., Matsuda Y.: Inorg.Chem. *40*, 2218 (2001).
51. Bassindale A. R., Pourny M., Taylor P. G., Hursthouse M. B., Light M. E.: Angew.Chem. Int.Ed. *42*, 3488 (2003).
52. Marciniec B., Maciejewski H.: Coord.Chem.Rev. *223*, 301 (2001).
53. Murugavel R., Voigt A., Walavalkar M. G., Roesky H. W.: Chem.ev. *96*, 2205 (1996).
54. Veith M., Hreleva H., Biegler J., Huch V., Rammo A.: *Phosphorus, Sulfur, and Silicon and Relat. Elem.* 179, 651 (2004).
55. King L., Sullivan A. C.: Coord.Chem.Rev. *189*, 19 (1999).
56. Haiduc I.: Organometallics *23*, 3 (2004).
57. Murugavel R., Chandrasekhar V., Roesky H. W.: Acc. Chem.Res. *29*, 183 (1996).
58. Roesky H. W., Anantharaman G., Chandrasekhar V., Jancik V., Singh S.: Chem.Eur.J. *10*, 4106 (2004).

59. Lorenz V., Fischer A., Giessmann S., Gilje J. W., Gunko Y., Jacob K., Edelmann F.T.: *Coord.Chem.Rev.* 206-207, 321 (2000).
60. Purkayastha A., Baruah J. B.: Appl.Organometal. Chem. *18*, 166 (2004).
61. Montero M., Voigt A., Teichert M., Uson I., Roesky H. W.: Angew.Chem., Int. Ed. Engl. *34,* 2504 (1995).
62. Murugavel R., Bhattacharjee M., Roesky H. W.: Appl. Organometal.Chem. *13*, 227 (1999).
63. Feher F. J., Budzichowski T. A.: Polyhedron *14*, 3239 (1995).
64. Duchateau R.: Chem.Rev. *102*, 3525 (2002).
65. Duchateau R., Dijkstra T. W., van Santen R. A., Yap G. P. A.: Chem.Eur.J. *10*, 3979 (2004).
66. Lorenz V., Edelmann F. T.: Z. Anorg.Allg.Chem. *630*, 1147 (2004).
67. Hanssen R. W. J. M., van Santen R. A., Abbenhuis H. C. L.: Eur.J.Inorg.Chem. *675* (2004).
68. Pescarmona P. P., van der Waal J. C., Maschmeyer T.: Chem.Eur.J. *10*, 1657 (2004).
69. Pescarmona P. P., Maschmeyer T.: Austr.J.Chem. *54*, 583 (2001).
70. Abbenhuis H. C. L.: Chem.Eur.J. *6*, 25 (2000).
71. Schwab J. J., Lichtenhan J. D.: Appl.Organometal. Chem. *12*, 707 (1998).
72. Phillips S. H., Haddad T. S., Tomczak S. J.: Curr.Op. Solid State & Mater. Sci. *8*, 21 (2004).
73. Costa R. O. R., Vasconcelos W. L., Tamaki R., Laine R. M.: Macromolecules *34*, 5398 (2001).
74. Zhang X., Haxton K. J., Ropartz L., Cole-Hamilton D. J., Morris R. E.: J.Chem.Soc., Dalton Trans. 3261 (2001).
75. Li G., Wang L., Ni H., Pittman Jr. C. U.: J.Inorg. Organometal.Polym. *11*, 123 (2001).
76. Pittman Jr. C. U., Li G., Ni H.: Macromol.Symp. *196*, 301 (2003).
77. Zhang C., Babonneau F., Bonhomme C., Laine R. M., Soles C. L., Hristov H. A., Yee A. F.: J.Am.Chem.Soc. *120*, 8380 (1998).
78. Wright J. D., Sommerdijk N. A. J. M.: *Sol-Gel Materials, Taylor and Francis*, London 2001.
79. Kansal P., Laine R. M., Babonneau F.: J.Am.Ceram. Soc. *80*, 2597 (1997).
80. Fujdala K. L., Tilley T. D.: J.Catal. *216*, 265 (2003).
81. Terry K. W., Ganzel P. K., Tilley T. D.: Chem.Mater. *4*, 1290 (1992).
82. Sanchez C., Lebeau B., Chaput F., Boilot J.-P.: Adv.Mater. *15*, 1969 (2003).
83. Shea K. J., Loy D. A.: Chem.Mater. *13*, 3306 (2001).
84. Loy D. A., Shea K. J.: Chem.Rev. *95*, 1431 (1995).
85. Baney R. H., Itoh M., Sakakibara A., Suzuki T.: Chem.Rev. *95*, 1409 (1995).
86. Cerveau G., Corriu R. J. P., Framery E.: Chem.Mater. *13*, 3373 (2001).
87. Pierre A. C., Pajonk G. M.: Chem.Rev. *102*, 4243 (2002).
88. Hüsing N., Schubert U.: Angew.Chem.Int.Ed. *37*, 22 (1998).
89. Lin H.-P., Mou C.-Y.: Acc. Chem.Res. *35*, 927 (2002).
90. Goltner-Spickermann C.: Curr.Op.Colloid & Interface Sci. 7, 173 (2002).
91. Hunks W. J., Ozin G. A.: Chem.Mater. *16*, 5465 (2004).
92. Ying J. Y., Mehnert C. P., Wong M. S.: Angew.Chem. Int.Ed. *38*, 56 (1999).
93. Zhao X. S., Lu G. Q., Miller G. J.: Ind.Eng.Chem.Res. *35*, 2075 (1996).
94. Stein A., Melde B. J., Schroden R. C.: Adv.Mater. *12*, 1403 (2000).
95. Ciesla U., Schüth F.: Micropor.Mesopor.Mater. *27*, 131 (1999).
96. Corma A.: Chem.Rev. *97*, 2373 (1997).
97. Patarin J., Lebeau B., Zana R.: Curr.Op.Colloid & Interface Sci. *7*, 107 (2002).
98. Liu Y., Pinnavaia T. J.: J.Mater.Chem. *12*, 3179 (2002).
99. Sayari A.: Chem.Mater. *8*, 1840 (1996).
100. Moller K., Bein T.: Chem.Mater. *10*, 2950 (1998).
101. Maschmeyer T., Thomas J. M., Masters A. F. in: *New Trends in Materials Chemistry*, p. 461-494, Ed. Catlow C. R. A., Cheetham A., NATO ASI Series. Series C, Mathematical and Physical Sciences, No. 498, Kluwer, Dordrecht 1997.
102. Maschmeyer T.: Curr.Op.Solid State & Mater. Sci. *3*, 71 (1998).
103. Sayari A., Hamoudi S.: Chem.Mater. *13*, 3151 (2001).
104. Walcarius A., Etienne M., Lebeau B.: Chem.Mater. *15*, 2161 (2003).
105. Soler-Illia G. J. de A. A., Sanchez C., Lebeau B., Patarin J.: Chem.Rev. *102*, 4093 (2002).
106. Corriu R. J. P., Leclercq D.: Angew. Chem., Int. Ed. Engl. *35*, 1420 (1996).
107. Vioux A., Leclercq D.: Heterogeneous Chem.Rev. 3, 65 (1996).
108. Hay J. N., Raval H. M.: Chem.Mater. *13*, 3396 (2001).
109. Cundy C. S., Cox P. A.: Chem.Rev. *103*, 663 (2003).
110. Francis R. J., O'Hare D.: J.Chem.Soc., Dalton Trans. *3133* (1998).
111. Serrano D. P., van Grieken R.: J.Mater.Chem. *11*, 2391 (2001).
112. Ikeda T., Akiyama Y., Oumi Y., Kawai A., Muzikami F.: Angew. Chem.Int. Ed. *43*, 4892 (2004).
113. Fyfe C. A., Brouwer D. H., Lewis A.R., Villaescusa L. A., Morris R. E.: J.Am.Chem.Soc. *124*, 7770 (2002).
114. Fitzgerald J. J., Ed.: *Solid-state NMR Spectroscopy of Inorganic Materials*, ACS Symp. Ser. 717, 1999.
115. Mackenzie K. J. D., Smith M. E.: *Multinuclear Solidstate NMR of Inorganic Materials*, Pergamon, Elsevier Science, Oxford 2002.
116. Kinrade S. D., Donovan J. C. H., Schach A. S., Knight C. T. G.: J.Chem.Soc., Dalton Trans. *1250* (2002).
117. Söger N., Binnewies M.: Z.Anorg.Allg.Chem. *629*, 232 (2003).
118. Bussian P., Sobbot F., Brutschy B., Schrader W., Schüth F.: Angew.Chem.Int.Ed. *39*, 3901 (2000).
119. Lafargue P. E., Gaumet J.-J., Muller J. F., Labrosse A.:

J.Mass Spectrom. *31*, 623 (1996).

120. Lafargue P. E., Gaumet J.-J., Muller J. F.: Chem.Phys. Lett. *288*, 494 (1998).

121. Groenewold G. S., Kessinger G. F., Scott J. R., Gianotto A. K., Appelhans A. D., Delmore J. E.: Anal. Chem. *73*, 226 (2001).

122. Gianotto A. K., Rawlinson J. W., Cossel K. C., Olson J. E., Appelhans A. D., Groenewold G. S.: J.Am. Chem.Soc. *126*, 8275 (2004).

123. Gidden J., Kemper P. R., Shammel E., Fee D. P., Anderson S., Bowers M. T.: Int. J. Mass Spec. *222*, 63 (2003).

124. Wagler J., Doert T., Roewer G.: Angew.Chem.Intl. Ed. *43*, 2441 (2004).

125. Gostevskii B., Silbert G., Adear K., Sivaramakrishna A., Stalke D., Deuerlein S., Kocher N., Voronkov M.G., Kalikhman I., Kost D.: Organometallics *24*, 2913 (2005).

126. Kocher N., Henn J., Gostevskii B., Kost D., Kalikhman I., Engels B., Stalke D.: J.Am. Chem.Soc. *126*, 5563 (2004).

127. Knight C. T. G, Kinrade S. D.: J.Phys.Chem. B *106*, 3229 (2002).

128. Kirschhock C. E. A., Ravishankar R., Verspeurt F., Grobet P. J., Jacobs P. A., Martens J. A.: J.Phys.Chem. B *106*, 3333 (2002).

129. Kragten D. D., Fedeyko J. M., Sawant K. R., Rimer J. D., Vlachos D. G., Lobo R. F., Tsapatsis M.: J.Phys.Chem. B *107*, 10006 (2003).

130. Mora-Fonz M. J., Catlow C. R. A., Lewis D. W.: Angew.Chem.Intl.Ed. *44*, 3082 (2005).

131. Schüth F.: Angew.Chem.Intl.Ed. *42*, 3604 (2003).

132. Kruk M., Dufour B., Celer E. B., Kowalewski T., Jaroniec M., Matyjaszewski K.: J. Phys.Chem. B *109*, 9216 (2005).

133. Akporiaye D. E., Dahl I. M., Karlsson A., Wendelbo R.: Angew.Chem.Int.Ed. *37*, 609 (1998).

134. Klein J., Lehmann C. W., Schmidt H.-W., Maier W. F.: Angew.Chem.Int.Ed. *37*, 3369 (1998).

135. Moliner M., Serra J. M., Corma A., Argente E., Valero S., Botti V.: Micropor.Mesopor.Mater. *78*, 73 (2005).

CHEMIE KŘEMIČITANŮ A HLINITOKŘEMIČITANŮ

JIŘÍ PINKAS

Katedra anorganické chemie, Masarykova univerzita v Brně, Kotlářská 2, 611 37 Brno

V tomto přehledu jsou stručně shrnuty nejzajímavější současné směry výzkumu v široké oblasti anorganické a organometalické chemie křemičitanů a hlinitokřemičitanů. Ohromný rozsah studované problematiky má za následek to, že výběr témat není vyčerpávající, ale spíše ilustrativní. Zahrnuté příklady podtrhují v současnosti dosažené výsledky a naznačují perspektivy budoucího vývoje ve směrech jako jsou chemie sloučenin křemíku s koordinačními čísly pět a šest nebo s neobvyklými ligandy na bázi S a N, vývoj charakterizačních technik pro oligomerní křemičitany v roztoku nebo v plynné fázi nebo syntéza polysilanolů a jejich derivátů - metalosilikátů a silsesquioxanů - a jejich aplikace v homogenní a heterogenní polymerační katalýze. Jsou zde také zdůrazněny pokroky v organokovové chemii na povrchu oxidu křemičitého, nové sol-gelové metody přípravy oxidů a hybridních materiálů založené na hydrolytických a nehydrolytických kondenzačních reakcích, postupy přípravy mezoporézního SiO_2 spolu se způsoby chemické modifikace vnitřních povrchů pórů a syntéza molekulových modelů stavebních jednotek zeolitů. Vývoj v oblasti SIMS hmotnostní spektrometrie s použitím těžkých projektilů a pokročilé metody charakterizace silikátů pomocí NMR spektrometrie uzavírají tento přehledný článek. Mezi citovanou literaturu byly zahrnuty publikace a články od roku 1993.