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Review

Bridged Polysilsesquioxanes as a Promising Class of Adsorbents. A Concise Review*

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Bridged polysilsesquioxanes (BPs) are an emerging group of organic-inorganic hybrid materials in which organic moieties are built into a siloxane matrix by hydrolytically stable covalent carbon-silicon bonds. The formation of these solids is kinetically controlled, *i.e.*, all synthesis parameters that can influence the kinetics of the sol-gel process affect both physical and chemical properties of target materials. Structure-adsorption characteristics such as porosity, specific surface area, pore volume or surface composition are also easily modulated during sol-gel processing by a suitable choice of synthesis conditions. The possibility of tailoring the properties makes BPs potential candidates for adsorption applications – several works describing such attempts have appeared in the literature to date. In this paper, the synthesis strategy, creation of porosity and some examples of using BPs as adsorbents are briefly discussed.

INTRODUCTION

Organic-inorganic hybrid materials are currently attracting particular interest because they combine the advantages of inorganic and organic components, and the sol-gel process is perfectly suited for their synthesis. Bridged polysilsesquioxanes (BPs) are a class of such nanostructured materials. The smallest »molecular building block« of a polysilsesquioxane structure includes a bridge of organic origin linking two or more Si atoms by Si–C bonds. BP precursor can be presented as a bissilylate structure $R(SiX_3)_n$, where X denotes hydrolysable groups (mostly alkoxy groups) and R refers to the organic bridge (spacer). Linking these blocks into a three-dimensional, crosslinked structure leads to a material in which organic and inorganic parts are mixed on the molecular level: the siloxane matrix is elaborated around the organic moiety by hydrolytically stable covalent Si–C bonds. The key to the success of such materials lies in the unique structural feature of the BP sol-gel precursor, *i.e.*, organic moieties are parts of a crosslinked network rather than end-chain groups. One of the great advantages of the chemistry of these materials is a continuously increasing number of BP precursors with a wide variety of organic bridges that can be finally incorporated in target materials. Some of them are presented in Figure 1. It is out of the scope of this short paper to describe the methods of synthesizing such precursors. A very good survey is given by Shea *et al*. and references therein.[1]

The influence of the synthesis conditions on the properties of target materials has been determined with re-

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* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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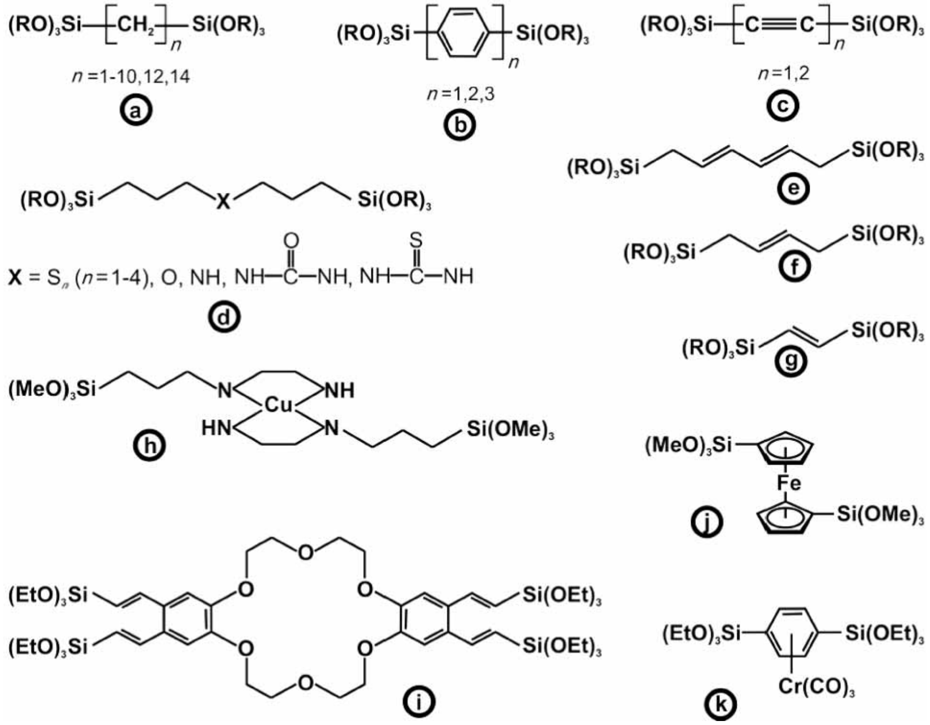


Figure 1. Representative bridged polysilsesquioxane monomers.

markable accuracy. As the sol-gel process is kinetically controlled, the resulting properties of fabricated materials are a function of all synthesis conditions: type and concentration of precursor, type and concentration of catalyst, type of solvent, temperature, time of ageing, mode of drying, *etc*. The influence of these factors on the textural characteristics of BPs has been extensively described in literature.[2–8] On the one hand, a wide variety of tunable parameters is a great advantage, but on the other, it fails to provide exactly the same conditions during the processing, which impedes recurrence of the properties of the final materials. A small change in experimental conditions can lead to a completely different texture and properties of the final material. It was accurately pointed out somewhere that »*the reproducibility is difficult to obtain and is observed only when the experimental conditions and the purity of chemicals are carefully controlled with the precision used in physical or analytical measurements*«.[6] Fortunately, a precise level of such control has been achieved, allowing reproducible synthesis of these materials with tailored structure-adsorption characteristics.

A wide choice of organic precursors coupled with the possibility of controlling the properties of final materials during the sol-gel processing leads to materials with controlled porosity, mechanical strength, *etc*. This makes BPs excellent smart materials in different fields such as optics,[9] coatings,[10] separation media[11] or catalysis.[12] Although the control of porosity has been well described in the literature since BP appearance, these materials have been used in the field of adsorption only for the last few years. In recent years, some papers have appeared testing BPs as a potential adsorbent of organic compounds from the gas phase[13,14] and organic compounds and ions from the liquid phase.[15–25] Results obtained by different research groups are very encouraging. In this short survey, the main factors influencing the porosity and adsorption properties during sol-gel processing are discussed as well as the strategy for synthesis and post-synthesis treatment of porous BPs. Examples of using these novel materials as adsorbents are also presented.

Sol-Gel Processing

The sol-gel route has attracted much attention in materials science due to its unique advantages, such as the low temperature process, high homogeneity of the final products and the capability to create materials with controlled surface properties and a wide range of pores. The sol-gel method deals with the one-pot process and the possibility of using »mild« conditions of synthesis.[26] Similarly to the large variety of organic-inorganic hybrid compounds, BPs are also obtained by sol-gel synthesis, on the basis of which a large number of sophisticated materials have been prepared. The sol-gel process consists of hydrolysis of molecular precursors, their subsequent polycondensation, ageing and drying, leading to the target material. During these steps, evolution of the organic-inorganic matrix occurs through formation of a colloidal suspension (sol) and gelation of the sol to form a net-

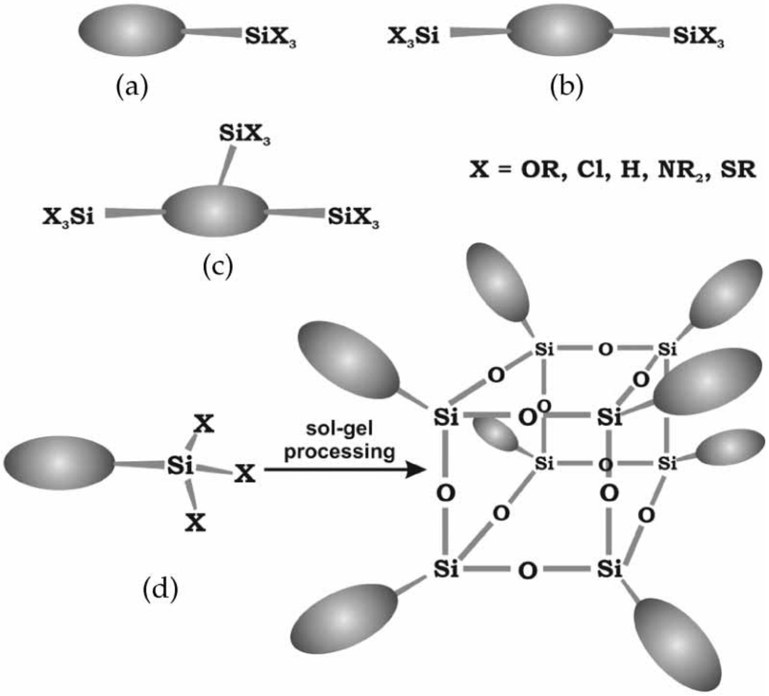


Figure 2. Monofunctional precursor (a), difunctional precursor (b), trifunctional precursor (c), and oligosilsesquioxane structure formed by the sol-gel processing of monofunctional precursor (d).

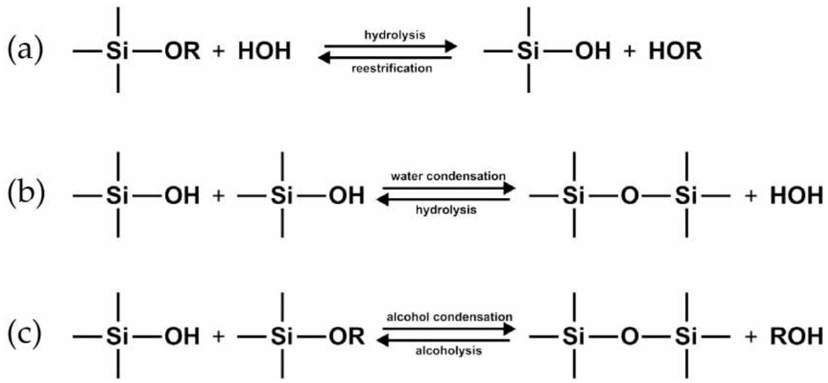
work in a continuous liquid phase (gel) and further materials. The initial stages of sol-gel processing proceed in the solution, and the porosity of the final product is most easily tailored during these initial stages by a careful choice and control of the synthesis parameters such as the type of solvent, monomer, and catalyst. Such a control makes the sol-gel method a reliable and practical technology for creating advanced nanostructured materials.

BPs can have an organic group attached to one, two or more silicon atoms (see Figure 2a,b,c, respectively). In practice, in almost all cases under conventional sol-gel processing, a simple organosilicon precursor $RSiX_3$ leads to low-molecular weight, soluble materials known as oligosilsesquioxanes due to steric hindrance of the spacers (see Figure 2d). Under these conditions, gelation rates are continuously decreasing. These difficulties can be circumvented by using a polyfunctional precursor (Figure 2b,c), having at least six reactive alkoxygroups. This results in rapid gelation and steric hindrance is overcome by attaching more silicon atoms to the organic spacer. $RSiX_3$ precursors are frequently called just polysilsesquioxanes rather than bridged polysilsesquioxanes because, in fact, R is not an organic bridge in that case but a side organic group.

Hydrolysis and Polycondensation

At the functional group level, three reactions are generally used to describe the stages of the sol-gel process. During hydrolysis, the alkoxyl groups of the precursor react with the water forming silanol (≡Si–OH) groups (see Figure 3a). During the subsequent condensation stage, these silanol groups, in reaction with other silanol groups or alkoxy groups, form siloxane linkages (≡Si–O–Si≡) with simultaneous elimination of water or alcohol, respectively (Figure 3b,c). Under most conditions, condensation starts before hydrolysis is complete; however, by tuning the conditions such as pH, molar ratio H_2O/Si and type of catalyst it is possible to complete hydrolysis before condensation begins. Additionally, because water and alkoxide are immiscible in all proportions, it is necessary to add a solvent to make them miscible and facilitate hydrolysis.[27] Simple alcohols or tetrahydrofuran are the most commonly used solvents. Although hydrolysis can occur without addition of a catalyst, it becomes faster when catalysis is employed. Polycondensation is usually catalyzed by mineral acids (HCl), bases (NaOH, KOH) or nucleophilic species (NH_4F). The type of catalyst has a substantial influence on the final material structure:

- Acid catalysis generally produces weakly-crosslinked gels that easily compact under drying conditions, yielding a microporous structure. The resulting material displays a type I nitrogen adsorption isotherm according to the IUPAC classification.[28]
- Neutral or basic catalysis results in a relatively mesoporous structure after drying, since rigid clusters a few nanometers across pack to form mesopores. The clusters themselves may be microporous. The resulting material displays a type IV nitrogen adsorption isotherm.



$$\text{(a)}\quad \equiv\text{Si—OR} + \text{HOH} \underset{\text{reestrification}}{\overset{\text{hydrolysis}}{\rightleftarrows}} \equiv\text{Si—OH} + \text{HOR}$$

$$\text{(b)}\quad \equiv\text{Si—OH} + \equiv\text{Si—OH} \underset{\text{hydrolysis}}{\overset{\text{water condensation}}{\rightleftarrows}} \equiv\text{Si—O—Si}\equiv + \text{HOH}$$

$$\text{(c)}\quad \equiv\text{Si—OH} + \equiv\text{Si—OR} \underset{\text{alcoholysis}}{\overset{\text{alcohol condensation}}{\rightleftarrows}} \equiv\text{Si—O—Si}\equiv + \text{ROH}$$

Figure 3. Reaction involved in hydrolysis and condensation steps of the sol-gel process: (a) hydrolysis, (b) water condensation, and (c) alcohol condensation.

- Under certain conditions, base-catalyzed and two-step acid-base catalyzed gels (initial polycondensation under acidic conditions and further gelation under basic conditions) exhibit hierarchical structure and complex network topology.

The type of catalyst is one of the key factors influencing porosity and structure-adsorption characteristics in final materials. Use of a basic catalyst results in a larger amount of mesopores in the final material while an acidic catalyst shifts porosity towards microporosity. This fact can be explained by taking into consideration the mechanism of polycondensation and intermediate products.[27]

However, the type of catalyst is only one of the factors influencing the structure-adsorption characteristics of final materials. Among other parameters affecting the rate of hydrolysis and condensation reaction are the pH, temperature, time of reaction, reagent concentrations, catalyst concentration, H_2O/Si molar ratio. However, one should keep in mind that even the velocity of stirring or the size of the reaction flask can influence the final properties.

Gelation

The »visible« effect of hydrolysis and condensation is sol – a viscous liquid composed of polymers, oligomers, aggregates and solvent. As the number of siloxane bonds produced by hydrolysis and condensation increases, the individual molecules are joined and aggregated in the sol to such an extent that links form between silica sol particles and a giant cluster is formed across the flask. At this point, the mixture has high viscosity but low elasticity, so that it does not pour even if the vessel is tipped. At the gelling point, there is no discrete chemical change apart from a sudden increase of viscosity. One of the most distinguishing features of the sol-gel processing of organosiloxanes is the extreme ease with which BPs form gels. Six reactive alkoxide groups participating in reactions make the gelation process very rapid even at a low monomer concentration (in minutes to hours for the majority of BPs at 0.4 mol dm^{-3} monomer concentration, even at 0.1 for some of them).[29] Sometimes, especially at a higher concentration, gelation proceeds so quickly that it is not possible to agitate the reaction flask. Cyclization reactions (which can delay or even prevent the formation of gels) are important in the case of BP processing only when intramolecular condensations lead to carbosiloxane rings. Then, the formation of cyclics results in retarding, or even preventing, gelation.[1] As cyclization reactions alter the structure of the building block, which eventually forms a crosslinked network of the final material, these reactions surely contribute meaningfully to its bulk properties, among others to porosity.[29]

Ageing

Although the reaction rates and physical changes slow down in the solid state, the sol-system is still dynamic and the ageing conditions have a drastic effect on the final structure of the material. The time-consuming ageing step is usually considered one of the disadvantages of the sol-gel process but it improves the properties of the material and can be tuned by varying several parameters, such as the pH, temperature, pressure and the ageing liquid medium. Ageing covers a wide range of processes, including further formation of a crosslinked structure, associated shrinkage and hardening of the gel. Several processes can be distinguished here: syneresis, coarsening (ripening) and phase transformation.[27]

Syneresis is the process by which a liquid is expelled from a gel owing to further shrinking. Syneresis is a direct effect of solid-phase crosslinking – a weak interaction between surface hydroxyl and alkoxy groups, which are changed into new siloxane bonds. Such shrinkage leads to expulsion of the liquid from the pores, so the gel is continuously changed from a homogeneous material to a shrunken solid monolith immersed in liquid.[27] The influence of syneresis during sol-gel treatment has a profound effect on the porosity and texture of the resulting xerogels.

Coarsening is another process associated with ageing. It involves dissolving of the material on the surface and its deposition on the necks joining aggregated particles. This process strengthens the solid and changes the size and shape of the pores. Like previous stages of the sol-gel process, it depends on the temperature and pH, pressure and type of solvent.

Another ageing-related effect that can occur is the phase transformation. In the case of rapid gelation or the presence of several moieties of different miscibility with water, the gel can have isolated regions of unreacted precursor and because of this difference in miscibility these regions can react distinctly resulting in different regions differing in structure and chemical composition.

Cerveau *et al.*[8] investigated thoroughly the influence of the ageing step on the final texture of BPs. They suggested that the final texture of xerogels depends on two sets of parameters: one influences the structure formation in the solution (by controlling the hydrolysis and polycondensation reaction occurring at silicon atoms); the other is connected with the rearrangements that occur in the solid gel during ageing. The pressure, temperature, type of solvent and pH belong to the second group of parameters. During the ageing step, the solid gel undergoes a reorganization of the structure, which changes the pore size distribution and influences the specific surface area. An increase in ageing temperature causes a loss of micropores and favors creation of mesopores with a narrow pore size distribution.[8] Such »shifting« of porosity is probably due to a redistribution reaction involving the surface of the gel (syneresis and coarsening) occurring without any significant change of the polycondensation degree at silicon atoms. The temperature of ageing also influences the specific surface area. An increase in ageing temperature is followed by an increase of the specific surface area, so it is possible to control the texture of xerogels during ageing.

Drying

The gel drying process consists of removal of water from the gel system, with a simultaneous collapse of the gel structure, under conditions of constant temperature, pressure, and humidity. Initially the aged gel shrinks, which is connected not only with evaporation of water and solvent but also with rapid crosslinking and syneresis. As the stiffness increases, at some critical point the gel becomes stiff enough to resist further shrinkage during liquid evaporation. From this moment the liquid begins to recede into the pores, resulting in very high surface tension because of capillary forces. This may even lead to a crack of the structure, especially when the gel is weakly crosslinked. After some time, the meniscus of the liquid recedes from the surface. To avoid problems connected with stress and cracking, supercritical drying is often performed, during which distinction between liquid and vapor no longer exists. In this process, water is first exchanged with alcohol and then removed under supercritical conditions. Nowadays, supercritical carbon dioxide is used most frequently because of the mild condition required to carry out such drying: 31 °C and 7.4 MPa (for ethanol it is 243 °C and 6.4 MPa).[27] Materials obtained in that way are called aerogels while those dried by a conventional method are called xerogels. The drying step can be of the utmost importance following the nature of the leaving group at silicon. An important evolution of polycondensation at silicon was observed in the case of OEt and O^{i}Pr leaving groups. In the case of OMe leaving groups, the polycondensation at silicon does not cause any evolution during the drying procedure.[8] As far as the porous structure is concerned, the mode of drying has a strong effect on porosity – the values of the specific surface area of xerogels are usually up to 1000 m^2/g, while aerogels exhibit specific surface areas much larger than 1000 m^2/g.[1]

Advantages vs. Disadvantages of Sol-Gel Processing

All stages involved in BPs' formation by sol-gel processing are presented schematically in Figure 4. From the point of view of potential applications in the field of adsorption, the most valuable advantages of the sol-gel route are:

- mild conditions of synthesis (the so called *chemie douce*), *e.g.*, low (usually room) temperatures of processing,
- high purity of the precursors, which makes the products pure as well,
- homogeneity of the final gel (although homogeneity in the solution does not guarantee homogeneity in the solid),
- possibility of tuning the particle size, pore size, porosity and surface functionalities by a proper choice of synthesis conditions,
- possibility of using entrapped organic moieties as templates for creating pores with a controlled size and shape. After these moieties are removed, »molecular footprints« are left,
- possibility of introducing functional groups that will be eventually presented on the surface by a simple co-condensation of the monomer with a functional group carrier (instead of grafting these groups after the synthesis).

Despite all these advantages, there are also some serious limitations of sol-gel processing: the precursors are usually expensive (if commercially available), sensitive to moisture and the sol-gel process is time-consuming, particularly when careful ageing and drying are required – this definitely limits large scale production. These sig-

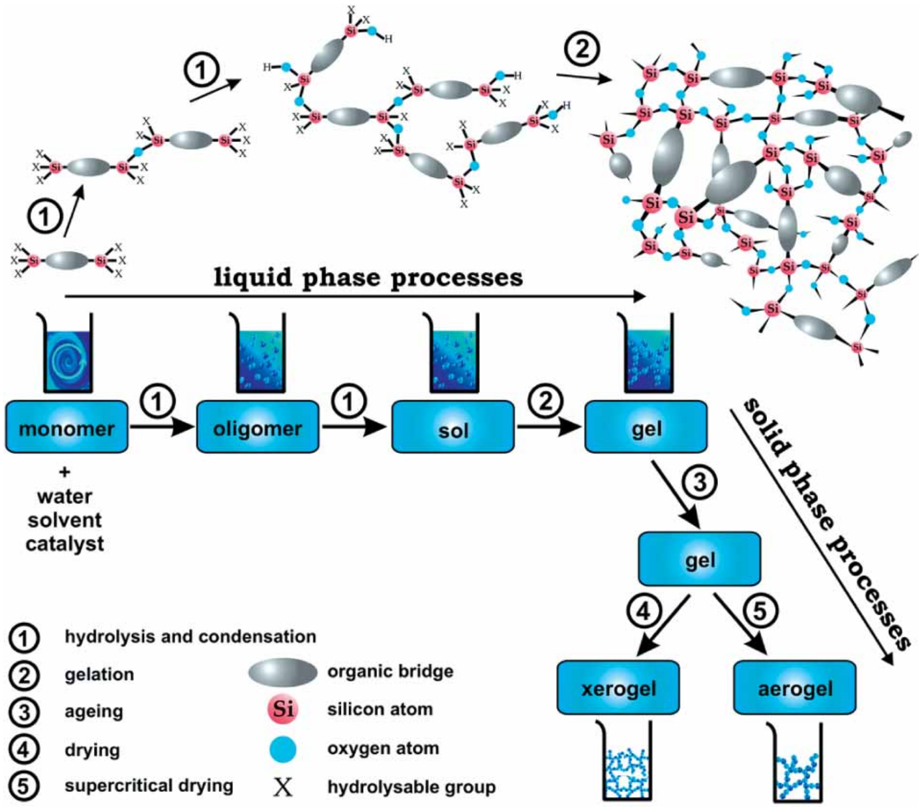


Figure 4. Scheme of the sol-gel processing of BPs.

nificant limitations can be at least partially overcome by optimizing the sol-gel synthesis of BPs and taking advantage of these materials in fields where they would reveal properties not attainable by other synthetic approaches.[27]

Engineering of Porosity by the Choice of the Bridge

The type of the organic bridge is one of the key parameters in controlling porosity and surface chemistry – the final materials have as much as up to 60 % of the weight of organic moieties after the sol-gel process. Bridges between alkoxysilyl groups can have a different nature, *e.g.,* they can be representative of a homologous series of saturated (Figure 1a) or aromatic hydrocarbons (Figure 1b). Apart from different composition, they have a different length, form and, in consequence, rigidity. Hence, by changing the nature and geometry of organic bridges it is possible to influence both chemical and physical properties, including the structure-adsorption characteristics. Flexibility of the organic bridge plays a very important role in creating a porous structure. It was found that an increase in the length of a carbon backbone chain in a homologous series of alkene-bridged polysilsesquioxane xerogels results in reduction of the value of a specific surface area: from 729 m^2/g (for two methylene units) to 94 m^2/g (for 10 units).[3]

Xerogels obtained in the acid medium are nonporous if the number of carbon atoms in the organic bridge is more than five. Xerogels synthesized in the alkaline medium with the same number of carbon atoms keep the high value of a specific surface area. Furthermore, at the same length of the organic bridge, formation of mesoporous materials is observed in the alkaline medium and formation of microporous materials in the acid medium. Thus, the pH of the reaction medium (the nature of the catalyst) has also a strong influence on the textural characteristics of BP xerogels *(vide supra)*. A less compliant network created in the presence of a basic catalyst gives more condensed networks, which retain porosity after drying. BPs can give materials with a surface area as large as 1800 m^2/g.[30] The mean pore diameter is roughly proportional to the length of the bridging groups (see Figure 5).[4] Using unsaturated or aromatic spacers instead of alkylene ones prevents the collapse of pores during drying.

Cerveau *et al.* examined thoroughly a series of BPs with different bridges to establish the influence of the nature of the organic precursor on the texture and structure of the solid.[5] They reported a drastic effect of the chemical structure of organic moiety on the properties of the solid. Systems with rigid bridges gave hydrophilic materials with high values of the specific surface area while systems with flexible bridges were hydrophobic with values of the specific surface area close to zero. Obviously, the nature of the organic precursor is not the only factor

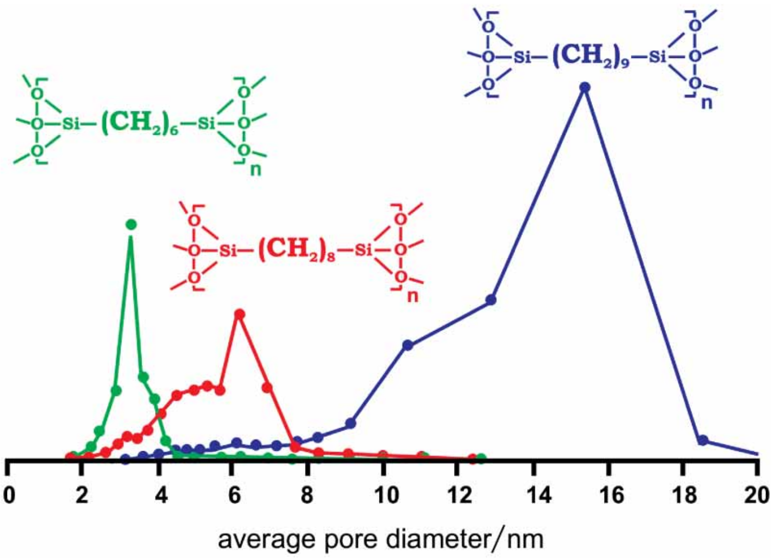


Figure 5. Influence of the spacer length on the average pore diameter (Figure adopted from Ref. 4).

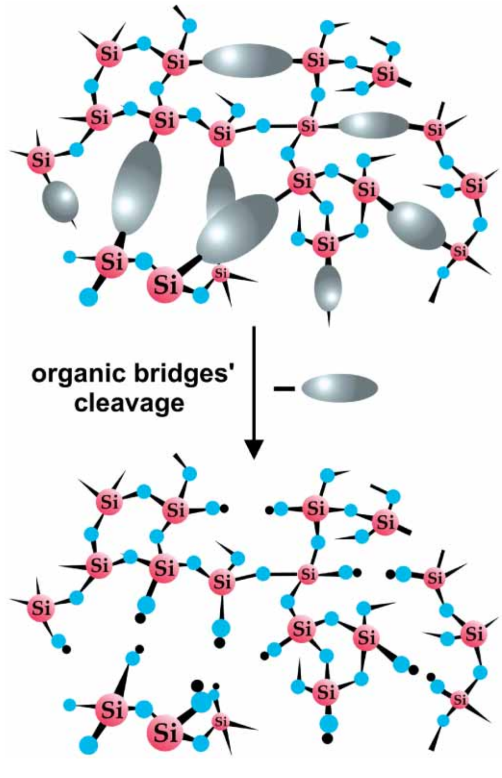


Figure 6. Creation of porosity by selective removal of organic bridges.

influencing the porosity of the final material – one has to consider a series of kinetic parameters such as the above mentioned nature of the catalyst, type of solvent, concentrations of all species involved during sol-gel processing as well as parameters controlling the solid-state reactions during ageing. Finally, the mode of drying (xerogels *vs.* aerogels) has a strong impact on the final structure. Such a variety of factors allows control of the porosity not by the choice of the bridge but rather by the proper set of reaction conditions. Thus, having only one monomer, it is possible to fabricate solids with desired values of the specific surface area, average pore size, *etc*. It is even possible to predict structure-adsorption properties under a given set of reaction conditions before processing. This is a remarkable advantage of the chemistry of BPs.

Post Synthesis Treatment

Several strategies have been used to modify the organosilsesquioxane gels using secondary chemical processes.[31] One of the approaches is preparation of a porous or nonporous xerogel using an organic bridge as template and its selective removal by chemical or physical treatment taking advantage of the differences in thermal or chemical properties of siloxane and organic components, *e.g.*, by thermal oxidation, plasma oxidation or fluoride-catalysis Si–C bond cleavage. This is schematically shown in Figure 6. When nonporous materials are used, the mean pore size after the organic part removal is proportional to the length of the organic bridge after such treatment. If the materials are porous before oxidation, the mean pore diameter increases. Such strategy has been successfully applied by several research groups to generate porous materials. For example, alkylene and arylene bridging groups were selectively removed using low temperature inductively coupled oxygen plasma to burn away the organic component.[32] The possibility of selective removal of some part of hybrid materials leads to another technique – molecular imprinting, which involves incorporation of a template into the host matrix by combining it with host monomers that polymerize around the template and form a porous bulk phase. Subsequent removal of the template results in tailored porous material that contains imprint cavities of favorable size, shape and chemical environment to selectively rebind the template molecules. Structural similarities between BPs and other organosilanes make the BPs excellent candidates for uniform incorporation of the functional ligands into the mesoporous silsesquioxane network.[21]

Organic bridging groups or residual alkoxy or silanol groups can also be used as platforms to attach other functional groups (*e.g.,* metal ligands). Several research groups used amino- and mercapto- functional groups to bind metal centers and generate siloxane gels with homogeneously dispersed metal clusters.[33] The presence of reactive silanol groups is very important, since they can be submitted to further reaction and in this way the surface functionalities can be added (*e.g.,* this plays an important role when the degree of hydrophobicity has to be changed). The techniques of such surface grafting are analogous to those for traditional silica materials. Obviously, such post-synthesis grafting is not the only way to change the chemical character of the surface – one-pot synthesis can also be used, which comprises stages of self-assembly and co-condensation, where the additional functional groups are introduced into the silica framework during sol-gel processing.[34,35]

The Surfactant Template Approach

Surfactant molecules are used to form supramolecular assemblies in solution. These self-assembled structures act as templates for the formation of a porous matrix. BP precursors can undergo hydrolytic polycondensation around these surfactant assemblies. Removal of the organic template *via* calcination or extraction effectively engineers the porosity of the resulting material. The final structure of such materials depends on many factors connected not only with BP sol-gel processing conditions (solvent, catalyst, ageing and drying mode) but also on the surfactant chain length and charge, solution and pH. Nowadays, the surfactant template approach is also used to engineer the porosity of a wide variety of tailored materials. Inagaki *et al.* have developed a novel methodology to synthesize porous hybrid materials based on the sol-gel processing of a single bridge-silsesquioxane precursor.[36] In the case of the surfactant templated, phenylene-bridged polysilsesquioxane, periodic organization of the »molecular building blocks« was established.[37] Melde *et al.* reported a synthesis of ordered materials with ethane and ethylene bridges,[38] while Burleigh *et al.* used the surfactant template approach to synthesize mesoporous ethane and phenylene BPs.[23] Recently, Alauzun *et al.* described a synthesis of mesoporous silica with two types of antagonistic functional groups on the surface (basic amino *vs*. acidic sulfate groups) existing without interaction.[39] It seems that this approach is very convenient for increasing the mesoporosity; moreover, it facilitates obtaining an ordered structure with a homogenous distribution of pore sizes. Such organization of the hybrid structure around soft (surfactant-based) or hard (polymer-based) templates will surely be used more and more frequently in the future because the field for the application of such ordered nanoporous hybrid materials is extensive.

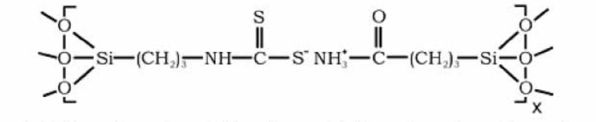
Bridged Polysilsesquioxanes as Adsorbents

Modern sorption technologies use adsorbents with highly advanced porous surfaces, high values of sorption capacity, selective properties and stability in aggressive environments.[40] The synthesis of such sorbents should be simple, reproducible and should enable affecting physicochemical and structural-adsorption characteristics of the final materials. From this point of view, BPs are attractive compounds. Thus far, several attempts to use these materials as novel sorbents have been described.

Russian scientists from Novosibirsk have performed extensive research concerning different metal ion sorption from aqueous solutions. Dithiocarbamato-bridged polysilsesquioxane xerogel (Figure 7a) was used for adsorbing Hg^{II}, Au^{III}, Pt^{IV}, Pd^{II} and Rh^{III} from solutions of hydrochloric acid (0.1–5.0 mol/dm^3) and Ag^{I} from solutions of nitric acid.[15] These authors determined by IR spectroscopy that Hg^{II} and Ag^{I} ions react with both sulfur atoms according to the coordination mechanism and the remaining ions involve both sulfur and nitrogen atoms. Figure 8 presents values of the observed and theoretical static sorption capacities for ions studied on the assumption that complexes are formed with bridges in the ratio 1:1. As can be seen from Figure 8, the synthesized sorbents have a promising sorption capacity towards noble metal ions, especially Hg^{II} and Au^{II} ions.

Vanadium(V) sorption from an aqueous solution by several BPs (Figure 7b,c) has been investigated.[16] To show the selective properties of such adsorbents, the VO_2^+ sorption from a multicomponent solution of Co^{II}, Cd^{II}, Cu^{II}, Ni^{II}, Zn^{II}, Mo^{VI} and U^{VI} ions was studied. It was found that a 100-fold excess of the majority of these species does not hinder V^{V} sorption by two synthesized adsorbents (Figure 7b,c), which makes these sorbents candidates for concentration and separation of V^{V} ions from multicomponent solutions. Values of static sorption capacities for these two materials are $\approx$400 mg/g. The adsorbed ions were easily desorbed by such common chemical agents as hydrochloric acid, ammonium hydroxide and sodium carbonate without any substantial change of the sorbent structure, so the xerogels obtained could be used repeatedly.

Sorption of lanthanides such as La, Ce, Pr, Nd^{III}, Pm, Sm^{III}, Eu, Gd, Tb, Dy, Ho, Er^{III}, Tm^{III}, Yb, Lu from acidic solutions was thoroughly studied by the same Russian research group.[17] Several BP sorbents (Figure 7b,c,d,e) were used. Values of static sorption capacity were in the range of 76-215 mg/g. The observed differences between



poly(3-silsesquioxanylpropylthiocarbamato)-3-silsesquioxanylpropylamonnium

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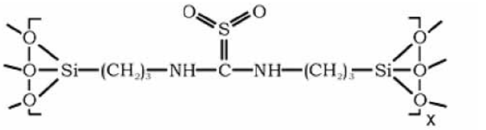

poly[*N*,*N'*-bis-(3-silsesquioxanylpropylamino)-*S*-dioxothiourea]

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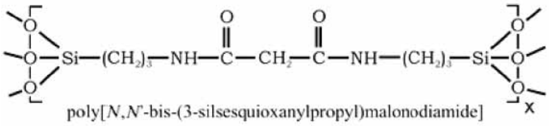

poly[*N*,*N'*-bis-(3-silsesquioxanylpropyl)malonodiamide]

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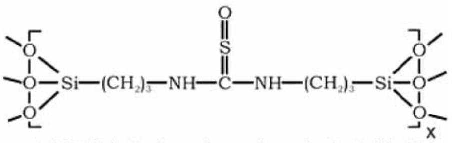

poly[*N*,*N'*-bis-(3-silsesquioxanylpropylamino)sulfoxide]

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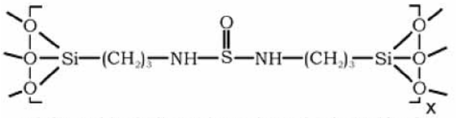

poly[*N*,*N'*-bis-(3-silsesquioxanylpropylamino)sulfone]

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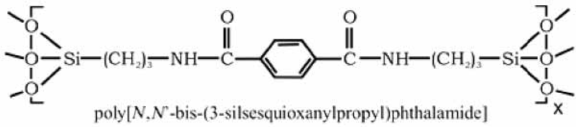
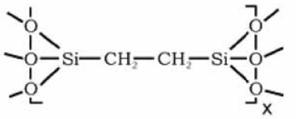


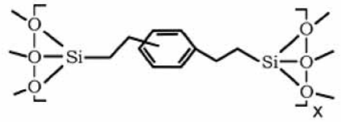
poly[*N*,*N'*-bis-(3-silsesquioxanylpropyl)phthalamide]

ⓕ



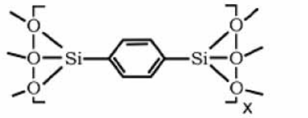
poly[1,2-bis(3-silsesquioxanyl)ethane]

ⓖ



poly[1,4-bis(3-silsesquioxanylethyl)benzene]

ⓗ



poly[1,4-bis(3-silsesquioxanyl)benzene]

ⓘ

Figure 7. Organic bridges used in adsorption applications.

the sorption activity of lanthanides (the lowest activity for La-Gd elements, low for Tb-Ho elements and very high for Er-Lu elements) in the case of the sorbent represented in Figure 7e make it a good candidate for the isolation of Er^{III}, Tm^{III}, Yb^{III} and Lu^{III} in the presence of other lanthanides. This sorbent turned out to be very effective in a selective recovery of erbium from a multicomponent solution of Cd^{II}, Zn^{II}, Cu^{II}, Ni^{II}, Co^{II} ions – the degree of erbium extraction was more than 99 %, so this sorbent (Figure 7e) can be used for the recovery of traces of Er^{III} and other lanthanides from industrial sludge. The regenerated adsorbents retained sorption activity, so they could be reused in further measurements; however, the efficiency decreased significantly after 10 cycles of work.

V^{VI}, Mo^{VI}, W^{VI}, Th^{IV} and U^{VI} sorption from acidic solutions in the presence of interfering ions such as Cu^{II}, Zn^{II}, Ni^{II} and Cd^{II}, Co^{II} was also studied.[18,19] The results have shown that even at the ratio of ions 1:1000 (ions : interfering ions) the selective sorption of Mo^{VI} and W^{VI} is not stopped. Selective sorption of V^{V} was also observed at 1:100 ratio (V^{V} ions : interfering ions). The most pronounced influence of contaminant metals was found in the case of Th^{IV} and U^{VI} recovery. The sorbents used by the authors (Figure 7b,c,f) were regenerated by several eluents – even after the use of 6 mol dm^{-3} HCl, which turned out to be the most versatile eluent, the materials retained their sorption properties. Sorption cloth-filter with one of the monomers (Figure 7c) grafted to a cellulose surface was manufactured and used for the U^{VI} sorption. The resulted sorption capacity was 25 mg/g of the cloth.[18] It is worth noting that mono-functional silsesquioxanes ($RSiX_3$ – see Figure 2a) were also used to examine the sorption of other toxic metal ions such as Hg^{II}, Bi^{III} and Cd^{II} from acidic solution.[20]

Burleigh *et al.* synthesized selective sorbents for Cu^{II}, Ni^{II} and Zn^{II} ions by a template approach.[21] The use of the ions as templates improved selectivity by favorable incorporation of ethylenediamine moieties in pairs due to formation of 1:2 complexes. Removal of the metal ions created cavities within the material with selective rebinding characteristics. Cations of copper, nickel, zinc and cadmium are common constituents of man-made waste and are very often present together in municipal wastewater, electroplating waste, acid mine drainage and landfill leachates, so the authors also tested the selectivity of copper adsorption from such solutions.[21] It was shown that from a mixture of these metal ions in solution (10^{-3} mol dm^{-3} with respect to all these ions), copper can

TABLE I. Structural adsorption characteristics and values of phenol uptake by bridged polysilsesesquioxanes obtained by Burleigh *et al.*[23]

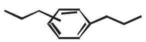
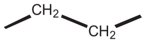
Organic bridge	Structural-adsorption characteristics			4-Nitrophenol		4-Chlorophenol		4-Methylphenol	
				0.1 mmol dm^{-3}	1 mmol dm^{-3}	0.1 mmol dm^{-3}	1 mmol dm^{-3}	0.1 mmol dm^{-3}	1 mmol dm^{-3}
	S_{BET} / (m^2/g)	V_t / (cm^3/g)	d / nm	Uptake / %					
	550	0.40	30	99.4	96.9	98.6	90.0	97.9	92.4
	1300	1.10	33	16.5	15.2	–	–	–	–

TABLE II. Structural adsorption characteristics and values of organic compounds uptake from the gas phase by functionalized bridged polysilsesesquioxanes obtained by Dąbrowski *et al.*[13]

Sample		Structural-adsorption characteristics				Uptakes at p/p_0 = 1 / (g/g)					
Bridge	Functional group	Concn.	Specific surface area	Pore volume	Pore diameter	n-Hexane	n-Heptane	Cyclohexane	Benzene	Triethyloamine	Acetonitrile
		mmol/g	m^2/g	cm^3/g	nm						
$–C_2H_4–$	$–NH_2$	1.4	690	0.57	9	0.51	0.54	0.55	0.67	0.55	0.05
$–C_2H_4–$	–SH	1.9	750	0.78	5	0.27	0.27	0.22	0.37	0.36	0.03
$–C_6H_4–$	$–NH_2$	1.4	850	0.73	5	0.33	0.34	0.32	–	0.27	0.03

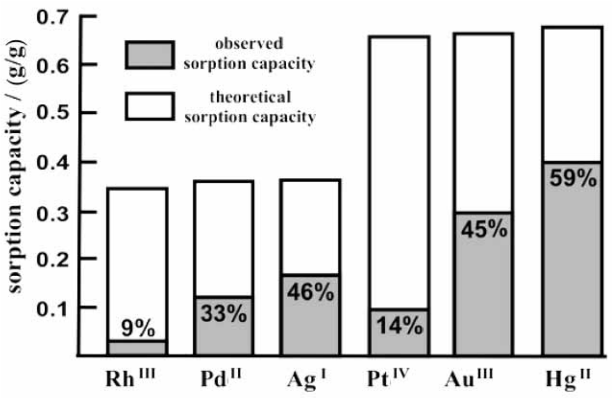


Figure 8. Theoretical and observed static sorption capacities for different metals observed by Ref. 15 (Figure adopted from Ref. 15).

be selectively adsorbed by using a Cu^{II}-selective sorbent, while the amounts of zinc, nickel and cadmium adsorbed were approximately 15, 5, and 1 %, respectively. Imprinted sorbents exhibit not only better selectivity but also higher capacity for the metal ion templates than for the nonprinting analogues. The Cu^{II} imprinted materials exhibit excellent metal ion adsorption kinetics, removing > 99 % Cu^{II} from 30 ppm solution in 60 s and can be regenerated by washing in diluted nitric acid.

A molecular imprinting approach was used for selective chemical sensors of DDT.[22] First, DDT was chemically linked to two molecules of organosilane. After that, a molecularly imprinting matrix was formed by sol-gel co-condensation of such DDT-linked-organosilane with bridged polysilsesquioxane. After the reaction DDT was removed, which created adsorption sites corresponding to the shape and size of removed DDT molecules. A rough outline of the approach used by these authors[22] is represented in Figure 9. It was found that the obtained materials exhibited increased adsorption of DDT particles and other particles of a similar shape. The detection limit for DDT was established as ≈ 50 ppt DDT in aqueous solutions.

Burleigh *et al.* used 1,4-bis(trimethoxysilylethyl)benzene- and 1,2-bis(triethoxysilyl)ethane-bridged xerogels (Figure 7g,h) prepared *via* a surfactant template approach as sorbents of selected phenols from solution.[23] Surfactant templating was used to increase the porosity and surface areas. In Table I, selected results obtained by the authors are presented. Despite the facts that the specific surface area of ethylene-bridged sample is two times bigger and the pore volume is three times bigger than those of the arylene-sample, the former removed only 16.5 % of 4-nitrophenol from 1×10^{-4} mol dm^{-3} solution and 15.2 % from 1×10^{-3} mol dm^{-3} solution of 4-nitrophenol, while the analogous values for the latter are 99.4 and 96.9 %, respectively. It is clearly evident that an important role is played by surface heterogeneities, namely, arylene bridges which promote the adsorption of phenols *via* π-π interaction between the aromatic bridges of the adsorbent and adsorbate. Results obtained for the three phenols show that the arylene-bridged sorbents exhibit efficient adsorption of all phenols used and adsorption capacities are comparable with commercial active carbons. The high degree of regeneration (98 % of 4-nitrophenol was removed from the arylene-bridged sorbent simply by its washing with ethanol, while only 1-2 % was removed by analogous treatment from the active carbon) allowed the authors to conclude that »*ease of regeneration is a potential advantage in the use of the porous polysilsesquioxanes over conventional activated carbons for the removal of phenolic compounds from aqueous solutions*«.[23] In fact, a 1,4-bis(trimethoxysilylethyl)benzene-bridged sorbent has been proved to be an effective sorbent for phenols. Some results obtained by the authors are presented in Table I.

Recently, we tried to use ethylene- and phenylene-bridged polysilsesquioxanes (Figure 7g,i) functionalized with amino and thiol groups as adsorbents of volatile organic compounds from the gas phase.[13] Several organic compounds: n-hexane, n-heptane, cyclohexane, benzene, triethyloamine, acetonitrile were adsorbed to investigate the functionalized BP behavior towards these compounds. The sorbents used exhibited a remarkable affinity for organic adsorbates, which makes them also potential candidates for adsorbents of volatile organic compounds. The uptake values are given in Table II. In particular, the sorbent obtained by co-condensation of the ethylene-bridge precursor and amino-group carrier showed high affinity to all the vapors adsorbed, which is connected with the different type of the porous structure created during sol-gel processing compared to other synthesized materials.[35]

Examples of BP application shown here testify to a great potential of these materials as sorbents. BPs can partially fill the gap caused by the limited use of other types of sorbents due to their complex production technology, low chemical and mechanical stability, low efficiency or selectivity. Two significant advantages should be underlined here. The first possibility is that of a homogenous distribution of organic moieties accessible to the adsorbate particles. This allows creation of adsorption sites that force selectivity of the adsorption process by promoting a particular type of the adsorption force involved, *e.g.,* donor-acceptor or π-π interactions. Secondly, precise control of structure parameters such as the specific surface area, pore diameter induces adsorbents with predetermined characteristics. The small number of papers in the up-to-date literature devoted to the use of BPs in the adsorption field is probably connected with relatively high costs of the starting materials and the time-consuming sol-gel process in the majority of cases. Nevertheless, further researches in this field are strongly desirable, since the opportunities which lie in these materials can easily overcome the above-mentioned disadvantages.

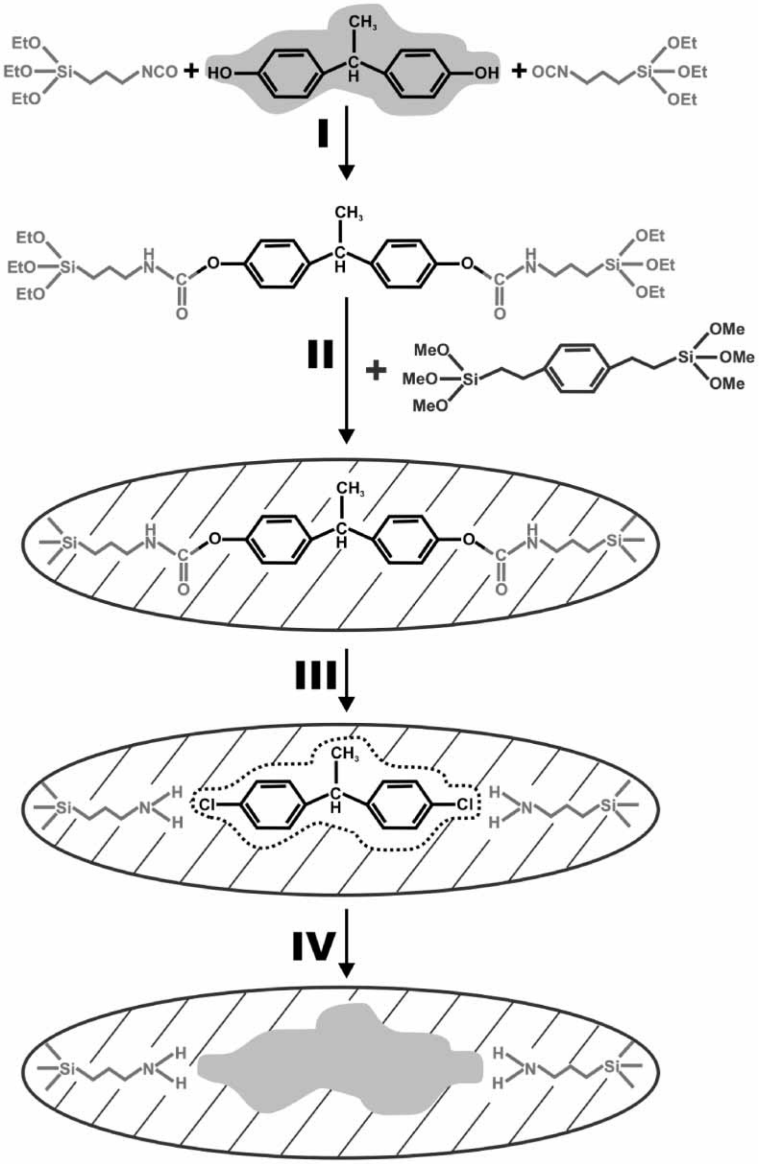


Figure 9. Molecular imprinting approach used for synthesizing the DDT sensor (Figure adopted from Ref. 22): I – forming template spacers, II – building a porous silsesquioxane matrix around the spacers by the sol-gel method, III – removal of template spacers, and IV – as a result size and shape selective pockets are created in the porous matrix.

CONCLUSIONS

The sol-gel process, which gained much notoriety in the past, can be effectively used to synthesize sorbents based on bridged polysilsesquioxanes. The possibility of using a wide range of organic bridges of different nature and geometry coupled with a precise degree of the control of structural-adsorption characteristics *via* a proper choice of the conditions of sol-gel treatment provides a significant prospect for the molecular design of new porous materials with predetermined characteristics. Despite the complex origin of porosity, the mechanism of creation of the porous structure is comprehensible. The continuously increasing number of attempts at bridged polysilsesquioxanes adsorption applications demonstrates that such understanding is an invaluable advantage in the creation of novel nanostructured sorbents.

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SAŽETAK

Premošteni polisilseskvioksani kao obećavajuća grupa adsorbenata – sažeti pregled

Andrzej Dąbrowski i Mariusz Barczak

Premošteni polisilseskvioksani (BPs) čine skupinu organsko-anorganskih hibridnih materijala kod kojih su organski sastojci ugrađeni u siloksansku matricu putem hidrolitički stabilnih kovalentnih veza ugljik–silicij. Nastajanje tih krutina kinetički je kontrolirano, tj. svi parametri sinteze koji mogu utjecati na kinetiku sol-gel procesa utječu i na fizikalna i na kemijska svojstva ciljanih materijala. Strukturno-adsorpcijske karakteristike poput poroznosti, specifične površine, volumena pora i sastava površine moguće je također, pomoću odgovarajućeg izbora uvjeta sinteze, jednostavno modulirati tijekom sol-gel procesa. Takva mogućnost krojenja svojstava čini premoštene polisilseskvioksane potencijalnim kandidatima za primjenu kod adsorpcije – do danas je objavljeno već nekoliko radova koji opisuju takve pokušaje. U ovom radu se raspravlja o strategiji sinteze, stvaranju poroznosti, te daju neki primjeri korištenja premoštenih polisilseskvioksana kao adsorbenata.