Synthesis of Inorganic-Organic Hybrids from Bridged-type Organic Precursors via Sol-Gel Processes

ゾル−ゲル法による架橋型前駆体を用いた無機−有機ハイブリッドの合成

Hitomi SAITO

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Thesis Submitted To Waseda University

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Inorganic-organic hybrids have attracted considerable attention lately because of the various combinations of organic functional groups and inorganic networks involved. Among several approaches to synthesizing the hybrids, the sol-gel process is an excellent and frequently employed method of forming the hybrids under mild conditions. This means that the organic groups introduced in the precursors can be immobilized in the resultant hybrids with no damage, after which they exhibit the desired properties effectively. The use of bridged-type precursors enables gel to be formed easily under various reaction conditions, moreover, compared to the use of non-bridged-type precursors. Although several advantages of bridged-type precursors have already been reported, much still remains to be studied.

This thesis introduces two different inorganic-organic hybrids among bridged-type precursors, bridged polysilsesquioxane and titanium-oxygen-phosphorus (Ti-O-P) hybrids, and discusses their applications.

It is widely considered that the hydrolysis reaction speed of the two alkoxy groups in a precursor is almost the same and that it is gradually decreased by the inductive effect under acidic conditions. It is shown, however, that one ethoxysilyl group in the precursor is hydrolyzed preferentially only when the precursor possesses an organic group that can form hyperconjugation.

Dimanganese complexes are known as catalysts for decomposition reactions of harmful hydrogen peroxide. Although many types of dimanganese complexes have been reported, their thermal stability is relatively low, when their application for
polymer electrolytes in fuel cells is considered. Immobilizing them to bridged polysilsesquioxane is an effective approach to maintaining not only their catalytic properties but also their thermal stability and exhibits promising catalytic properties after thermal treatment.

Metal-oxygen-phosphorus (M-O-P) hybrids derived from organophosphonic acids are similar to bridged polysilsesquioxanes. Utilizing the distinctive features of phosphonic acid, such as, its high affinity for many metals and its heterocondensation, porous Ti-O-P hybrids are synthesized \textit{via} a non-hydrolytic sol-gel process. The resultant hybrids exhibit relatively high specific surface areas with no use of a structure-directing reagent.

LiClO$_4$-doped poly(ethylene oxide) is known to exhibit high ionic conductivity. Although the polymer possesses good ionic conductive properties, it loses its ionic conductivity below its crystallization temperature (~65°C). Introducing oligomeric ethylene oxide chains to the precursors of Ti-O-P hybrids is a novel approach to maintaining conductivity below 65°C. The resultant LiClO$_4$-doped Ti-O-P hybrids exhibit high ionic conductivity at ambient temperature compared to the hybrids possessing oligomeric ethylene oxide chains reported in previous studies.

This thesis describes an approach to preparing inorganic-organic hybrids derived from four different bridged-type precursors. The applications described in this thesis show promising property of inorganic-organic hybrids.
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Introduction
1.1. Concept and Definition of Inorganic-Organic Hybrids

Inorganic-organic hybrids have attracted considerable attention recently, because the resultant hybrids can possess not only optical and mechanical properties derived from inorganic components, but also functional properties derived from organic components, and because they offer applications in various fields, as shown in Figure 1.1.

Several approaches to obtaining desirable inorganic-organic hybrids have been reported: dispersing layered materials or nanoparticles into polymers; modifying the surfaces of layered materials, porous materials, and nanoparticles with organic groups; and utilizing the tailor-made inorganic precursors containing organic groups as so-called “building blocks.” Controlling the interfaces between inorganic and organic components is very

Figure 1.1 Overview of the application of inorganic-organic hybrids. \(^1\)
important for obtaining the desired properties. Inorganic-organic hybrids can be classified into two categories, class I and class II: class I hybrids have weak interactions such as Van der Waals force, coordination bonds, ionic bonds and hydrogen bonds, while class II hybrids, on the contrary, have strong bonds such as covalent bonds (Figure 1.2).³-⁵

![Figure 1.2. Schematic structures in class I and class II hybrids.](image)

\textit{Chimie Douce} (soft chemistry) reactions are carried out under mild conditions.²,⁶ The \textit{Chimie Douce} approach is excellent for obtaining class II hybrids, because the resultant hybrids can be synthesized without the thermal treatment such as conventional ceramic processing, and this means that the organic group can be retained in the final materials. Thus, the \textit{Chimie Douce} approach can avoid not only decomposition of the organic groups, but also drastic changes in their inorganic structures. The \textit{Chimie Douce} approach consists of such topochemical reactions as ion-exchange, intercalation, and de-intercalation reactions⁷ and such non-topochemical reactions as sol-gel processes, hydrothermal processes, and reactions utilizing molten salts and acid-leaching.⁶ Among the non-topochemical processes, sol-gel process has been investigated extensively, because this process enables the formation of inorganic networks directly from precursor
solutions. Ceramics and glasses can be obtained easily by hydrolysis and condensation, with subsequent thermal treatment. Multicomponent products can be synthesized from a single precursor, moreover, than from a mixture of several compounds. In the synthesis of inorganic-organic hybrids, the sol-gel process is excellent for dispersing organic groups effectively without any thermal treatment when utilizing appropriate organic groups containing precursors.

 Among the several procedures for introducing organic groups into inorganic networks, organo-bridged precursors are more effective than non-bridged precursors for synthesizing homogeneous inorganic-organic hybrids with high loading of functional groups. Thus, in this chapter, we focus on hybrids derived from organo-bridged precursors \textit{via} a sol-gel process. In the following section, the preparation methods of inorganic-organic hybrids are discussed.

\section*{1.2. Preparation Methods of Inorganic-Organic Hybrids}

\subsection*{1.2.1. Sol-Gel Process}

\subsubsection*{1.2.1.1. Sol-Gel Process of Tetraalkoxysilanes}

The sol-gel process is a conventional method of synthesizing metal-oxo polymers and dispersing them in solvents \textit{via} hydrolysis and condensation reactions by using metal alkoxides \([\text{M(OR)}_y]\), where M=Si, Sn, Ti, Zr, Al, Mo, V, W, Ce; OR: \(\text{OC}_n\text{H}_{2n+1}\) as precursors. \cite{8} The two reactions occur under kinetic control, indicating that the final materials depend heavily on the experimental conditions. \cite{9} The final products are formed \textit{via} highly complex steps: precursor
(monomer)→oligomer→polymer (sol) →gel.\textsuperscript{10} Despise the lack of precise and detailed knowledge concerning the mechanism of gel formation, this research area is absolutely fascinating, because it offers a variety of preparation routes. An overview of use of the sol-gel process to control the final morphology of the products is shown in Figure 1.3.\textsuperscript{11}

![Figure 1.3 Overview of the sol-gel process and the types of final morphology of the products.\textsuperscript{11}](image)

In the sol-gel process, a metal alkoxide is hydrolyzed first, as shown in Eq (1.1).

\[
\text{Hydrolysis} \quad \text{M-OR} + \text{H}_2\text{O} \rightarrow \text{M-OH} + \text{R-OH} \quad (1.1)
\]

After reactive hydroxyl groups are formed, they are condensed via two competing mechanisms, oxolation Eq (1.2) and olation Eq (1.3).

\[
\begin{align*}
\text{Oxolation} & \quad \text{M-OH} + \text{XO-M} \rightarrow \text{M-O-M} + \text{XOH} & (1.2) \\
\text{Olation} & \quad \text{M-OH} + \text{HO-M} \rightarrow \text{M(OH)}_2\text{M} & (1.3)
\end{align*}
\]

(X = H or alkyl group)

The structures and morphology of the resultant metal-oxopolymers depend on the respective rates of these reactions. The intermediate species should be
controlled to tailor the final structures by changing such parameters as the bulkiness of R, the water content, the solvent, the reaction temperature, the types of catalysts, and additives. The various factors affecting the sol-gel process are listed in Table 1.1. As the metal alkoxide employed most commonly is silicon alkoxide, the sol-gel process of silicon alkoxide is further discussed.

Table 1.1 Sol-gel processing variables and their impact on the sol-gel process.\textsuperscript{12}

<table>
<thead>
<tr>
<th>Sol-gel processing variable</th>
<th>Impact on sol-gel process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomer</strong></td>
<td></td>
</tr>
<tr>
<td>Ractive groups</td>
<td>Hydrolysis and condensation kinetics</td>
</tr>
<tr>
<td>Organic substituents</td>
<td>Polymer and gel structure</td>
</tr>
<tr>
<td>Metal</td>
<td>Chemical and physical properties of gels</td>
</tr>
<tr>
<td>Concentration</td>
<td>Gel times</td>
</tr>
<tr>
<td><strong>Water: monomer ratio</strong></td>
<td></td>
</tr>
<tr>
<td>(1) Substoichiometric</td>
<td>No gels; fibers and coating</td>
</tr>
<tr>
<td>(2) Stoichiometric</td>
<td>Gelation: alcohol producing condensation</td>
</tr>
<tr>
<td>(3) Excess</td>
<td>Complete hydrolysis: slow gelation and/or particulate-based gels</td>
</tr>
<tr>
<td><strong>pH of solution</strong></td>
<td></td>
</tr>
<tr>
<td>(1) Low pH</td>
<td>Faster hydrolysis, slower condensation, reaction at less condensed metal oxide sites</td>
</tr>
<tr>
<td>(2) Isoelectric point</td>
<td>Slowest condensation rate</td>
</tr>
<tr>
<td>(3) High pH</td>
<td>Slower hydrolysis, faster condensation, more condensed colloids</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td></td>
</tr>
<tr>
<td>(1) Acid</td>
<td>Mineral acids-gelation faster; organic acids-slower gelation</td>
</tr>
<tr>
<td>(2) Base</td>
<td>No catalyst residue with ammonia; residue with metal hydroxides</td>
</tr>
<tr>
<td>(3) Fluoride</td>
<td>Rapid condensation at low pH with fluoride catalysts</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td></td>
</tr>
<tr>
<td>(1) Polarity</td>
<td>Moderately polar to help mix hydrophobic monomer and water</td>
</tr>
<tr>
<td>(2) Hydrogen bonding</td>
<td>Hydrogen bonding and polarity effect reaction and gelation rates</td>
</tr>
<tr>
<td>(3) Coreactant</td>
<td>Alcohol solvents: participant in hydrolysis and condensation. Can slow hydrolysis and functionalize silanols</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Faster reaction and gelation rates; used with slow gelting monomer formulations</td>
</tr>
<tr>
<td><strong>Ionic strength</strong></td>
<td></td>
</tr>
<tr>
<td>Salt effect</td>
<td>Increased hydrolysis/condensation and gelation rates</td>
</tr>
<tr>
<td><strong>Aging time</strong></td>
<td></td>
</tr>
<tr>
<td>Stronger gels; less cracking; coarsening of porosity</td>
<td></td>
</tr>
<tr>
<td><strong>Drying method</strong></td>
<td></td>
</tr>
<tr>
<td>(1) Xerogels or “dry gels” with loss of volume and porosity using air drying; slow process</td>
<td></td>
</tr>
<tr>
<td>(2) Aerogels or “air gels” with no cracking and less shrinkage using supercritical drying; faster, but requires autoclave</td>
<td></td>
</tr>
</tbody>
</table>

The hydrolysis mechanisms differ based on the type of catalyst. Under acidic conditions, alkoxy groups are protonated first, and the electron density is then decreased by withdrawing electrons from the Si atom, as a result of which the Si atom becomes more electrophilic and susceptible to attack by water. The mechanism is thought to be of the S_N2-type. The reaction is described below.
Scheme 1.1 $S_N2$-type hydrolysis reaction under acidic conditions.  

Under basic conditions, on the other hand, alkoxide groups are hydrolyzed through two transition states ($S_N2^{**}$-Si and $S_N2^*$-Si) by forming five-coordinated intermediates.

Scheme 1.2 $S_N2$-type hydrolysis reaction under basic conditions.

The degree of condensation varies based on the pH range. Under acidic conditions, the polymers tend to be linear due to limited condensation, whereas under basic conditions, the polymers tend to be three-dimensional networks due to high condensation. Shea et al. demonstrated sol-gel polymerization with 1,6-bis(triethoxysilyl)hexane, for example, to demonstrate the differences between acidic and basic conditions. The integrals of signals in the upfield region increased as the pH increases, as shown in Figure 1.4, a result corresponding to the proposed mechanism.

Figure 1.4 Solid-state $^{29}$Si CP/MAS NMR spectra of hexalene-bridged polysilsesquioxane aerogels prepared under acidic and basic conditions.
Steric hindrance plays the most important role in attaining stability of organosilane with respect to hydrolysis. As the bulkiness of the alkoxy group increase, the hydrolysis rate is obviously decreased, as shown in Table 1.2.

Table 1.2 Rate constants $k$ for acid hydrolysis of tetraalkoxysilane $\text{Si(OR)}_4$ at 20°C.

<table>
<thead>
<tr>
<th>R</th>
<th>$k / 10^5\text{-mol}\cdot\text{s}\cdot\text{[H}^+\text{]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_5$</td>
<td>5.1</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9$</td>
<td>1.9</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{13}$</td>
<td>0.83</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CH(CH}_2)_2\text{CH(CH}<em>3)</em>\text{CH}_2$</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Inductive effects are investigated with methylethoxysilane, $\text{Si(OC}_2\text{H}_5)_4\_x$, where $x$ varies from 0 to 3. The hydrolysis rate increases according to increases in the substitution of $x$ under acidic conditions, whereas the reverse trend is observed under basic conditions. Figure 1.5 shows the accelerating effect of substitution at the Si atom on the hydrolysis reaction. The extent of alkyl substitution does not affect the hydrolysis mechanism. Inductive effects work positively and negatively under acidic and basic conditions, respectively, depending on the type of substituent.

Figure 1.5 Inductive effects of substituents attached to silicon atom.
1.2.1.2. Sol-Gel Processes Employing Other Metal Alkoxides

Chemical modifications of metal alkoxides with alcohols, acidic or basic catalysts, or chelating reagents are useful methods of retarding the rate of hydrolysis and condensation reactions.\(^8,^{15}\) The modification occurs due to an \(S_N2\) reaction between a nucleophilic reagent (XOH) and a metal alkoxide to form a new molecular precursor, or when metal (M) is unsaturated \((N-z\geq2)\) by nucleophilic addition (\(A_N\)):

\[
\text{XOH} + \text{M(OR)}_z \rightarrow \text{M(OR)}_z(\text{XOH})_{N-z}
\]

The reactivity of the alkoxide increases when \(\delta(M) \gg 1\) and \((N-z) \geq 2\) or when XOH is a strong nucleophile.\(^{16}\) The hydrolysis and condensation behavior depends on the stability of the modifying reagents. In general, less electronegative reagents are preferentially removable during hydrolysis, whereas more electronegative reagents are removed slowly during condensation.\(^{16}\) Thus, complexes with more stable ligands form materials with lower condensation and promote gelation.

Metal alkoxo-acetates can be formed by the reaction of acetic acid (HOAc) with metal alkoxides.\(^{17}\) Though the addition of HOAc retards the gelation of silicon alkoxide, it accelerates that of titanium and zirconium alkoxides. Livage\(^{18}\) and Sanchez\(^{15}\) conducted some careful experiments that revealed that the bridging AcO\(^-\) ligands remained to be bonded to titanium through hydrolysis, and that alkoxide groups, on the other hand, were preferentially hydrolyzed. The ligands changed the condensation pathway and promoted the formation of linear polymers consisting of edge-shaped octahedra.
Titanium isopropoxide [Ti(O'Pr)₄]-acetylacetone (acac) systems were also examined by $^1$H, $^{13}$C NMR, IR, and XANES. The XANES spectrum showed a single pre-peak, excluding the octahedral Ti coordination. The addition of acac increased the coordination from 5 to 6, as shown in Figure 1.6.

![Figure 1.6 Schematic formation of the Ti-complex precursor.](image)

When water was added to the complex precursor, O'Pr groups were hydrolyzed preferentially, but even with a large excess of water, not all the acac ligands bonded to titanium could be hydrolyzed. A general scheme was shown in Figure 1.7.

![Figure 1.7 Structural evolution during hydrolysis of Ti(O'Pr)₃-acac complex.](image)
1.2.1.3 Non-Hydrolytic Sol-Gel (NHSG) Process

Dearing and Reid first discovered the non-hydrolytic sol-gel (NHSG) process in 1928. Corriu et al. applied the concept of the NHSG process to nanoparticle synthesis. The NHSG process is developed for synthesis of metal oxides in systems excluding water. Because most transition oxide precursors are too reactive to control in sol-gel processes, it is difficult to obtain the desired morphology and homogeneity of complex multicomponent oxides. The resultant gels often require a thermal process to induce crystallization after the sol-gel process. With an NHSG process, on the other hand, it is relatively easy to control the reaction parameters and induce only particle growth, or destruction of well-defined particle morphology. Non-hydrolytic condensation can be applied to thermal decomposition and atomic layer deposition, as well as to surface modification. NHSG processes can be classified according to the type of metal precursor, such as halide, alkoxide, or acetylacetonate; the type of oxygen donor, such as alkoxide, alcohol, or ether; and the types of the predominantly eliminated molecules. The main reactions of the NHSG processes are described in Eqs (1.5-1.7), and these reactions proceed under mild conditions.

Alkyl halide elimination \[ \equiv M-X + R-O-M \equiv \rightarrow \equiv M-O-M \equiv + R-X \] (1.5)

Alkoxylation \[ \equiv M-X + R-O-R \rightarrow \equiv M-O-R + R-X \] (1.6)

Ether elimination \[ \equiv M-OR + R-O-M \equiv \rightarrow \equiv M-O-M \equiv + R-OR \] (1.7)

An NHSG process can be a valuable alternative pathway to a hydrolysis-condensation system, because NHSG processes are kinetically
controllable and can be extended to many metal oxide nanoparticles, such as TiO$_2$, FeO$_x$, MnO, Mn$_3$O$_4$, CeO$_2$, CuO$_x$, Cr$_2$O$_3$, Co$_3$O$_4$, CoO, NiO, ReO$_3$, ZrO$_2$, Hf$_2$O$_2$, Zr$_{1-x}$O$_2$, V$_2$O$_5$, ZnO, Y$_2$O$_3$:Eu, In$_2$O$_3$, SnO$_2$, WO$_x$, Sm$_2$O$_3$ and ferrites.

1.2.2. Hydrothermal Process

The hydrothermal process, which is a well-established method of synthesizing crystallized compounds such as zeolite, is acquiring widespread use for synthesizing metastable materials such as aluminum phosphates (AlPO$_3$), transition metal polychalcogenides, other transition metal phosphates, coordination polymers, and clusters. The typical hydrothermal processes are illustrated in Figure 1.8. The starting materials are dissolved or dispersed in water and introduced into an autoclave, and the autoclave is then heated. As the internal pressure increases in the heating process, a unique reaction proceeds to crystalize the resultant material.

![Figure 1.8 Hydrothermal processes of the (A) solution-mediated transport mechanism and the (B) solid-hydrogen transformation crystallization mechanism.](image-url)
Hydrothermal processes can be applied to the synthesis of inorganic-organic hybrid materials such as coordination polymers and clusters. Selection of the organic functional groups and metal oxides can be used to tune the structures of the hybrids from 1D (linear) to 3D (framework). Hybrids consisting of CuL(VO$_2$)(PO$_4$)$_3$ [L=4,4’-bipyridine (4,4’-bipy), 1,10-phenanthroline (1,10-phen), and 2,2’-bipyridine (2,2’-bipy)], for example, were synthesized via hydrothermal reactions. A hybrid employing 2,2’-bipy (Figure 1.9 a) and 1,10-phen (Figure 1.9 b) formed an 1D infinitive chain, whereas that of 4,4’-bipy forms a 2D layered structure (Figure 1.9 c). When the metal was Zn, the hybrid possessed a cluster structure (Figure 1.9 d).

Figure 1.9 The structures of the (a) 1D chain of Cu(2,2’-bipy)(VO$_2$)(PO$_4$)$_3$, the (b) 1D chain of Cu(1,10-phen)(VO$_2$)(PO$_4$)$_3$, the (c) 2D layered structure of Cu(4,4’-bipy)(VO$_2$)(PO$_4$)$_3$ along the $b$-axis, and the (d) cluster structure of $[\text{Zn(en)}_2]_6(\text{VO})_{12}\text{O}_6\text{B}_{13}\text{O}_{39}(\text{OH})_3\cdot13\text{H}_2\text{O}$. 

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1.2.3. Surface Modification

1.2.3.1. Silylation

Silylating reagents such as chlorosilanes (R_{4-x}SiCl_x), alkoxy silanes [R_{4-x}Si(OR)_x], and silylamines [R_{4-x}Si(NH)_2x], where x varies from 1 to 4, have widespread applications for surface modification, as shown in Scheme 1.3. Silanes are the most familiar modifiers for metal oxide surfaces. The grafting reaction is extremely easy to conduct in a one-step process and is applicable to numerous metal oxides, such as SiO_2, Al_2O_3, TiO_2, SnO_2, ZrO_2 and V_2O_5. The reactivities of di- and tri-chlorosilanes, R_{4-x}SiCl_x (x=2,3), are high without heating and addition of a catalyst such as water, and these compounds thus react multifunctionally to surfaces, producing by-products such as alcohols and alkylammonium halides, which are difficult to separate. Thus, monochlorosilanes are more often used than di- and trichlorosilanes, even though they require base catalysts such as amines. By contrast, silazane-based silylation reactions proceed at a relatively slow rate under mild conditions and exhibit a monolayer surface reaction. The excess silylamines are removed easily, moreover, by thermal treatment.

Scheme 1.3  Representative silylation reactions.

\[ \text{Silane + Base} \rightarrow \text{Silane + HCl} \]  
\[ \text{Silane + ROH} \rightarrow \text{Silane + H}_2 \text{O} \]  
\[ 2 \text{Silane + NH}_3 \rightarrow 2 \text{Silane + NH}_3 \]  
\[ 2 \text{Silane + CF}_3\text{CF}_2\text{OSiMe}_3 \rightarrow 2 \text{Silane + CF}_3\text{CF}_2\text{ONH}_2 \]  
\[ 2 \text{Silane + H}_2\text{SiH}_3 \rightarrow 2 \text{Silane + H}_2 \]
1.2.3.2. Grafting with Organophosphonic Acids

Organophosphorus acids, salts and esters (phosphoric, phosphonic and phosphinic; the general formula is $R_xPO(OX)_{3-x}$; $x=1$ or 2, $X=H$, Na, alkyl, and organic group) are thought to play a complementary role as organosilanes. They show excellent affinities toward many metals and transition metals, their oxides, hydroxides, carbonates, and phosphates. Thus, metal-oxygen-phosphorus (M-O-P) bonds can be formed easily, and the P-OH bonds are fairly stable with respect to homocondensation under mild conditions. A phosphoryl group can act as a Lewis base to coordinate Lewis acid sites on the surface of metals and metal oxides. The types of M-O-P coordination are described in Figure 1.8.

![Figure 1.8](image)

Figure 1.8 Schematic possible binding modes of organophosphonic acid: (a) monodentate, (b, c) bridging bidentate, (d) bridging tridentate, (e) chelating bidentate; (f-h) additional hydrogen-bonding interfaces.

Organophosphonic acids are also used for surface modification and the formation of polyoxometalates. Surface modifications of metals such as titanium and stainless steel, metal oxides such as titania, and non-oxide inorganic materials such as calcium hydroxyapatite were performed by organophosphonic acid [$RP(O)(OH)_2$, $R$= phenyl, $n$-C$_{12}$H$_{24}$SH, $n$-C$_8$H$_{17}$, $n$-C$_{18}$H$_{37}$, and $n$-C$_8$F$_{17}$(CH$_2$)$_2$].
The grafted materials, namely self-assembled monolayers (SAMs), were applied to biosensors and electrochemical devices.

The acid dissociation content (pK_a) is often taken into consideration for the reaction mechanism. Freedman gathered pK_a values of a variety of organophosphonic acids. Phenylphosphonic acid is a dibasic acid, for example, and the first one is rather small (pK_a1 ~ 1.4), while the second one is reported to be much larger (pK_a2 ~ 6.9). The pK_a values depend on the substitution group.

1.3. M-O-P Compounds Prepared from Organophosphonic and Organodiphosphinic Acids

1.3.1. Preparation of Organophosphonic Acids

Freedman introduced several approaches to organophosphonic acid preparations such as Grignard’s reactions, Michaelis-Arbuzov rearrangement reactions, and various reactions employing organophosphonic chlorides. Novel procedures forming organophosphonic acids via the organic reactions such as cross-coupling reactions, oxidative Heck reactions, and Michaelis-Becker reactions have since been studied extensively. The schematic process of the Grignard’s reaction is shown in Scheme 1.4.

\[
\text{Scheme 1.4 Synthetic procedure of the Grignard’s reaction.}^{75}
\]
The schematic process of the Michaelis-Arbuzov rearrangement reaction is shown in Scheme 1.5. The advantage of this reaction is that it can be applied to a variety of organophosphonic acids and di- and multi-phosphonic acids.

Scheme 1.5 Synthetic procedure of the Michaelis-Arbuzov reaction.

The schematic processes of the Heck reaction and the cross-coupling reaction are shown in Scheme 1.6 and Scheme 1.7, respectively. It is characteristic for the oxidative Heck reaction to be used for the synthesis of intermediate products, whereas the cross-coupling reaction is used directly for the formation of P-C bonds.

Scheme 1.6 Synthetic procedure of the Heck reactions: (a) basic oxidative Heck reaction, (b) synthetic procedure of organophosphonic acid with oxidative Heck reaction.

Scheme 1.7 Synthetic procedure of the cross-coupling reaction.
1.3.2. Cage-type Structures

Metal phosphonates have been studied with various metals and have formed layered structures,\textsuperscript{154} and cage-type structures containing clusters.\textsuperscript{79, 156, 157} Layered $\text{M(OC}_n\text{H}_{2n+1})_2\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Mg, Mn, Zn}, \ n = 1-12; \ \text{M} = \text{Ca, Cd}, \ n = 1-4$), $\text{M(O}_3\text{PC}_6\text{H}_{2n+1})_2\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Mg, Mn, Zn}$), $\text{Ca(HO}_3\text{PC}_6\text{H}_5)_2$, and $\text{Ca(HO}_3\text{PC}_n\text{H}_{2n+1})_2$ ($n>5$) are synthesized \textit{via} the precipitation method.\textsuperscript{154}

Cage-type metal phosphonates are synthesized in various structures (Figure 1.9). Some cages act as postulated building blocks, known as secondary building units, and affect the final framework structures.\textsuperscript{79}

Several metals, such as Al, Si, Ti, and Ga, formed D4R and D6R structures with organophosphonic acids. Al-containing D4R and D6R structures were synthesized, for example, with $\text{AlMe}_3$ and $t$-$\text{BuP(O)(OH)}_2$ (Figure 1.10 a). More complicated gallium-phosphonates were synthesized by a simple alkane elimination reaction between the precursor $\text{MGaMe}_4$ ($\text{M}=$Li, Na, and K) and $t$-$\text{BuP(O)(OH)}_2$.
Figure 1.10 Structures of (a) Aluminum organophosphonate of D4R and D6R, and (b) gallium organophosphonate.

Among cage-type structures, following tin, aluminum, and vanadium organophosphonate clusters \([\text{Me}_2\text{Sn}_2(\text{OH})(\text{O}_2\text{P} \cdot \text{O} \cdot \text{Ph})_2]_3\)\((\text{O}_3\text{POP})_3\)_2\), \([\text{t-BuPO}_3\text{AlEt}_2]_3\)\(\text{Na}_3\), and \([\text{(VO)}_4\text{(3,5-Me}_2\text{PzH)}_8\text{(CCl}_3\text{PO}_3)_4]\), (Pz=pyrazole) were synthesized, and their crystalline structures were characterized.

Polyoxometalates have attracted considerable attention and offer various potential applications, such as bifunctional catalysis and antiviral and antitumoral chemotherapy. Organophosphonic acids were reacted with the divacant Keggin tungstate anions \([\gamma\text{-SiW}_{10}\text{O}_{36}]\) to obtain hybrid derivatives \([\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RPO})_2]\) (R = H, Et, n-Bu, t-Bu, C\(_2\)H\(_4\)COOH, and Ph). The phenylphosphoryl polyoxotungstate \((\text{NBu}_4)_2\text{-(NET}_4)\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{C}_6\text{H}_5\text{PO})_2]\) formed a monoclinic structure with virtual \(C2\) symmetry with two phenylphosphonic groups grafted to the surface of the divacant tungstosilicate (space group \(P2_1\)). The two phenyl rings were rotated by about \(\pi/2\) and oriented parallel to the plane of the divacant surface of the polyanion (Figure 1.11).
1.3.3. Lamellar Structures

Lamellar metal organophosphonates and organodiphosphonates, whose metals are La, Zr, Cu, Zn, Fe, have also been studied. Not only can lamellar metal organophosphonates possess functionality derived from organic groups, but they can also act as novel hosts for intercalation. In addition, several metal organophosphonates can possess cross-linked porous structures with bridged-type diphosphonic acids present between the layers. Thus, they can be applied to catalysts, sorbents, and ion exchangers.

The organic derivative of γ-Zirconium phosphate Zr[PO₃-O(CH₂CH₂O)₁₃]₂·nH₂O was synthesized via an ion-exchange reaction (Figure 1.13). After doping with LiClO₄, ionic conductivity was observed in the range between 10⁻⁵ and 10⁻⁸ S·cm⁻¹ in the temperature range of 450-300 K.
Figure 1.13 Structure of the organic derivative of $\gamma$-Zirconium phosphate $\text{Zr}\{\text{O}_3\text{PO(CH}_2\text{CH}_2\text{O})_{1.8}\text{H}]_2\cdot n\text{H}_2\text{O}$ with LiClO$_4$ and THF. $^{86}$

The structure of La(\text{O}_3\text{PC}_6\text{H}_5)(\text{HO}_3\text{PC}_6\text{H}_5)$ was triclinic, and its space group was $P\overline{1}$, where $a = 8.410$ (3), $b = 15.696$ (7), $c = 5.636$ (1) Å, $\alpha = 90.24$ (4)$^\circ$, $\beta = 108.99$ (1)$^\circ$, $\gamma = 85.59$ (4)$^\circ$, and $Z = 2$ (Figure 1.12). $^{84}$

Figure 1.12 Lanthanum benzylphosphonate as view down from a axis, with dark circles corresponding to lanthanum atoms and dotted circles corresponding to oxygens of water molecule. $^{84}$

Fe$^{II}$\text{(C}_2\text{H}_3\text{PO}_3)\cdot \text{H}_2\text{O}$ formed roughly coplanar layers and its crystal structure was $P1n1$ ($Z = 2$) with parameters $a = 4.856(8)$, $b = 10.33(1)$, $c = 5.744(3)$ Å, and $\beta = 91.0(1)^\circ$. The resultant material indicated antiferromagnetism with field-induced weak ferromagnetism below $T_c = 24.5$ K. $^{88}$
1.4. Inorganic-Orga13nic Hybrids Derived from Bridged-type Precursors

1.4.1. Advantages of Bridged-type Precursors over Non-bridged Precursors

Inorganic-organic hybrids derived from bridged-type precursors have several advantages over non bridged-type precursors. The precursors of bridged polysilsesquioxanes are taken as examples here, because bridged polysilsesquioxanes are the most extensively studied among inorganic-organic hybrids using bridged-type precursors. Bridged polysilsesquioxanes can be prepared simply from their precursor, \((\text{RO})_3\text{Si-R'-'Si(OR)}_3; \text{R: alkyl, R': functional organic group, whereas many porous silica supports require multiple steps for surface modification. Bridged-type precursors can also form gel rapidly regardless of the type of organic group, even as a dilute solution. Gelation develops within minutes to hours for many bridged polysilsesquioxanes at a 0.4 M monomer concentration, or approximately one-fifth the concentration of that of \(\text{Si(OEt)}_4\) used in typical sol-gel formations, which require days for gelation. \(\text{R'Si(OR)}_3\), by contrast, which comprises the majority of organoalkoxysilanes, cannot form gel independently under any sol-gel conditions.\(^{13,89}\) This tendency corresponds to the gelation of Ti-O-P hybrids derived from bridged-type organodiphosphonates. The gelation conditions of Ti-O-P hybrids derived from phenylphosphonic acid and TiCl\(_4\) or Ti(OR)\(_4\) are relatively narrow compared to those derived from diphenylphosphonic acid\(^{90}\) and bridged-type diphosphonic acid (Chapter 4).
The organic group can be dispersed homogeneously into the inorganic network, moreover, when a bridged-type precursor is used. Bridged polysilsesquioxanes can obtain a wide variety of organic groups and offer potential applications for optics, electronics, separation and catalysts.  

1.4.2. Precursors of Bridged Polysilsesquioxanes

1.4.2.1. Synthesis of Precursors of Bridged Polysilsesquioxanes

Various precursors of bridged polysilsesquioxanes have been prepared in recent decades. The designed precursors are generally synthesized in 1 to 2 steps from readily available starting materials. The precursors are commonly synthesized via (1) metalation of aryl, alkyl, or alkynyl precursors; (2) hydrosilylation of dienes (or polyenes) or diynes; or (3) reaction of a bifunctional organic group with an organotrialkoxysilane-bearing functional group.

(1) Metalation: Metalation consists of the Grignard reaction (Scheme 1.8 a),
lithium-halogen exchange (Scheme 1.8 b), and deprotonation (Scheme 1.8 c).

```
(a) Br-Br → 1) Mg²⁺, THF, reflux 2) > 5 Si(OMe)₃
(b) Br
     1) d eq. iBuLi, ThF, -78 °C
     2) >2 eq (EtO)₃SiCl
     Si(OMe)₃
(c) Si-Br → 1) 2 BuLi, ThF, -78 °C
     2) >2 eq (MeO)₃Si
     Si(OMe)₃
```

Scheme 1.8 Synthetic procedures of metal-halogen exchange or metalation.
(2) Hydrosilylation: Hydrosilylation (Scheme 1.9 a) is a useful reaction for synthesizing the precursors of bridged polysilsesquioxanes from starting compounds bearing two or more terminal olefins in high yield.\textsuperscript{95, 96} The addition of the Si-H group to trichlorosilanes or trialkoxysilanes is catalyzed with a platinum complex such as chloroplatinic acid or Karstedt’s catalyst.\textsuperscript{97} The Si-C bond is generally formed preferentially in the terminal position of a double bond due to regioselectivity. Trichlorosilanes are easily converted into trialkoxysilanes with trialkoxylorthoformates (Scheme 1.9 b),\textsuperscript{95} alcohols, and amines (Scheme 1.11 b).\textsuperscript{91}

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

Scheme 1.9  Synthetic procedures of hydrosilylation.\textsuperscript{13}

(3) Functionalization of Organotrialkoxysilanes: This synthetic route widens the variety of the available precursors. An electrophilic substituent of organotrialkoxysilane can react with many organic compounds possessing nucleophilic groups, such as isocyanates (Scheme 1.10 a-1.10 b)\textsuperscript{98} and alkyl or benzyl halides (Scheme 1.10 c).\textsuperscript{99} At the same time, organotrialkoxysilanes possessing nucleophilic groups can also react with organic compounds possessing electrophilic groups, such as sulfonyl chlorides, acid chlorides (Scheme 1.10 d)\textsuperscript{100}.
or Schiff bases (Scheme 1.10 e). There are also additional routes to synthesizing the precursors via a ruthenium-catalyzed silylation/desilylation (Scheme 1.11 d), a photochemical isomerization (Scheme 1.11 e), a Heck reaction (Scheme 1.11 f), or a Diels-Alder reaction (Scheme 1.11 g).

Scheme 1.10 Representative precursors derived from organoalkoxysilanes.

Scheme 1.11 Representative precursors derived from various compounds.
1.4.2.2. Examples of the Precursors

In this section, representative precursors of bridged polysilsesquioxanes are shown in Figures 1.14-1.18 according to classification of their structural properties or functionalities.  

Figure 1.14 Representative precursors of bridged polysilsesquioxanes.

Figure 1.15 Representative precursors possessing urea group.
Figure 1.16 Representative precursors possessing chirality group. 104

Figure 1.17 Representative precursors possessing metal-complex. 104

Figure 1.18 Representative precursors of bridged polysilsesquioxanes. 104
1.4.2.3. Non-Template Method with Bridged Polysilsesquioxane

Most bridged polysilsesquioxanes tend to adopt an amorphous form with no use of a structure-directing reagent. As described previously, bridged polysilsesquioxanes can contain a variety of organic groups in siloxane networks homogenously, and thus the application of bridged polysilsesquioxanes is widespread.

The primary application of bridged polysilsesquioxanes is for surface modification of coupling reagents and coating formations. With the use of functionalized precursors, the surface is easily protected and can form relatively tough and hard films. Bridged polysilsesquioxanes incorporating dye moieties can be applied to optical and electronic products, such as waveguides, lasers, sensors, light-emitting diodes, and nonlinear optical (NLO) materials. Dithienylene-bridged polysilsesquioxane, for example, was a photoreversible photochromic material obtained by changing its refractive index (Scheme 1.12). This approach were applied to second-order NLO bridged polysilsesquioxane, whose precursor contained 4-nitro-N,N-bis[(3-trioethoxysilyl)propyl]aniline (Figure 1.19). Thin optical film was prepared by spin coating with concomitant electric field poling. The \( \chi \) value corresponded to the \( d_{33} \) coefficient (18.9 pm V\(^{-1}\)), and the \( r_{33} \) value is 4.7 pm V\(^{-1}\).
Bridged polysilsesquioxanes can be doped with nanoparticles, and they maintain transparency after doping. Complex materials of this type can be applied for the catalytic membranes of electrooptical devices. Bridged polysilsesquioxanes doped with CdS-nanoparticles were prepared with successive washes with CdNO₃ and Na₂S. The CdS particles were dispersed uniformly in the xerogel, and the average CdS size correlated closely with the average pore size of the xerogel (Scheme 1.13).
Scheme 1.13 (a) Schematic process of bridged polysilsesquioxane doping with CdS-nanoparticles, and (b) HRTEM image of a xerogel X-2. The dark spots within the fragment (average diameter 90 Å) are microcrystalline CdS particles.  

Palladium complexes homogeneously immobilized into bridged polysilsesquioxanes (Pd-SiO$_2$) were reported. The Pd-SiO$_2$ catalyst were separated easily from the reaction solution and recycled several times without degrading the catalytic activity for the hydrogenation of arenes (PhCO$_2$Me, PhOH, toluene, PhOCH$_3$, PhCO$_2$Et, 4-CH$_3$C$_6$H$_4$CO$_2$Et, dimethyl terephthalate) to cyclohexanes.

Another application was a separation media for HPLC columns obtained by using the precursor with robust phenylene groups.

1.4.2.4. Template Method with Tetraalkoxysilane

Thanks to the development of the Chimie Douce approach, a variety of inorganic or hybrids materials can be obtained by slightly changing the experimental parameters such as the monomer concentration, pH, temperature, solvent or organic additives. The final structures of the resultant materials still rely on the synergy
between the inorganic and organic components, however, and it is thus difficult to form a well-ordered structure. A novel approach employing an organic template (structure-directing reagent) has therefore been developed.

Kuroda et al. used alkylammonium ions as a template to synthesize three-dimensional ordered mesoporous SiO₂ from a layered silicate Kanemite.¹⁰⁸ Kresge also reported MCM-41 molecular sieves synthesized from tetraalkoxysilane through the use of hexadecyltrimethylammonium ions as a template.¹⁰⁹,¹¹⁰ Both discovered a simple procedure for synthesizing uniformly ordered and size-controlled mesoporous materials by tuning the length of the alkyl ammonium chain. Since the discovery of mesoporous silica, various templates such as emulsion droplets, latex beads, bacterial threads, colloidal templates, organoammonium ions, and block copolymers have been employed to create pores on a nano- and meso-scale.¹¹¹-¹¹⁴

The typical mechanisms for templates are shown in Figure 1.20.¹¹⁵ In route A, molecular/supermolecular templates such as surfactant molecules, amphiphilic block copolymers, and dendrimers are preorganized or self-assembled as mesostructures in the synthesis media, and the replication of inorganic networks then occur around accessible interfaces of the templates. After the formation of the inorganic networks, the templates are removed by chemical or thermal treatment. In route B, the precursors and templates are self-assembled at the same time. In other words, they are cooperatively self-assembled to form well-organized structures.
Figure 1.20  Representative approaches for formation of well-ordered mesoporous structure. 115

When the templates form structures such as spheres, rods, cylinders or platelets, 116-118 they are interacted with inorganic precursors with different forces, such as H-bonding, electrostatic interactions, and coordination bonds. These interactions can be retained after formation of an inorganic network. Figure 1.21 shows examples of interactions between templates and the resultant metal oxides. Table 1.3 lists well-ordered porous materials classified according to the interaction.

Figure 1.21  Different types of silica-surfactant interfaces. S: surfactant molecule; I: inorganic framework; M⁺ and X: corresponding counter ions; triangles: solvent; dashed lines: H-bonding interactions. 115
Table 1.3  List of meso-structured inorganic materials with different interactions between the surfactant and the inorganic frameworks.  

<table>
<thead>
<tr>
<th>surfactant type</th>
<th>interaction type</th>
<th>example materials (structure)</th>
<th>References</th>
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<tr>
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<td>$Me(OEt)_2$</td>
<td>Nb, Ta (hex)</td>
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</tbody>
</table>

*hex, hexagonal; lam, lamellar; cub, cubic.

1.4.2.5. Template Method with the Precursors of Bridged Polysilsesquioxanes

Since the first discovery of ordered mesoporous silicas, a variety of ordered mesoporous materials have been synthesized with surfactants used as templates. When organoalkoxysilanes $[R^*-Si(OR)_3]$ and tetraalkoxysilane $[Si(OR)_4]$ are co-condensed in the presence of surfactants, the resulting mesoporous materials have a microscopically heterogeneous inorganic framework with an organic layer bound to it. Unfortunately, these materials often have a poor structural organization and low loading of organic components. Thus, a homogeneous dispersion of
inorganic and organic components in the framework and high loading of organic components should be achieved in ordered porous materials.

One possibility is to utilize the bridged-type organosilane precursor [(RO)₃Si-R’-Si(OR)₃]. As hybrids can obtain high periodicity with templates, they are called periodic mesoporous organosilicas (PMOs), whose preparation is shown in Figure 1.22. The PMOs possess uniform pores, high stability, and control of the framework composition and morphologies. It can be applied to sensors, optical, electronic, and electro-optical devices for communication and data storage as well as in diverse fields of nanotechnology and a wide range of information technologies.

Figure 1.22 (a) Schematic process of periodic mesoporous organosilica with bridged-type precursor and (b) TEM image of periodic mesoporous structure of the ethylene-bridged precursor.

In addition, the pore walls of PMO with their robust organic spacers can be crystallized. Inagaki reported that the PMO possessed crystalline pore walls resulting from the assembly of [(EtO)₃SiC₆H₄Si(OEt)₃] and trimethylalkylammonium chloride surfactants (Figure 1.23).
1.4.3. Metal-Oxygen-Phosphorus Hybrids Prepared via the Sol-Gel Process

1.4.3.1. Bridged-type Di- and Multi-Phosphonic Acids

Similarly to bridged polysilsesquioxanes, many types of bridged-type di- and multi-phosphonic acids have been synthesized during recent decades. Representative bridged-type di- and multi-phosphonic acids with rigid spacers are shown in Figure 1.24. The simplest ones were aryldiphosphonic acid (1),\textsuperscript{140-142} and naphthalene-bridged analogues (5) were also reported\textsuperscript{143}. Triphosphonic acids (3, 7) were prepared by a procedure similar to that used for diphosphonic acid (1).\textsuperscript{144-146} Tetraphosphonic acid (9) was prepared by a completely different procedure based on the palladium-catalyzed cross-coupling reaction.\textsuperscript{147} This synthesis was started from the tetraiodo derivative of adamantane and reacted with a diethylphosphite.
[(EtO)₂P(OH)] in the presence of dichlorodi(triphenylphosphine)palladium(II) [PdCl₂(PPh₃)₂]. Tetraphosphonic acid was obtained from its ester via a hydrolysis reaction. Hexaphosphonic acid (10) has been reported recently. The hydrated crystals of hexaphosphonic acid had excellent proton conduction due to precise positioning of the conducting groups. Unlike Nafion 117 and other polymers, this rather rigid system had constant proton conductivity (3.2×10⁻³ S cm⁻¹) above 160°C, even higher than that of Nafion 117.

Figure 1.24 Representative bridged-type di-and multi-phosphonic acids with rigid spacers.
At the same time, several bridged-type di- and multi-phosphonic acids with flexible spacers were also reported, as shown in Figure 1.25. The simplest alkyl-bridged diphosphonic acid and its derivatives (11, 16) were synthesized via a Michaelis-Arbusov reaction. Hydroxy-, amino- and carboxylalkane-bridged multiphosphonic acids (12, 13, 18, 20) were also studied for pharmacological applications. Ethylene diamine- and diethylene triamine-bridged multiphosphonic acids and their derivatives (15, 17, 19) were synthesized to utilize the preparation of porous titanium organophosphonates. The resultant hybrids had photocatalytic activity and heavy metal adsorption capabilities. Crown ether-bridged diphosphonic acid (21) bound to a zirconium phosphate interlayer was also prepared for the application of separation.

Figure 1.25  Representative bridged-type di-and multi-phosphonic acids with flexible spacers.
1.4.3.2. Titanium Organophosphonate

Organophosphonic acids can be utilized to form various titanium organophosphonates, and the resultant hybrids possess amorphous, cluster and porous structures. Mutin et al. succeeded in synthesizing several types of titanium organophosphonate clusters, as shown in Figure 1.26, by controlling the reaction conditions. There have been no reports of titanium organodiphosphonate clusters, because the steric effect is too high to form a cluster structure using bridged-type diphosphonic acids.

![Figure 1.26](image)

Figure 1.26: Titanium organophosphonate clusters of $[\text{Ti}_4(\mu_3-O)(\text{O'iPr})_3(\mu-O'iPr)(\text{PhPO}_3)_3]\cdot\text{THF}$ (left), $[\text{Ti}(\text{O'iPr})(\text{O}_2\text{PPh}_2)]_4$ (center), and $[\text{Ti}(\text{O'iPr})_2(\text{BuPO}_3)]_4$ (right).

A highly porous titanium organotetraphosphonate was obtained via a template-free route based on a sophisticated architecture of organic subunits in the precursor, dendritic tetraphosphonic acid. The specific surface area measured by the Brunauer-Emmet-Teller (BET) method was 557 $\text{m}^2\text{g}^{-1}$, and the isotherm exhibited a typical profile of mesoporous material (Figure 1.27 a). The pore size distribution was narrow, centered at 1.35 nm (Figure 1.27 b). Another titanium organodiphosphonate derived from HO-$\text{CH}_2$-$\text{CH(PO}_3\text{H}_2)_2$ also possessed a high specific surface area (257 $\text{m}^2\text{g}^{-1}$).
Figure 1.27  (a) BET isotherm and (b) pore size distribution curves of the titanium organotetraphosphonate derived from dendritic tetraphosphonic acid (Figure 1.24 9).

The values for the porosity of the titanium organophosphonates differ according to the choice of different titanium precursors, even when the same organophosphonic acid is used. 160 Three titanium organophosphonates were reported, for example, that were obtained using TiCl₃, TiCl₄, and titanium (IV) fluorocomplex: the specific surface areas of the products were 61 m² g⁻¹ for the product using TiCl₃, 143 m² g⁻¹ for the product using TiCl₄ and 79 m² g⁻¹ for the product using titanium (IV) fluorocomplex. 160

Porous titanium organophosphonates were also synthesized with templates such as Brij56 161 and dodecyl sulfate surfactants.162

Ionic exchange and adsorption properties have also been targeted for these titanium organo-polyphosphonates for trapping metal cations. 153, 159, 163 In a similar fashion, titanium organophosphonates were reported to serve as supports for catalyst. 164-166

Titanium phosphate sulfophenylphosphonate, [Ti(HPO₄)₁.₀₀(O₂PC₆H₄SO₃H)₀.₈₅(OH)₀.₃₀nH₂O], exhibited protonic conductivity when mixed with Nafion. 167 The protonic conductivity was increased up to about
0.1 S cm\(^{-1}\) by increasing the number of water molecules per sulfonic group from 2 to 14, while the activation energy was decreased from 12.6 to 4.3 kcal mol\(^{-1}\).

### 1.4.3.3. Other Metal Organophosphonates

Layered metal organodiphosphonates, especially zirconium organodiphosphonate, have attracted considerable attention. Covalent pillared \(\alpha\)-zirconium phosphite diphosphonate had high surface area (405 m\(^2\) g\(^{-1}\)) due to micropores (0.5 nm) formed using 3,3',5,5'-tetramethyl-diphenyldiphosphonic acid (Figure 1.28). \(^{66, 168}\)

![Figure 1.28 Microporous zirconium phosphite diphosphonate. Circle: hydrogen, and rectangular: organic spacer.](image)

Layered Sn (II)--organodiphosphonates were synthesized with \(\text{H}_2\text{O}_3\text{PCH}_2\text{PO}_3\text{H}_2\) and \(\text{H}_2\text{O}_3\text{PC(OH)(CH}_3\text{)PO}_3\text{H}_2\) via the precipitation method. With single crystal X-ray diffraction, \(\text{Sn[HO}_3\text{PCH}_2\text{PO}_3\text{H}]}\cdot\text{H}_2\text{O}\) formed a 1D structure of linear chains of \(\{\text{SnO}_3\}\) pyramids bridged by \((\text{HO}_3\text{PCH}_2\text{PO}_3\text{H})\) groups, whereas \([\text{Sn}_2\{\text{O}_3\text{PC(OH)(CH}_3\text{)PO}_3\}]\) formed a 3D tetrahedral-pyramidal framework under acidic conditions (pH 3.5). \(^{155}\)

Cu(II), Co(II), and Mn(II) complexes with organodiphosphonic acid,
H$_2$O$_3$PCH$_2$NH$_2$•CH$_2$PO$_3$H$^-$, were also reported. The Cu$_3$[NH$_2$(CH$_2$PO$_3$)$_2$]$_2$ complex formed a 3D framework of corner-sharing layers assignable to the orthorhombic space group $Pbca$, with unit cell parameters: $a = 9.4430(10)$, $b = 9.3681(10)$, $c = 16.0755(17)$ Å, $V = 1422.1(3)$ Å$^3$, and $Z = 4$.

The Co$_3$[NH$_2$(CH$_2$PO$_3$)$_2$]$_2$ complex formed tetranuclear 16-membered rings with both ends of the diphosphonic acid bound to Co(II) ions via O atoms, and the characterization of the complex was assignable to the orthorhombic space group $P2_12_12$ with unit cell parameters: $a = 10.7346(8)$, $b = 13.3704(10)$, $c = 5.3699(4)$ Å, $V = 770.72(10)$ Å$^3$, and $Z = 2$.

The Mn{[NH$_2$(CH$_2$PO$_3$H)$_2$]$_2$(H$_2$O)$_2$} complex formed a 1D chain architecture stitched together by hydrogen bonds, and the characterization of the complex was assignable to the monoclinic space group $P2_1/n$, with unit cell parameters: $a = 7.3668(11)$, $b = 8.1540(12)$, $c = 14.090(2)$ Å, $\beta = 103.935(-2)^\circ$, $V = 821.4(2)$ Å$^3$, and $Z = 2$.

Mesoporous zirconium titanium organodiphosphonate was prepared according to the useful approach using polyacrylonitrile-F-127-templated beads. The resultant hybrids possessed wormhole-like structures and exhibited 215 and 185 m$^2$ g$^{-1}$ after calcination at 500 and 600°C, respectively. The resultant hybrid modified with aminotris-methylene phosphonic acid exhibited better adsorption properties (~90 %) for the extraction of uranyl sulfate complexes from the acidic solution examined (pH 1~2) than the hybrids modified with 4-amino,1-hydroxy,1,1-bis-phosphonic acid.\textsuperscript{170}
Self-assembled vanadium diphosphonate clusters were reported for the use of phenylene and biphenylene diphosphonic acid (Figure 1.29). The dimensions and inner cavities were tailored spontaneously and according to the aromatic ligands used.

![Figure 1.29 Vanadium diphosphonate clusters.](image)

### 1.4.4. Metal-organic-Framework

The synthesis and characterization of infinitive one, two, and three dimensional inorganic-organic networks have recently been studied intensively. Coordination polymers, known as metal-organic-frameworks (MOFs), are formed via a type of covalent metal-ligand bonding and consist of metal ions as connectors and ligands as linkers. As shown in Figure 1.30, the ligands must be from a bridging organic group, and the metal atoms must be bridged independently by the ligands in at least one extended dimension. Ligands have widely diversified topologies, and the possible properties of the MOF networks thus vary to a large extent. Representative linkers are shown in Figure 1.31. By choosing appropriate stopper ligands, the coordination number of metal ion is restricted to four or six, and the shape of the metal building unit can then be controlled to exhibit the desired coordination geometry. One example of different structures with the same metal and different ligands is shown in
Figure 1.30 Schematic of MOFs versus other extended metal-ligand structures (E, E’:organic ligand, M:metal ion). \(^{173}\)

Figure 1.31 Representative bridging groups. \(^{171}\)

Figure 1.32 Examples of MOFs with various bond combinations: a) 3D framework (the B net in CaB\(_6\)) of \([\text{[Ag(pyz)}_3]\text{SbF}_6]_n\), \(^{174}\) b) 2D sheet structure (left) and the stacking of two sheets linked by amide hydrogen bonds (right) in \([\text{Co(NCS)}_2(3\text{-pna})_2]_n\), \(^{175}\) c) 2D network consisting of helical chains linked by Ag-Ag bonds (dashed lines) in \([\text{Ag(2,4’-bpy)}]\text{ClO}_4]_n\). \(^{176}\)
Bridged-type organodiphosphonic acids are applied to synthesize MOF, as shown in Figure 1.33. The hybrid Cu₃[O₃P(C₆H₄)₂PO₃](4,4-bipy)(OH)₂ (Figure 1.33 a) was synthesized under hydrothermal synthesis and exhibited magnetic properties.

The hybrid had asymmetric units containing two distinct Cu(II) ions, a ligand [O₃P(C₆H₄)₂PO₃], a 4,4-bipy ligand, and a coordinated hydroxyl group which form a 3D pillared-layered structure. The hybrid exhibited antiferromagnetism between the Cu (II) centers, and its χₘT value was 0.93 cm³ mol⁻¹ K per Cu₂ ion at room temperature, which was slightly larger than the spin value for two S=1/2 Cu (II) ions (0.75 cm³ mol⁻¹ K for g=2.0). The hybrid of Cu₅[(O₃P)₂C₆H₃CO₂]₂(H₂O)₆ (Figure 1.34 b) was synthesized from a rigid heretotrifunctional building block, 1,3-diphophonobenzoic acid, via hydrothermal synthesis. The crystal structure of the hybrid was assigned to the triclinic P̅1 space group, and the cell parameters are 
a=9.968(7), b = 11.141(4), c = 13.825(6) Å, α = 68.75(3), β = 89.67(5), and γ = 63.70(4)°. The magnetic susceptibility χ of the hybrid is increased continuously to reach 0.4 emu/mol at 2 K when the sample is cooled to below room temperature.

Figure 1.33 MOF derived from organodiphosphonic acid, (a) Cu₃[O₃P(C₆H₄)₂PO₃](4,4-bipy)(OH)₂ and (b) Cu₅[(O₃P)₂C₆H₃CO₂]₂(H₂O)₆.
The porous properties of MOFs have attracted considerable attention recently due to demand for industrial applications, such as separation, heterogeneous catalysts, and gas storage. Unlike conventional porous materials such as activated carbons, aluminum phosphates, and zeolites,\textsuperscript{110, 179, 180} MOFs have crystallographically well-defined pore shapes whose cross-sections are squares, rectangles, triangles, and so on. Thus, the pore shapes of the MOFs are not necessarily modeled by slit-like and cylindrical pores. The pores of the MOFs with flexible and dynamic frameworks based on weak interactions such as coordination bonds, hydrogen bonds, $\pi-\pi$ stacking interactions, and van der Waals forces can be transformed from non-porous to microporous during the gas adsorption (Figure 1.34).

![Figure 1.34 Adsorption isotherms with the transformation from nonporous to porous structure: broken line: the Type I (micropore filling) and dotted line: Type II (surface adsorption) isotherms. Points A and B indicate the gate-opening and gate-closing pressures which accompany the start and end of the structure transformation, respectively.\textsuperscript{171}](image-url)
1.5. Objectives of This Thesis

As described in the previous section, the Chimie Douce approach is extremely important for preparation of new materials through a variety of combinations of inorganic and organic components, and among the Chimie Douce approaches, the sol-gel process is an especially useful and convenient method of synthesizing class II hybrids. In sol-gel-derived hybrids, inorganic components form network structures, and a variety of functional properties can be provided by their organic moieties. The structures and properties of sol-gel-derived hybrids can be optimized by designing the starting materials and controlling the reaction conditions.

This thesis describes the use of bridged-type precursors to form inorganic-organic hybrids via hydrolytic sol-gel processes. In chapters 2 and 3, preparation of bridged polysilsesquioxanes, typical class-II hybrids, prepared from bridged-type precursors via hydrolytic sol-gel processes is described. The initial hydrolysis reaction of the precursor of phenylene-bridged polysilsesquioxane was investigated using liquid-state $^{29}$Si NMR spectroscopy (Chapter 2). The precursor possessing a dimanganese complex moiety, the catalyst for the decomposition of hydrogen peroxide was synthesized via a hydrosilylation reaction, and its catalytic applications were investigated (Chapter 3). In chapters 4 and 5, bridged-type diphosphonic acids, whose structures are similar to those of bridged polysilsesquioxanes precursors, were synthesized via Michaelis-Arbuzov reactions and reacted with TiCl$_4$ via non-hydrolytic sol-gel processes to prepare Ti-O-P hybrids. Porous Ti-O-P hybrids were prepared from phenylene-bridged diphosphonic acid and TiCl$_4$ in DMSO (Chapter
4). Ti-O-P hybrids possessing a tetraethylene oxide chain were synthesized, doped with LiClO₄, and then measured for ionic conductivity (Chaper 5).

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Chapter 2

Hydrolysis Behavior of the Precursor for the Bridged Polysilsesquioxane [1,4-Bis(triethoxysilyl)benzene]: a $^{29}$Si NMR study
2.1 Introduction

Bridged polysilsesquioxanes are typical class II inorganic–organic hybrid materials\textsuperscript{1-4} derived \textit{via} the sol–gel processes, and have applications in various fields, such as optics, biology and electrochemistry, when functional organic groups are incorporated as spacers.\textsuperscript{5} Bridged polysilsesquioxane can be prepared from a precursor typically consisting of an organic spacer group and two terminal alkoxydimethyl groups. The molecularly designed precursors possessing functional organic groups can be converted into materials with desired shapes, such as porous materials (xerogel), coating films and fibers. Bridged polysilsesquioxanes possessing rigid organic spacers are of particular interest, since they have very high surface areas: up to 1,150 m\textsuperscript{2} g\textsuperscript{-1} for biphenylene-bridged polysilsesquioxane and up to 960 m\textsuperscript{2} g\textsuperscript{-1} for phenylene-bridged polysilsesquioxane.\textsuperscript{5-8}

Organoalkoxysilanes \([R'_{x}Si(OR)_{3-x}\ (x = 1-3)]\)\textsuperscript{9-13} have been employed as precursors for sol–gel processing of inorganic–organic hybrids, and the effects of several factors, such as the composition of the starting materials, the type of catalyst, solvent polarity and temperature, on the hydrolysis and polycondensation reactions have been thoroughly investigated. It is well recognized that the hydrolysis behavior and mechanism of organoalkoxysilanes depend on the type of catalyst. Under acidic conditions, the hydrolysis rate tends to increase with an increase in the number of the substituted electron-donating groups (R’), such as alkyl groups.\textsuperscript{11,14,15} Under basic conditions, on the other hand, the hydrolysis rate increases with an increase in the number of substituted electron-withdrawing groups, and the polycondensation reaction

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proceeds faster than the hydrolysis reaction. 16

Siloxane networks derived from organoalkoxysilanes have been investigated mainly with solid-state $^{29}$Si cross polarization/magic angle spinning nuclear magnetic resonance ($^{29}$Si CP/MAS NMR) spectroscopy. 1,17–22 Several studies have also been reported on the hydrolysis behavior of organoalkoxysilanes using liquid-state $^{29}$Si NMR, 9, 11, 14, 15, 23–34 since hydrolysis and the initial polycondensation behavior of organosiloxanes affect the final siloxane networks. With respect to the siloxane networks of bridged polysilsesquioxanes, Shea et al. investigated the siloxane network structures of bridged polysilsesquioxanes using solid-state $^{29}$Si CP/MAS NMR spectroscopy 6, 18 and reported that the siloxane networks depended on the type of catalyst. Although the liquid-state $^{29}$Si NMR spectra of hydrolyzed solutions of bridged polysilsesquioxane precursors were reported, 35–38 no detailed study of the hydrolysis behavior of the precursors has been reported so far.

This chapter describes the hydrolysis behavior of 1,4-bis(triethoxysilyl)benzene (BTB) using liquid-state $^{29}$Si NMR spectroscopy and compares to that of 1, 2-bis(triethoxysilyl)ethane (BTE). The major hydrolysis path is revealed based on the evolutionary behavior of the hydrolyzed species, and the reaction mechanism is discussed.

2.2 Experimental Section
Materials. BTB was used without further purification. Ethanol (EtOH) was distilled over Mg and I$_2$. Tetramethylsilane (TMS) and chromium triacetylacetonate
[Cr(acac)_3] were used as received. To obtain NMR lock signals, ethanol-d_1
[CH_3CH_2OD; EtOD] was included as a part of ethanol.

**Preparation of samples.** Samples were prepared in the BTB-ethanol-water-HCl systems with BTB:ethanol:H_2O:HCl = 1:10:x:0.8 \times 10^{-4} (x = 3, 6 and 9). Samples were also prepared in the 1, 2-bis(triethoxysilyl)ethane (BTE)-ethanol-water-HCl system with BTE:ethanol:H_2O:HCl = 1:15:6:1.7 \times 10^{-4}. A trace of Cr(acac)_3 (Si/Cr \approx 100) was added to shorten the relaxation time. BTB was dissolved in ethanol (EtOH + EtOD) in a glass vial. A mixture of EtOH, water and 0.1 mol/L HCl was added dropwise to the BTB solution with a needle-tipped syringe while stirring. The mixture was stirred further for 3 min to obtain a clear homogeneous solution. A sample solution with traces of Cr(acac)_3 and TMS was then put into a 5 mm glass NMR tube.

**29Si NMR.** All liquid-state 29Si NMR spectra were recorded on a JEOL Lambda-500 spectrometer at ambient temperature with an inversely-gated decoupling pulse sequence. The intervals between two pulse sequences were 10 s. The chemical shifts were reported with respect to internal TMS. For a sample with water/ BTB = 6, a spectrum was measured every 30 min during initial 2 h and then once every 1 h. For other samples with water/ BTB = 3 and 9, the spectra were measured every 2 h.

**2.3 Results and Discussion**

**29Si NMR spectra.** The liquid-state 29Si NMR spectra of the solutions in all three systems (BTB:ethanol:H_2O:HCl = 1:10:x:0.8 \times 10^{-4}; x = 3, 6 or 9) are measured from
The signal due to BTB shifts downfield gradually as hydrolysis proceeds. Since hydrolysis causes a change in the compositions of solvents, the observed shift should be ascribed to solvent effect. \(^{39-41}\) Similar observation was reported for hydrolysis of DMDES. \(^{14}\) Signals at > -60 ppm form four sub-regions: from -58.5 to -57.5 ppm [D], from -56.5 to -55.5 ppm [C], from -55.0 to -54.0 ppm [B] and from -53.5 to -52.5 ppm [A].

Previous studies of organoalkoxysilanes \(^{15, 32, 42, 43}\) revealed that signals showed downfield shifts as an alkoxy group was replaced with a hydroxyl group. Actually, in the \(^{29}\)Si NMR spectra of hydrolyzed species of phenyltriethoxysilane \([\text{PhSi(OEt)}_3]\) (PTES), \(^{42}\) signals due to \(\text{T}^0_{(0\text{OH})}[\text{PhSi(OEt)}_3]\), \(\text{T}^0_{(1\text{OH})}[\text{PhSi(OH)(OEt)}_2]\), \(\text{T}^0_{(2\text{OH})}[\text{PhSi(OH)}_2(\text{OEt})]\) and \(\text{T}^0_{(3\text{OH})}[\text{PhSi(OH)}_3]\) appeared at -57, -55, -53.5 and -52 ppm at almost even intervals. Although the observed signals show upfield shifts compared to the corresponding signals of PTES and PTES-derived species, the number of sub-regions is the same as that observed in the hydrolysis behavior of PTES and the intervals are similar to those of \(\text{PhSi(OH)}_x(\text{OEt})_{3-x}\), indicating similar shifts in the present system. \(^{42}\) In terms of the effect of water content, the intensities of signals in the downfield sub-region increase with an increase in water content. When water/BTB = 9, in particular, the BTB signal in the sub-region [D] disappears after 4.25 h and signals due to condensation products [\(\text{T}^1(-\text{Si(OSi)}(\text{OH})_{x}(\text{OEt})_{2-x}; x = 0-2)\)] appear in the range from -62 to -64 ppm. We can thus conclude that the four observed sub-regions from [A] to [D] should be assigned to \(-\text{Si(OH)}_x(\text{OEt})_{3-x}\) environments of monomeric species as demonstrated in Scheme 2.1.
To examine the hydrolysis behavior more closely, the hydrolysis behavior of a sample with BTB:EtOH:water:HCl = 1:10:6:0.8×10^{-4} was studied using $^{29}$Si NMR from 0.25 h to 8.25 h, and the enlarged profiles in the range from -52 to -60 ppm are shown in Figure 2.2. Though the signals of the hydrolyzed species do not appear at 0.25 h, they begin to appear in the spectra measured after 0.75 h in the four sub-regions, and signals besides that of BTB develop drastically up to 4.25 h. It is clearly demonstrates that each of the four sub-regions consists of four signals. After 0.25 h, signal D3 [(EtO)$_3$Si-] and signal C4 [(EtO)$_2$(HO)Si-] develop, and the intensities of these two signals are very similar in all the spectra. Thus, the D3 and C4 signals are assignable to [(EtO)$_3$Si-C$_6$H$_4$-Si(OH)(OEt)$_2$], indicating that the downfield shift from D4 [(EtO)$_3$Si-C$_6$H$_4$-Si(OE)] to D3 [(EtO)$_3$Si-C$_6$H$_4$-Si(OH)(OEt)$_2$] is caused by the replacement of one ethoxy group with one hydroxy group at the other silicon atom. This assignment is consistent with a previous report on a $^{29}$Si NMR spectrum of a hydrolyzed BTB solution.\(^2\) In a similar fashion, D2 [(EtO)$_3$Si-] and C4 [(EtO)$_2$(HO)Si-] behave similarly, and D1 [(EtO)$_3$Si-] and A4 [(OH)$_3$Si-] exhibit similar intensities in all the spectra. Thus, D2 and C4 are assignable to [(EtO)$_3$Si-C$_6$H$_4$-Si(OE)] and D1 and A4 are due to [(EtO)$_3$Si-C$_6$H$_4$-Si(OH)$_3$]. It is also concluded that the presence of four signals in the sub-region [D] [(EtO)$_3$Si-] is caused by the effect of substituents of the other Si atom through the phenylene group. For the other sub-regions ([A] - [C]), four signals are assigned in a similar fashion, as shown in Table 2.1. It should be noted that pairs of signals due to these assignments show very similar intensities and development behavior; (A2-B1), (A3-C1), (A4-D1),
Signals A1 [(HO)₃Si-C₆H₄-Si(OH)₃], B2 [((OEt)(HO)₂Si-C₆H₄-Si(OH)²(OEt))] and C3 [((HO)(EtO)₂Si-C₆H₄-Si(OH)(OEt)₂] as well as D4 (BTB) should not make pairs.

**Relative amounts of BPB and hydrolyzed species.** The evolution of monomeric species is discussed based on the assignments. To estimate the amount of the monomeric species, the arithmetic averages of integrated intensities are used for paired signals and halved integrated intensities are used for the four signals A1, B2, C3 and D4. The calculation results are shown in Tables 2.2 and 2.3. The abbreviations of the species are also listed in Table 2.1.

Figure 2.3 shows the evolution of the relative amount of each species. As shown in Figure 2.3, the relative amount of (1-0), in which one of six ethoxy groups is hydrolyzed, initially increases rapidly, and the relative amount of (1-0) then decreases after 2 h, indicating that it undergoes further hydrolysis. While the relative amount of (1-1), in which one ethoxy group at each silicon atom is hydrolyzed, does not show a clear increase, the relative amount of (2-0) increases gradually. Moreover, the relative amount of (3-0) increases in a way similar to that of (2-0). Thus, once one ethoxy group is hydrolyzed at a silicon atom, there is a tendency for another ethoxy group bound to the same silicon atom to be further hydrolyzed. Based on these results, the hydrolysis reaction can be summarized as shown in Scheme 2.2.

Since one -Si(OEt)₃ group of BTB tends to be preferentially hydrolyzed to the -Si(OH)₃ group in a hydrolysis process, hydrolysis is promoted with an increase in the degree of hydrolysis. Generally, the hydrolysis behavior of tetraalkoxysilanes is
discussed based on the inductive effect, which produces electron polarization within a molecule through a $\sigma$ bond with the gap in electron negativity. As the electron negativities of oxygen and silicon are 3.5 and 1.8, respectively, oxygen atoms withdraw electrons from silicon atoms in tetraalkoxysilanes (and their hydrolyzed species), leading to lower electron densities of the silicon atoms. When the inductive effect becomes dominant under acidic conditions, the electron density of a silicon atom in tetraalkoxysilane decreases after substitution of an alkoxy group with a hydroxyl group because the electron-withdrawing property of the hydroxyl group is stronger than that of the alkoxy group. In the hydrolysis mechanism of tetraalkoxysilanes under acidic conditions, an alkoxy group is protonated, and water molecule then attacks the silicon atom to form a pentacoordinate intermediate as a transition state. The protonated alkoxy group is then eliminated from the pentacoordinate intermediate as an alcohol. When the electron density of the silicon atom decreases, the replacement of the alkoxy group with the hydroxyl group destabilizes the development of a positive charge, leading to a decrease in the hydrolysis rate. The hydrolysis rate thus decreases under acidic conditions with an increase in the degree of hydrolysis of tetraalkoxysilanes, and a similar tendency is expected for organotrialkoxysilanes. It is therefore concluded that the observed hydrolysis behavior of BTB under acidic conditions is opposite to the hydrolysis behavior predicted based on the inductive effect.

As demonstrated in Figure 2.2, all sub-regions of $^{29}$Si NMR spectra consist of four signals, and this splitting of the same local environment is caused by the influence
of the environment of the other silicon atom: as an ethoxy group bound to the other silicon atom is replaced with a hydroxyl group, the signal shifts downfield. This phenomenon can be caused by an intra-molecular interaction, such as a ‘through-space’ (TS) interaction\textsuperscript{36,46-52} and negative-hyperconjugation\textsuperscript{53-59}. When an ethoxy group in a -Si(OEt)\textsubscript{3} group is hydrolyzed, the decrease in the electron density of the silicon atom upon the replacement of an ethoxy group with a hydroxyl group is compensated by electrons from the other silicon atom by TS interaction and/or negative-hyperconjugation, leading to a decrease in the electron density of the other silicon atom in the unhydrolyzed -Si(OEt)\textsubscript{3} group. Thus, the resulting -Si(OEt)\textsubscript{2}(OH) group is more reactive towards hydrolysis, and, at the same time, the other -Si(OEt)\textsubscript{3} group, which is acted as a donor, becomes less reactive towards hydrolysis. A decrease in the electron density of the other silicon atom is accelerated upon further hydrolysis. As a consequence, one -Si(OEt)\textsubscript{3} group is hydrolyzed while hydrolysis of the other -Si(OEt)\textsubscript{3} group is suppressed, leading to 2-0 and 3-0 as dominant species in the latter part of hydrolysis.

The comparison to alkylene spacer. The hydrolysis behavior of 1,2-bis(triethoxysilyl)ethane (BTE) was also investigated as shown in Figure 2.4. The signals of the hydrolyzed species began to appear at 0.75 h and in the four sub-regions ([A]-[D]) after 1.25 h. The same phenomenon as BTB is observed that each of the four sub-regions consists of four signals. Some signals can be made pairs because of the correspondence of their intensities and development behavior shown in Tables 2.4 and 2.5. Thus, all sixteen signals can be assigned to ten hydrolyzed species. To estimate
the amount of the monomeric species, calculations similar to those done for the BTB system were carried out to each signal. The abbreviations of the species are also listed in Table 2.6. The small signals which are appeared under -38.5 ppm are assigned to intermolecular ring compounds.35

Figure 2.5 shows the evolution of the relative amount of initial three species, that is, (1-0), (1-1) and (2-0). At initial stage of hydrolysis, there was no indication on preferential hydrolysis of one -Si(OEt)3 groups; two -Si(OEt)3 groups in BTE were hydrolyzed independently as shown in Figure 2.5. Moreover, there was obvious increase of (2-1) against that of (3-0) shown in Figure 2.6. This result indicates that one -Si(OEt)3 groups are hydrolyzed successively based on the inductive effect,11,44 and the effect of an intra-molecular interaction, such as a ‘through-bond’ (TB) interaction36,45,48 is lower than the inductive effect. These results strongly suggest that the pi orbitals in the phenylene group play an important role for intra-molecular interaction, which causes the electron density difference of two silicon atoms upon very initial hydrolysis, leading to the clear preferential hydrolysis.

In addition, since a silicon environment with one phenylene group and three ethoxy groups is relatively crowded, it is probable that less crowded C6H4-Si(OH)x(OEt)3-x groups are sterically advantageous for hydrolysis. As a consequence, in the hydrolysis of BTB, the steric effect could also affect hydrolysis behavior.
2.4 Conclusions

In this chapter, the hydrolysis behavior of BTB under acidic conditions has investigated with liquid-state $^{29}\text{Si}$ NMR spectroscopy, and all signals for the monomeric species are assigned. One silicon environment affected the electron density of the other silicon environment through the phenylene group to cause the appearance of four signals in the same local silicon environment. In the initial stage of hydrolysis, one $-\text{Si(OEt)}_3$ group of BTB was preferentially hydrolyzed to $-\text{Si(OH)}_3$, which is opposite to the tendency predicted based on the inductive effect. It is assumed that the electron density of the silicon atom in the hydrolyzed group, $-\text{Si(OH)}_x(\text{OEt})_{3-x}$ is compensated through the intra-molecular interaction, such as the TS interaction and negative hyperconjugation. This study clearly demonstrates the unique hydrolysis behavior of BTB, and this behavior should affect the polycondensation process of BTB.
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Figure 2.1 The variation in $^{29}$Si NMR spectra with hydrolysis time: (a) $\text{H}_2\text{O}/\text{BTB} = 3$, (b) $\text{H}_2\text{O}/\text{BTB} = 6$, and (c) $\text{H}_2\text{O}/\text{BTB} = 9$.

Scheme 2.1 The structures of hydrolysis species in sub-regions.
Figure 2.2 The variation of $^{29}$Si NMR spectra with hydrolysis time (BTB:ethanol:H$_2$O:HCl =1:10:6:0.8×10$^{-4}$).

Table 2.1 Assignments of $^{29}$Si NMR signals for BTB and hydrolyzed species.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Chemical shift / ppm</th>
<th>Formula</th>
<th>Abbreviation $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>-52.6</td>
<td>(HO)$_2$Si$_2$CH$_2$Si(OH)$_2$</td>
<td>2-3</td>
</tr>
<tr>
<td>A2</td>
<td>-52.7</td>
<td>(HO)$_2$Si$_2$CH$_2$Si(OH)$_2$</td>
<td>2-2</td>
</tr>
<tr>
<td>A3</td>
<td>-52.9</td>
<td>(HO)$_3$Si$_2$CH$_2$Si(OH)OEO</td>
<td>3-1</td>
</tr>
<tr>
<td>A4</td>
<td>-53.1</td>
<td>(HO)$_3$Si$_2$CH$_2$Si(OEO)</td>
<td>3-0</td>
</tr>
<tr>
<td>B1</td>
<td>-54.0</td>
<td>(EO)$(HO)H_2$Si$_2$CH$_2$Si(OH)</td>
<td>2-3</td>
</tr>
<tr>
<td>B2</td>
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<td>2-2</td>
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<tr>
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<td>(EO)$(HO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>2-1</td>
</tr>
<tr>
<td>B4</td>
<td>-54.6</td>
<td>(EO)$(HO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>2-0</td>
</tr>
<tr>
<td>C1</td>
<td>-55.6</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OH)</td>
<td>3-3</td>
</tr>
<tr>
<td>C2</td>
<td>-55.8</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>1-2</td>
</tr>
<tr>
<td>C3</td>
<td>-56.0</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>1-1</td>
</tr>
<tr>
<td>C4</td>
<td>-56.2</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>1-0</td>
</tr>
<tr>
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<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OH)</td>
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</tr>
<tr>
<td>D2</td>
<td>-57.6</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>0-2</td>
</tr>
<tr>
<td>D3</td>
<td>-57.9</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>0-1</td>
</tr>
<tr>
<td>D4</td>
<td>-58.2</td>
<td>(EO)$(EO)H_2$Si$_2$CH$_2$Si(OEO)</td>
<td>0-0</td>
</tr>
</tbody>
</table>

* The abbreviations of the species are composed of pairs of the numbers, which correspond to the numbers of the hydroxyl groups bound to silicon.
Table 2.2  Relative integrated intensities from C1 to D4.

<table>
<thead>
<tr>
<th>Time / h</th>
<th>Relative integrated intensity/ -</th>
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</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>0.25</td>
<td>0.884</td>
</tr>
<tr>
<td>0.75</td>
<td>0.762</td>
</tr>
<tr>
<td>1.25</td>
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</tr>
<tr>
<td>1.75</td>
<td>0.581</td>
</tr>
<tr>
<td>2.25</td>
<td>0.528</td>
</tr>
<tr>
<td>3.25</td>
<td>0.413</td>
</tr>
<tr>
<td>4.25</td>
<td>0.364</td>
</tr>
<tr>
<td>5.25</td>
<td>0.319</td>
</tr>
<tr>
<td>6.25</td>
<td>0.260</td>
</tr>
<tr>
<td>7.25</td>
<td>0.226</td>
</tr>
<tr>
<td>8.25</td>
<td>0.200</td>
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</tbody>
</table>

Table 2.3  Relative integrated intensities from A1 to B4.

<table>
<thead>
<tr>
<th>Time / h</th>
<th>Relative integrated intensity/ -</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B4</td>
</tr>
<tr>
<td>0.25</td>
<td>0.000</td>
</tr>
<tr>
<td>0.75</td>
<td>0.016</td>
</tr>
<tr>
<td>1.25</td>
<td>0.035</td>
</tr>
<tr>
<td>1.75</td>
<td>0.040</td>
</tr>
<tr>
<td>2.25</td>
<td>0.043</td>
</tr>
<tr>
<td>3.25</td>
<td>0.059</td>
</tr>
<tr>
<td>4.25</td>
<td>0.072</td>
</tr>
<tr>
<td>5.25</td>
<td>0.076</td>
</tr>
<tr>
<td>6.25</td>
<td>0.087</td>
</tr>
<tr>
<td>7.25</td>
<td>0.098</td>
</tr>
<tr>
<td>8.25</td>
<td>0.102</td>
</tr>
</tbody>
</table>
Figure 2.3 Change in relative amounts of BTB and hydrolyzed species.

1 - 0 • 2 - 0 □ 1 - 1 ■ 3 - 0 ▼ 3 - 2 ● 2 - 1 ○ 2 - 2 ▽ 3 - 1 ◇ 3 - 3

Scheme 2.2 Hydrolysis process of BTB.
Figure 2.4  The variation of $^{29}$Si NMR spectra with hydrolysis time (BTE:ethanol:H$_2$O:HCl =1:10:6:1.7×10$^{-4}$).

Table 2.4 Relative integrated intensities from C1 to D4.

<table>
<thead>
<tr>
<th>Time / h</th>
<th>D4</th>
<th>D3</th>
<th>D2</th>
<th>D1</th>
<th>C4</th>
<th>C3</th>
<th>C2</th>
<th>C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>0.784</td>
<td>0.089</td>
<td>0.011</td>
<td>0.000</td>
<td>0.087</td>
<td>0.010</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.25</td>
<td>0.616</td>
<td>0.121</td>
<td>0.030</td>
<td>0.016</td>
<td>0.114</td>
<td>0.025</td>
<td>0.012</td>
<td>0.000</td>
</tr>
<tr>
<td>1.75</td>
<td>0.520</td>
<td>0.111</td>
<td>0.038</td>
<td>0.023</td>
<td>0.114</td>
<td>0.041</td>
<td>0.016</td>
<td>0.010</td>
</tr>
<tr>
<td>2.25</td>
<td>0.439</td>
<td>0.109</td>
<td>0.045</td>
<td>0.023</td>
<td>0.109</td>
<td>0.042</td>
<td>0.024</td>
<td>0.015</td>
</tr>
<tr>
<td>2.75</td>
<td>0.368</td>
<td>0.106</td>
<td>0.047</td>
<td>0.025</td>
<td>0.105</td>
<td>0.049</td>
<td>0.033</td>
<td>0.024</td>
</tr>
<tr>
<td>3.25</td>
<td>0.322</td>
<td>0.095</td>
<td>0.043</td>
<td>0.022</td>
<td>0.104</td>
<td>0.048</td>
<td>0.031</td>
<td>0.021</td>
</tr>
<tr>
<td>3.75</td>
<td>0.277</td>
<td>0.089</td>
<td>0.050</td>
<td>0.023</td>
<td>0.092</td>
<td>0.044</td>
<td>0.038</td>
<td>0.031</td>
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<td>0.231</td>
<td>0.079</td>
<td>0.044</td>
<td>0.031</td>
<td>0.076</td>
<td>0.045</td>
<td>0.043</td>
<td>0.027</td>
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<td>0.073</td>
<td>0.048</td>
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<td>0.077</td>
<td>0.050</td>
<td>0.044</td>
<td>0.029</td>
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<tr>
<td>5.25</td>
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<td>0.074</td>
<td>0.042</td>
<td>0.021</td>
<td>0.068</td>
<td>0.039</td>
<td>0.056</td>
<td>0.033</td>
</tr>
<tr>
<td>5.75</td>
<td>0.158</td>
<td>0.062</td>
<td>0.035</td>
<td>0.016</td>
<td>0.063</td>
<td>0.044</td>
<td>0.045</td>
<td>0.031</td>
</tr>
<tr>
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<td>0.062</td>
<td>0.039</td>
<td>0.015</td>
<td>0.062</td>
<td>0.039</td>
<td>0.052</td>
<td>0.033</td>
</tr>
<tr>
<td>6.75</td>
<td>0.132</td>
<td>0.055</td>
<td>0.039</td>
<td>0.013</td>
<td>0.050</td>
<td>0.042</td>
<td>0.057</td>
<td>0.030</td>
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<tr>
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<td>0.028</td>
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<td>0.048</td>
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<td>0.046</td>
<td>0.034</td>
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<td>0.044</td>
<td>0.027</td>
<td>0.013</td>
<td>0.052</td>
<td>0.039</td>
<td>0.051</td>
<td>0.032</td>
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Table 2.5 Relative integrated intensities from A1 to B4.

<table>
<thead>
<tr>
<th>Time / h</th>
<th>Relative integrated intensity / -</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>B4</td>
</tr>
<tr>
<td>0.75</td>
<td>0.009</td>
</tr>
<tr>
<td>1.25</td>
<td>0.034</td>
</tr>
<tr>
<td>1.75</td>
<td>0.040</td>
</tr>
<tr>
<td>2.25</td>
<td>0.041</td>
</tr>
<tr>
<td>2.75</td>
<td>0.050</td>
</tr>
<tr>
<td>3.25</td>
<td>0.047</td>
</tr>
<tr>
<td>3.75</td>
<td>0.050</td>
</tr>
<tr>
<td>4.25</td>
<td>0.045</td>
</tr>
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<tr>
<td>5.25</td>
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<tr>
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<td>0.041</td>
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<tr>
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<td>0.034</td>
</tr>
<tr>
<td>7.25</td>
<td>0.035</td>
</tr>
<tr>
<td>7.75</td>
<td>0.032</td>
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</table>

Table 2.6 Assignments of 29Si NMR signals for BTE and hydrolyzed species.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Chemical shift / ppm</th>
<th>Formula</th>
<th>Abbreviation *</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>-38.9</td>
<td>(OH)2SiC2H5Si(OH)3</td>
<td>1/2</td>
</tr>
<tr>
<td>A2</td>
<td>-39.1</td>
<td>(OH)2SiC2H5Si(OH)2(OEt)</td>
<td>1/2</td>
</tr>
<tr>
<td>A3</td>
<td>-39.4</td>
<td>(OH)2SiC2H5Si(OEt)2(OH)</td>
<td>2/1</td>
</tr>
<tr>
<td>A4</td>
<td>-39.8</td>
<td>(OH)2SiC2H5Si(OEt)3</td>
<td>3/0</td>
</tr>
<tr>
<td>B1</td>
<td>-40.3</td>
<td>(OH)(OEt)SiC2H5Si(OH)3</td>
<td>2/3</td>
</tr>
<tr>
<td>B2</td>
<td>-40.5</td>
<td>(OH)(OEt)SiC2H5Si(OEt)2(OH)</td>
<td>2/2</td>
</tr>
<tr>
<td>B3</td>
<td>-40.9</td>
<td>(OH)(OEt)SiC2H5Si(OEt)3(OH)</td>
<td>3/1</td>
</tr>
<tr>
<td>B4</td>
<td>-41.3</td>
<td>(OH)(OEt)2SiC2H5Si(OEt)3</td>
<td>2/0</td>
</tr>
<tr>
<td>C1</td>
<td>-41.9</td>
<td>(OH)(OEt)2SiC2H5Si(OH)3</td>
<td>3/3</td>
</tr>
<tr>
<td>C2</td>
<td>-42.2</td>
<td>(OH)(OEt)2SiC2H5Si(OEt)(OEt)</td>
<td>2/2</td>
</tr>
<tr>
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<td>-42.6</td>
<td>(OH)(OEt)2SiC2H5Si(OEt)(OH)</td>
<td>1/1</td>
</tr>
<tr>
<td>C4</td>
<td>-43.1</td>
<td>(OH)(OEt)2SiC2H5Si(OEt)3</td>
<td>1/0</td>
</tr>
<tr>
<td>D1</td>
<td>-43.9</td>
<td>(OEt)SiC2H5Si(OH)3</td>
<td>0/3</td>
</tr>
<tr>
<td>D2</td>
<td>-44.2</td>
<td>(OEt)SiC2H5Si(OEt)(OEt)</td>
<td>0/2</td>
</tr>
<tr>
<td>D3</td>
<td>-44.6</td>
<td>(OEt)SiC2H5Si(OEt)(OH)</td>
<td>0/1</td>
</tr>
<tr>
<td>D4</td>
<td>-45.2</td>
<td>(OEt)2SiC2H5Si(OEt)3</td>
<td>0/0</td>
</tr>
</tbody>
</table>

* The abbreviations of the species are composed of pairs of the numbers, which correspond to the numbers of the hydroxyl groups bound to silicon.
Figure 2.5 Change in relative amounts of BTE and hydrolyzed species.

Figure 2.6 Change in relative amounts of BTE and hydrolyzed species.
Chapter 3

Sol-gel-derived Bridged Polysilsesquioxane as a Hydrogen Peroxide Decomposition Catalyst: Immobilization of a Dimanganese Complex and Its Improved Thermal Stability
3.1. Introduction

Fuel cells are expected to become a new source of clean energy. Among fuel cells, the polymer electrolyte fuel cell (PEFC) is an excellent candidate for batteries for use in portable electric apparatuses and electric vehicles.\(^1\)\(^-\)\(^3\) In the operation of PEFCs, hydrogen peroxide is formed by the crossleak and gradually degrades ionomer membranes such as acidic Nafion mediums as shown in Figure 3.1.\(^4\)\(^-\)\(^6\) Decreasing the volume of hydrogen peroxide is thus a problem to be solved. One effective method of removing the hydrogen peroxide formed is to employ catalysts to decompose it. Since PEFCs generally operate at 80-100 °C under acidic conditions, sufficient thermal stability is required of such catalysts.

Catalase enzymes decompose hydrogen peroxide in nature by a dismutation reaction as shown in Eq (3.1) and Scheme 3.1.\(^7\)

\[2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2\] (3.1)

Since catalase possesses two manganese ions, bio-inspired dimanganese complexes have been extensively designed.\(^8\)\(^-\)\(^{14}\) Immobilization in matrices is important for application of these complexes, and inorganic matrices are superior to organic matrices in terms of durability and thermal stability. The sol-gel process is one of the common methods for the formation of inorganic networks, such as siloxane (Si-O-Si) networks, and metal complexes can be immobilized into siloxane networks through covalent bonds by using appropriate precursors possessing trialkoxysilyl groups.\(^15\) The introduction of multiple trialkoxysilyl groups is advantageous for gel formation, and the resulting hybrids are called bridged polysilsesquioxane.\(^16\)\(^-\)\(^{29}\) Various bridged polysilsesquioxanes bearing metal complexes have thus been reported to date. A polysilsesquioxanes-bearing dimanganese complex moiety is
thus an attractive catalyst for the reduction of hydrogen peroxide in PEFCs.

This chapter describes the preparation of a new bridged polysilsesquioxane possessing a dimanganese complex moiety and its ability to achieve decomposition of hydrogen peroxide. The effect of co-condensation reagents is also investigated.

3.2. Experimental Section

**General information** All manipulations of hydrosilylation reaction were carried out under an inert atmosphere using standard Schrenk techniques\(^\text{30}\). The dimanganese complex \([\text{LMn}_2-\mu-\text{X}]\text{Y}_2\), where \(\mu-\text{X} = \text{p-CH}_2=\text{CHC}_6\text{H}_4\text{CO}_2\), \(\text{Y} = \text{CH}_3\text{O(CH}_2\text{CH}_2\text{O)}_n(\text{CH}_2)_4\text{SO}_3\) \((n = \sim 45)\), \(\text{L=} \text{N,N,N',N'-tetrakis(2-methylene-N-(4-stryrylmethyl)benzimidazole)-1,3-diaminopropa}-\text{n-2-olate},^8\) (abbreviated as Mn-STP, Scheme 3.2(a)), was synthesized from the precursor possessing \(\text{p-vinylbenzoate anion (Y} = \text{CH}_2=\text{CHC}_6\text{H}_4\text{COO)}\), which was identified by ESI-MS \((m/Z 1477.4)\), via an ion-exchange reaction. Ethanol (EtOH) was distilled over Mg and I\(_2\). Triethoxysilane (TES) was distilled and no existence of any by-products was confirmed by liquid-state \(^{29}\text{Si}\) nuclear magnetic resonance (\(^{29}\text{Si}\) NMR) spectroscopy on a JEOL JNM-EX500. The chemical shifts are referenced to tetramethylsilane (TMS) for \(^1\text{H}\) and \(^{13}\text{C}\) nuclei. Triethoxysilane (TES) was used after vacuum distillation, and a 0.1 mol/L xylene solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt’s catalyst) was used as received. Fourier-transfer infrared (FT-IR) spectra were measured on a JASCO FT/IR-460 spectrometer. Electron spin resonance spectroscopy (ESR) was recorded on a JEOL JES-TE200. Inductively coupled plasma (ICP) analysis was measured on a Variant Vista-MPX after dissolution in a mixture of 5 mL of conc. HNO\(_3\) (69-70
mass%), 5 mL of conc. H$_2$SO$_4$ (>96 mass%), and 10 mL of HF (46-48 mass%) at 200ºC for 2 h for Mn, whereas the measurement was performed after fusion with lithium metaborate for Si. Nitrogen adsorption-desorption isotherms were recorded on a Bel Japan Inc. BELSORP-mini II. The sample was degassed at 120ºC for 3 h under reduced pressure.

**Hydrosilylation of Mn-STP.** The hydrosilylation reaction of Mn-STP was manipulated under an inert atmosphere using standard Schrenk techniques.$^{31}$ Mn-STP (600 mg) was dissolved in dry ethanol (18 mL), and TES (0.37 mL) and Karstedt’s catalyst solution (0.33 mL) were then added to the solution. The mixture was allowed to react at 60ºC for four days with stirring. After cooling to room temperature and drying under a vacuum, 920 mg of the resultant product $N,N,N',N'$-tetrakis(2-methylene-$N$-(4-((triethoxysilyl)ethyl)benzyl)benzimidazole)-1, 3-diaminopropan-2-olate, (abbreviated as Mn-TES, Scheme 3.2(b)) was obtained. The dark brown color of Mn-STP was retained after hydrosilylation. The completion of hydrosilylation was confirmed by the Fourier transform infra-red (FT-IR) spectroscopy.

**Preparation of bridged polysilsesquioxane immobilized dimanganese moiety.** A hybrid gel was prepared by the sol-gel process under acidic conditions. A mixture of ethanol (1.9 mL), distilled water (240 µL) and 0.10 mol/L HCl (66 µL) was added dropwise to Mn-TES (200 mg) diluted in ethanol (5.0 mL) with stirring at room temperature, and the solution was then allowed to stand to form a wet gel via the formation of a siloxane (Si-O-Si) network. The wet gel was then dried under a
vacuum to yield Mn-hybrid (Scheme 3.2(c)).

The assessment of the catalytic decomposition reaction of hydrogen peroxide.
The catalytic activity of hydrogen peroxide decomposition was assessed at 80°C under acidic conditions, under which PEFCs in electric vehicles typically operates.\(^4\) Mn-hybrid (4.3 \(\mu\)mol/Mn) was dispersed in a solution (1.00 mL) of poly(sodium 4-styrenesulfonate), which was dissolved in a tartaric acid/sodium tartrate buffer solution. The buffer solution was prepared from a 0.20 mol/L aqueous tartaric acid and a 0.10 mol/L aqueous sodium tartrate solution by adjusting the pH to 4.0. Ethylene glycol (1.00 mL) was then added to the mixture and stirred. The resultant solution was stirred at 80°C for 5 min or 24 h as a pre-heat treatment before the catalytic assessment. A hydrogen peroxide aqueous solution (2.3 mmol) was then added to the Mn-hybrid solution to conduct a decomposition reaction of hydrogen peroxide at 80°C for 20 min. The generated gaseous oxygen was measured with a gas burette to assess the quantity of decomposed hydrogen peroxide. The volume \((v)\) of gaseous oxygen was converted to the volume \((V)\) under standard conditions \([0°C, 101325 \text{ Pa (760 mmHg)}]\) by using the Numerical Eq. 3.2.

\[
V = \frac{273v (P-p)}{760 (273 + t)}
\]

Parameters were shown as follows: \(P/\text{mmHg}\): the atmospheric pressure, \(p/\text{mmHg}\): vapor pressure of water, \(t/°C\): temperature, \(v/\text{mL}\): measured volume, and \(V/\text{mL}\): converted volume at 0°C and 101325 Pa (760 mmHg).
3.3. Results and Discussions

3.3.1. Hydrosilylation of Mn-STP.

Figure 3.2 shows the FT-IR spectra of triethoxysilane, Mn-STP, and Mn-TES. The spectrum of Mn-TES showed the disappearance of $\delta$(C=C) (950-1000 cm$^{-1}$) and $\alpha$(C=C) (545-555 cm$^{-1}$) bands originating from Mn-STP, as well as $\nu$(Si-H) (~2100 cm$^{-1}$) and $\alpha$(Si-H) (800-950 cm$^{-1}$) bands which were observed in the spectrum of TES. New adsorption bands due to $\nu$(C-H) at ~2950 cm$^{-1}$, $\nu$(C-O) at 1050-1100 cm$^{-1}$ and $\nu$(Si-C) at ~780 cm$^{-1}$, all of them originating from TES, were also observed in the spectrum of Mn-TES. The molar ratio of Si and Mn of Mn-TES was 6:2 measured by ICP analysis, whereas the theoretical value was 5:2. This result indicates that the hydrosilylation reaction was preceded not only with Mn-STP but also with $p$-vinylbenzoate anion which still remained after the synthesis of Mn-STP. The ESR spectrum of Mn-TES (Figure 3.3) exhibited the Mn$_2$(II, II) center, which was identical to that of Mn-STP in the region of $g \approx 2$, as 6-line signals (hyperfine splitting of $\approx$100 G), indicating that the hydrosilylation reaction did not affect the local structure of dimanganese complex.

3.3.2. Preparation of bridged polysilsesquioxane immobilized dimanganese moiety.

Figure 3.4 shows the FT-IR spectra of Mn-TES and Mn-hybrid. A $\nu$(C-O) band (1050-1100 cm$^{-1}$) due to the ethoxy group was decreased and a $\nu$(Si-O-Si) band (1030-1090 cm$^{-1}$) caused by the formation of siloxane networks appeared. The $\nu$(SiO-H) band (3200-3700 cm$^{-1}$) and $\nu$(Si-OH) band (900-820 cm$^{-1}$) were observed in the spectrum of Mn-hybrid, indicating that some Si-OH groups remained.
ν(C-H) band (1280-1250 cm\(^{-1}\)) and ν(Si-C) band (860-720 cm\(^{-1}\)) due to Mn-TES were observed in the spectrum of Mn-hybrid, indicating that the local structure of Mn-TES was retained in Mn-hybrid.

3.3.3. The assessment of catalytic activity for hydrogen peroxide decomposition.

The catalytic activity of Mn-hybrid was measured after 5-min and 24-h treatments as shown in Figure 3.5. A similar heterogeneous catalytic decomposition was also performed with the corresponding non-immobilized dimanganese complex, LMn\(_2(\mu\text{-OAc})(\text{CF}_3\text{SO}_3)_2\), L=\(N,N,N',N'\)-tetrakis(2-methylene(1-ethylbenzamidazolyl))-1,3-diaminopropan-2-olate,\(^8\) 34 (abbreviated as Mn-ETP) (8.4 μmol/Mn). The initial slope of the time-conversion plot at 5-min treatment for Mn-hybrid was almost equal to that of Mn-ETP, although the amount of catalyst employed for Mn-hybrid was less than that for Mn-ETP. These results indicate that the present immobilization does cause no deactivation of the dimanganese catalyst. The catalytic activity of Mn-hybrid was mostly retained, even after 24-h treatment, while that of Mn-ETP decreased significantly after 24 h. These results clearly demonstrate the thermal stability of Mn-hybrid upon immobilization. Although Mn-hybrid exhibited excellent thermal stability at 80ºC, the structure of Mn-hybrid could not be retained at 120ºC. Nitrogen adsorption-desorption isotherm of Mn-hybrid exhibited very low specific surface area (1.94 m\(^2\) g\(^{-1}\)), indicating the hybrid was nonporous. If Mn-hybrid was truly nonporous, hydrogen peroxide could not reach to dimanganese complex moiety in the hybrid and the hydrogen decomposition catalytic activity should be much
As the catalytic activities of after 5-min and 24-h treatments were similar to that of Mn-ETP, this result suggest that the degree of condensation was not enough to maintain of the porous structure originating from dimanganese complex after heat treatment before nitrogen adsorption-desorption measurement at 120°C.

Some unimmobilized catalysts such as dicopper (II) complex, 35 Mn- and Fe-metalloporphyrin 36 and heteronuclear CuMn and CuZn complexes 37 have been reported. Fe (II)-fulvate complex at pH 5 needed about 120 min to halve the concentration of hydrogen peroxide in phosphate buffer solution. 38 The hydrogen peroxide decomposition catalytic activity of N,N’-bis(acetylacetone)-o-phenylenediamine cobalt (II) Schiff base complex which was anchored to crosslinked functional polymeric beads synthesized via copolymerization of styrene, allylchloride and divinylbenzene in the presence of azobisisobutyronitrile was measured at 25°C in pH 8. 39 The activation energy of the supported Co complex was lower (42.37 kJ mol⁻¹) than that of unsupported catalyst (63.59 kJ mol⁻¹) within the same temperature range of 20°C to 50°C, indicating that immobilization in the polymer matrix led to the decrease in the activation energy of the decomposition of hydrogen peroxide, because the polymer matrix provided suitable interaction between Co complex and hydrogen peroxide. Copper(II) phthalocyanine tetrasulfonate, which was intercalated to layered double hydroxides (LDHs), exhibited thermal stability up to 400°C, though its hydrogen peroxide decomposition catalytic activity disappeared. 40 As shown above, metal complexes possessing both thermal stability and catalytic activity comparable to unimmobilized catalyst have never been reported. Thus, this study should have a huge impact in this research field.
Durability of dimanganese complex is also essential, on the other hand, for the application of PEFCs. PEFC for automobile, for example, have to be operated for at least 5,000 h, whereas Mn-hybrid only showed thermal stability for 24 h. Thus, the durability of Mn-hybrid should be further improved to a large extent.

3.4. Conclusions

This chapter describes the novel application of a bridged polysilsesquioxane possessing a dimanganese complex moiety prepared via the sol-gel process as a hydrogen peroxide decomposition catalyst. The thermal stability of hydrogen peroxide decomposition catalysis of a dimanganese complex under acidic conditions at 80°C was drastically improved by immobilization in siloxane networks with no deactivation. The present results strongly suggest that bridged polysilsesquioxanes bearing catalase moieties have potential for hydrogen peroxide decomposition catalyst in PEFC.

References


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Figure 3.1 Overview of polymer electrolyte fuel cell (PEFC).

Scheme 3.1 Proposed mechanism of dismutation reaction with dimanganese complexes. 7
Scheme 3.2  Schematic procedure of Mn-Hybrid.

Figure 3.2 IR spectra of (a) Triethoxysilane, (b) Mn-STM and (c) Mn-TES.
Figure 3.3 ESR spectra of (a) Mn-STP and (b) Mn-TES.

Figure 3.4 IR spectra of (a) Mn-TES and (b) Mn-hybrid.
Figure 3.5. Time-conversion plot for hydrogen peroxide decomposition catalysis of Mn-hybrid and Mn-ETP after 5-min and 24-h treatments under acidic conditions at 80°C: black circle: Mn-hybrid after 5-min treatment; black square: Mn-hybrid after 24-h treatment; broken line: Mn-ETP after 5-min treatment; dashed line: Mn-ETP after 24-h treatment.
Chapter 4

Preparation of Porous Ti-O-P Hybrid Derived from 1,4-Bis(phosphono)benzene and TiCl$_4$ via a Non-Hydrolytic Sol-Gel Process
4.1. Introduction

Porous inorganic-organic hybrid materials have been studied extensively and can be obtained as amorphous materials, pillared-layered materials, and metal-organic frameworks (MOFs).\textsuperscript{1-3} A sol-gel process, a \textit{Chimie Douce} approach involving hydrolysis and condensation reactions under mild conditions, is a particularly convenient and useful approach. Sol-gel-derived class II hybrid materials are usually prepared by co-hydrolysis of organoalkoxysilane [R\textsuperscript{'}\textsubscript{n}Si(OR)\textsubscript{4-n}, R, R\textsuperscript{'}, organic group, n=1, 2] and tetraalkoxysilane [Si(OR)\textsubscript{4}], because it is difficult for the majority of organoalkoxysilanes to form gel via hydrolysis and condensation.\textsuperscript{4, 5} The advantages of these hybrid materials are homogeneous dispersion of organic moieties in siloxane networks and thermal stability that is improved with respect to those of corresponding organic materials.\textsuperscript{6, 7} Bridged-type precursors, which consist of multiple trialkoxysilyl groups and organic spacers with a typical formula [(RO)\textsubscript{3}Si-R\textsuperscript{'}-Si(OR)\textsubscript{3}, R, R\textsuperscript{'}; organic group], can be used for preparation of porous hybrid materials called bridged polysilsesquioxanes, which possess high specific surface areas.\textsuperscript{4, 5, 8} The use of bridged-type precursors enables organic groups to be immobilized in the pore structures of the final hybrid materials, suggesting highly homogeneous dispersion and high accessibility of the organic groups. Thus, many functional organic groups have been introduced into inorganic networks, and the resultant hybrids have been applied in many fields such as catalysts, adsorbents and electrical and optical devices.\textsuperscript{9-11} High periodicity has been achieved by using structure-directing reagents such as amphipathic block copolymers\textsuperscript{12}, surfactants\textsuperscript{13}, and ionic liquids\textsuperscript{14, 15}, leading to the formation of periodic mesoporous organosilicas (PMOs)\textsuperscript{14, 15}. Porous hybrid materials can also be obtained from bridged-type
precursors bearing rigid organic groups with no use of structure-directing reagents.

The development of non-silica hybrid materials is very important for expanding the variations of inorganic frameworks, and metal-oxygen-phosphorus (M-O-P) network-based class II hybrid materials are promising, since various metals form M-O-P bonds and the P-C bonds are sufficiently stable. To date, various M-O-P-based class II hybrid materials have been prepared. 16-23 Organodiphosphonic acids [(HO)₂OP-R-PO(OH)₂; R: organic group] can also form M-O-P networks with various types of metals and enable immobilization of organic groups into metal-oxygen-phosphorus networks homogeneously.24-29 Among M-O-P hybrids, Ti-O-P hybrids are especially attractive, because Ti-O-P bonds are formed easily with various organodiphosphonic acids via a non-hydrolytic sol-gel process.24

In this chapter, we demonstrated template-free synthesis of porous Ti-O-P hybrids from phenylene-bridged diphosphonic acid and titanium tetrachloride via a non-hydrolytic sol-gel process, and estimated their specific surface areas.

4.2. Experimental section

General information All manipulations were carried out under an inert atmosphere using standard Schrenk techniques or a glove box filled with nitrogen.30 The reagents were used as received. Solvents were purified by conventional procedures before use. All liquid-state ¹H, ¹³C and ³¹P NMR spectra were obtained with a JEOL JNM-EX500 instrument at 500.00 MHz, 125.65MHz, and 128.27 MHz, respectively. The chemical shifts are referenced to tetramethylsilane (TMS) for ¹H and ¹³C and to 85% H₃PO₄ (external) for ³¹P nuclei. Solid-state ³¹P MAS NMR
spectra were recorded with a JEOL ECX-400 spectrometer with magnetic angle spinning techniques at 128.27 MHz (pulse delay, 5 s; pulse width, 3.3 μs; spinning rate, 14.1 kHz). The chemical shifts are referenced to external H₃PO₄. Fourier-transfer infrared (FT-IR) spectra were measured with a JASCO FT/IR-460 spectrometer. The XRD patterns were recorded with a Rigaku RINT-1100 diffractometer with Mn-filtered FeKα radiation. Thermogravimetry (TG) analyses were performed with a Perkin-Elmer TGA7 instrument from 50 to 800°C at a heating rate of 20°C min⁻¹ under an air flow. Energy dispersive X-ray spectrometry (EDX) analysis was performed with a Hitachi S-3000N microscope. Elemental analysis was performed with a Perkin-Elmer PE2400 II instrument. Field emission scanning electron microscopic (FE-SEM) images were taken with a Hitachi S-4500S microscope.

Nitrogen adsorption-desorption isotherms were measured by Prof. Kazuki Nakanishi at Kyoto University in Japan. The isotherms were recorded with a Bel Japan Inc. BELSORP-max. The samples were degassed at 150°C for 2.5 h under vacuum before N₂ adsorption−desorption measurement.

Raman spectra were measured at the Institut Charles Gerhardt of Université de Montpellier 2 (ICG-UM2) in France. The spectra were recorded with a HORIBA LabRAM ARAMIS IR2 with a blue diode laser at 473 nm.

Computational simulation was conducted by Prof. Hisako Sato at Ehime University in Japan. The simulation was carried out with a Gaussian Revision-A 02 by DFT level (B3LYP functional with Stuttgart ECP for Ti and 6-31G(d,p) for other atoms).
Synthesis of 1,4-bis(phosphono)benzene  

The ester of 1,4-bis(phosphono)benzene [(EtO)₂OP(C₆H₄)PO(OEt)₂; BPB ester] was synthesized from 1,4-dibromobenzene via the Michaelis-Arbuzov reaction. Triethylphosphate [P(OEt)₃] was added dropwise to 1,4-dibromobenzene with nickel chloride as a catalyst at 170°C, and ethylbromide, a by-product, was thoroughly eliminated. The molar ratio of triethylphosphate to 1,4-dibromobenzene was 3:1 and that of 1,4-dibromobenzene to nickel chloride was 30:1. After triethylphosphate was added, the solution was refluxed for 2 h and cooled down to ambient temperature. Hexane was added to the solution and the resulting solution was refluxed for approximately 5 min. The solution was then cooled down slowly, and white needle-like crystals of BPB ester were obtained. The characterization of the BPB ester was as follows: \(^{1}H\) NMR (500 MHz, CDCl₃), \(\delta\) (ppm): 1.25 (t, 12H, OCH₂CH₃), 4.05 (m, 8H, OCH₂CH₃), 7.87 (q, 4H, C₆H₄). \(^{31}P\) NMR (202.35 MHz, CDCl₃), \(\delta\) (ppm): 18.6.

The BPB ester was then hydrolyzed with concentrated hydrochloric acid at 80°C for 24 h. The solution was cooled down to ambient temperature and concentrated to obtain a slightly yellow powder. The characterization of BPB was as follows: \(^{1}H\) NMR (500 MHz, D₂O), \(\delta\) (ppm): 7.51 (q, C₆H₄). \(^{13}C\{\(^{1}H\}\) NMR (125.65 MHz, D₂O), \(\delta\) (ppm): 133.3 (o, d, \(J_{pc}=11.37\) Hz), 136.4 (m, d, \(J_{pc}=13.70\) Hz), 137.2 (ipso, d, \(J_{pc}=181.90\) Hz). \(^{31}P\) NMR (202.35 MHz, D₂O), \(\delta\) (ppm): 18.4. Elemental analyses exhibited experimental values for carbon and hydrogen of 30.4 wt% and 3.3 wt%, respectively. These values corresponded to the theoretical values; C (30.3 wt%) and H (3.4 wt%). The synthesis procedure for BTB is shown in Scheme 4.1.
Synthesis of Phenylene-bridged TiOP hybrids

Phenylene-bridged TiOP hybrids (abbreviated as Ph-TiOP hybrids) were synthesized from titanium tetrachloride (TiCl₄) and BPB via a non-hydrolytic sol-gel process²⁶,²⁷,³⁴ with distilled dimethyl sulfoxide (DMSO) in a glove box. In a typical synthesis, TiCl₄ was added dropwise to a half volume of total DMSO with vigorous stirring, since dissolution of TiCl₄ into DMSO to form a TiCl₄-DMSO complex is highly exothermic.³⁵,³⁶ BPB was also dissolved in the other half volume of DMSO, and the molar concentration of phosphonic acid group was fixed at 0.5 mol/L. The TiCl₄-DMSO solution was added to a BPB-DMSO solution under vigorous stirring to obtain a homogeneous solution. The resultant solution was stirred for additional 30 seconds, and then transported into an ampule. The solution became a transparent yellow gel within 3 min. The gel was aged for 1-5 days at 80°C, becoming turbid and whitening gradually during aging. After washing with distilled water and ethanol, it was dried under a vacuum. The P/Ti ratio was fixed at 2. Hybrids with aging periods of 1, 3 and 5 days were abbreviated as Ph-TiOP_1D, Ph-TiOP_3D, and Ph-TiOP_5D, respectively. The synthetic procedure is shown in Scheme 4.2.

4.3. Results and Discussion

The evolution of Ti-O-P networks with aging time was monitored using solid-state ³¹P MAS NMR (Figure 4.1). A ³¹P MAS NMR spectrum of the TiOP_1D (Figure 4.1, solid line) exhibited two broad signals at 12 and -3 ppm, and the signal at 12 ppm had shoulders on both sides (about 18 and 4 ppm). As the ³¹P NMR signal of BPB was observed at 18 ppm and larger upfield shifts were reported
for increasing numbers of Ti-O-P bonds, the broad 18-ppm signal was assignable to the -PO(OH)$_2$ environment and the 12, 4 and -3-ppm signals to the -PO(OH)(OTi), -PO(OTi)$_2$ and -P(OTi)$_3$ environments, respectively. The intensity of this signal increased with prolongation of the aging period. The intensities of the downfield signals also decreased gradually, suggesting that Ti-O-P bonds formed during aging.

The Ph-TiOP hybrids were further analyzed by FT-IR (Figure 4.2). Compared with the spectrum of BPB, the spectrum of Ph-TiOP$_{1D}$ (Figure 4.2(b)) showed the disappearance of $\nu$(P-OH) (1040-940 cm$^{-1}$) and $\nu$(PO-H) (2700-2100 cm$^{-1}$) bands originating from BPB (Figure 4.2(a)). New adsorption bands due to the $\nu$(P-O) (1100-900 cm$^{-1}$) mode were observed, on the contrary, in the spectra of Ph-TiOP$_{1D}$, Ph-TiOP$_{3D}$ and Ph-TiOP$_{5D}$, indicating of the formation of Ti-O-P bonds. New adsorption bands of the $\nu$(Ti-O) (950-700 cm$^{-1}$ and 600-400 cm$^{-1}$) modes were also observed in Ph-TiOP$_{1D}$, and these decreased as the length of the aging time increased, indicating that the amounts of the remaining Ti-Cl groups decreased before the hydrolysis process. As the adsorption bands of the $\nu_{ar}$(C=C) (1650-1430 cm$^{-1}$), $\omega_{ar}$(C-H) (830-810 cm$^{-1}$), and $\nu$(P-C) (ca. 1394 cm$^{-1}$) modes originating from BPB were observed in the spectra of the Ph-TiOP hybrids, the BPB moieties were clearly immobilized into the Ph-TiOP hybrids.

The Raman spectra of all the Ti-O-P hybrids showed similar profiles (Figure 4.3). New bands of $\nu$(P-O) (1100-1000 cm$^{-1}$) and $\nu_{s}$(O-P-O) (780-710 cm$^{-1}$) were assignable to the Ti-O-P bonds [Figures 4.3(b)-(d)]. Weak $\nu$(P=O) bands (1280-1240 cm$^{-1}$) observed in all the Ph-TiOP hybrids, indicating that a limited number of phosphoryl groups still remained. Weak band of the $\nu_{as}$(C-H)
(3100-3000 cm\(^{-1}\)) mode originating from BPB were observed in the spectra of the Ti-O-P hybrids, suggesting that the BPB moieties were immobilized into the Ph-TiOP hybrids. \(^{41}\)

The XRD patterns of the Ph-TiOP hybrids were shown in Figure 4.4. All the hybrids exhibited the appearance of a broad diffraction \((d\approx2.3\;\text{nm})\) and a sharp diffraction \((d=0.95\;\text{nm})\). The sharp diffraction was assignable to the distance of the two titanium atoms connecting to BPB, and the broad diffraction suggested weak periodicity of the porous structure.\(^{44}\) As the profiles of two diffractions were very similar in the XRD patterns of these three hybrids, the local periodicities showed similarity regardless of the aging time.

The nitrogen (N\(_2\)) adsorption-desorption isotherms were shown in Figure 4.5. All the curves of the hybrids were type IV isotherms, which are characteristic to meso- and macro-porous materials.\(^{45,46}\) The specific surface areas of Ph-TiOP\(_{1}\)D, Ph-TiOP\(_{3}\)D, and Ph-TiOP\(_{5}\)D were 286, 308, and 159 m\(^2\) g\(^{-1}\), respectively. These results were higher than those reported for metal phosphonates prepared with no use of templates, such as mesoporous titanium pentaphosphonate derived from diethylene triamine penta(methylene phosphonic acid) (128 m\(^2\) g\(^{-1}\))\(^{47}\) and titanium tetraphosphonate derived from dendritic tetrakis-1,3,5,7-(4-phosphonatophenyl) adamantine (117 m\(^2\) g\(^{-1}\)).\(^{28}\) In addition, the total pore volumes measured near saturation were 0.28 cm\(^3\) g\(^{-1}\) (P/P\(_0\)=0.985), 0.35 cm\(^3\) g\(^{-1}\) (P/P\(_0\)=0.989), and 0.17 cm\(^3\) g\(^{-1}\) (P/P\(_0\)=0.987), respectively. These results were also comparable to those of previously reported mesoporous titanium pentaphosphonate (0.28 cm\(^3\) g\(^{-1}\))\(^{47}\) and titanium tetraphosphonate (0.42 cm\(^3\) g\(^{-1}\)).\(^{28}\)

The SEM images of Ph-TiOP\(_{1}\)D, Ph-TiOP\(_{3}\)D, and Ph-TiOP\(_{5}\)D were
shown in Figure 4.6. All the hybrids exhibited an aggregation of fine particles from sponge-like surfaces. There were no obvious differences among the samples with respect to aging time.

The thermogravimetry (TG) analyses were shown in Figure 4.7. The TG analyses exhibited mass losses of Ph-TiOP_1D, Ph-TiOP_3D, and Ph-TiOP_5D of 22.4, 24.2 and 27.5 wt%, respectively, in the range of 250-600°C due to the loss of the phenylene group. SEM-EDX analyses indicated that the P/Ti ratios of Ph-TiOP_1D, Ph-TiOP_3D, and Ph-TiOP_5D were 2.16, 2.27, and 2.30, respectively. With the results of the TG and EDX analyses taken into consideration, the empirical chemical formulae of Ph-TiOP_1D, Ph-TiOP_3D, and Ph-TiOP_5D were determined to be TiP_{2.16}O_{6.48}H_{0.32}(C_6H_4)_{1.08}, TiP_{2.28}O_{6.84}H_{0.56}(C_6H_4)_{1.14}, and TiP_{2.30}O_{6.90}H_{0.60}(C_6H_4)_{1.15}. These results indicated that a limited amount of Ti was lost during aging at 80°C.

A possible micro-environment was simulated, as shown in Figure 4.8. When a four-membered ring in which the phosphonic acid moiety of BPB was bound to one titanium ion in a bidentate manner was assumed, the corresponding calculated Raman spectrum did not correspond to the observed Raman spectrum of the Ph-TiOP hybrids. A stable simulated environment contains two BPB moieties, whose edges are linked by two titanium ions. The calculated Raman spectrum of this simulated environment [Figure 4.3 (a)] partly corresponded (as indicated by the bands marked with asterisks) to those of the Ph-TiOP hybrids [Figures 4.3 (b)-(d)], suggesting that all the hybrids could contain this type of environment. The distance between two titanium atoms was approximately 0.92 nm, corresponding to the sharp XRD diffraction ($d=0.95$ nm).
All the Ph-TiOP hybrids formed homogeneous gels in this system. It has already been reported that non-bridged-type precursors $R'_{n}Si(OR)_{4-n}$, $R$, $R'$; organic group, $n=1$ or 2, scarcely form gels via hydrolysis without the presence of tetraalkoxy silanes,\textsuperscript{36, 37} whereas bridged-type precursors $[R'[Si(OR)_{3}]_{n}$, $R$, $R'$; organic group, $n\geq 2$] can form homogeneous gels easily upon hydrolysis.\textsuperscript{4} When rigid bridged-type precursors, such as those with phenylene and biphenylene spacers, are used, for example, they form homogeneous gels easily at concentrations lower than those required for tetraethoxysilane.\textsuperscript{4} Similar to bridged polysilsesquioxane, phenylene-bridged diphosphonic acid also enable formation of a homogeneous gel upon reaction with a metal compound. A homogeneous Ti-O-P hybrid gel can also be obtained from a similar precursor possessing a flexible organic spacer, an oligomeric ethylene oxide chain.\textsuperscript{48}

The relatively high specific surface areas of the Ph-TiOP hybrids were partly due to the rigidity of the phenylene spacer. In the case of bridged polysilsesquioxanes derived from 1,4-bis(triethoxy)benezene with no use of templates, the resultant bridged polysilsesquioxanes possessed high specific surface areas, whose exact values depended on the reaction conditions.\textsuperscript{8} The rigid phenylene spacer thus played an important role in forming the mesoporous structure during a hydrolytic sol-gel process.\textsuperscript{4} On the other hand, Ph-TiOP hybrids also formed porous structures with no use of templates via a non-hydrolytic sol-gel process. Neumann prepared porous titanium and vanadium tetraphosphonate materials with narrow pore size distribution via a non-hydrolytic condensation of metal alkoxide and dendritic tetraphosphonic acid with no use of templates.\textsuperscript{29, 28} In the present system, porous Ti-O-P hybrids were obtained easily without the use of
precursors bearing complex rigid organic spacers; porous structures were formed via condensation between phenylene-bridged diphosphonic acid and TiCl₄ with no use of a template and water. The specific surface areas of the Ph-TiOP hybrids were comparable to those reported in similar previous studies.²⁸,²⁹

4.4. Conclusions

In this chapter, phenylene-bridged titanium phosphonates were prepared via a non-hydrolytic sol-gel process via formation of a TiCl₄-DMSO complex. The condensation of phosphonic acids of the Ti-O-P hybrids proceeded gradually during aging. The specific surface areas of the resultant hybrids were high despite the fact that no structure-directing reagent was used. The values increased for up to 3 days, indicating a dependence on aging time. The combination of diphosphonic acid and TiCl₄ is excellent for the preparation of porous class II inorganic-organic hybrids.

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Scheme 4.1 Synthetic procedure of BPB.

Scheme 4.2 Synthetic procedure of Ph-TiOP hybrid via a non-hydrolytic sol-gel process.
Figure 4.1 $^{31}$P MAS NMR spectra of Ph-TiOP hybrids; solid line: Ph-TiOP_1D, dotted line: Ph-TiOP_3D, and broken line: Ph-TiOP_5D.

Figure 4.2 IR spectra of (a) BPB and (b)-(d) Ph-TiOP hybrids: (b) Ph-TiOP_1D, (c) Ph-TiOP_3D, and (d) Ph-TiOP_5D.

Figure 4.3 Raman spectra of (a) simulated Ph-TiOP and (b)-(d) Ph-TiOP hybrids: (b) Ph-TiOP_1D, (c) Ph-TiOP_3D, and (d) Ph-TiOP_5D.
Figure 4.4  XRD patterns of (a)-(c) Ph-TiOP hybrids: (a) Ph-TiOP _1D, (b) Ph-TiOP_3D, and (c) Ph-TiOP_5D.

Figure 4.5  Nitrogen adsorption-desorption isotherms of (a)-(c) Ph-TiOP hybrids: (a) Ph-TiOP _1D, (b) Ph-TiOP_3D, and (c) Ph-TiOP_5D. White circle: adsorption and black circle: desorption isotherm.

Figure 4.6  SEM images of (a)-(c) Ph-TiOP hybrids: (a) Ph-TiOP _1D, (b) Ph-TiOP_3D, and (c) Ph-TiOP_5D.
Figure 4.7  Thermogravimetry analyses of Ph-TiOP hybrids: solid line: Ph-TiOP_1D, dotted line: Ph-TiOP_3D, and broken line: Ph-TiOP_5D.

Figure 4.8  Simulated structure of a Ph-TiOP hybrid: red ball: oxygen, small white ball: hydrogen, gray ball: carbon, blue ball: titanium, and orange ball: phosphorus.
Chapter 5

Preparation of LiClO$_4$-doped Titanium Organodiphosphonates Possessing Oligomeric Ethylene Oxide Chains and Their Ionic Conductivity
5.1 Introduction

Solid polymer electrolytes (SPEs) have attracted considerable attention for their applications in lithium-ion batteries. Poly(ethylene oxide) (PEO) is an excellent polymer matrix for SPEs, because its ether oxygen atoms coordinate easily with lithium ions, leading to excellent ionic conductivity. As Li$^+$-ion transport is thought to be caused by segment movement of ethylene oxide chains, PEO’s amorphous state must remain flexible over a wide temperature range. Unfortunately, the mobility of PEO chains decreased below the crystallization temperature (~60°C), and ionic conductivity is thus decreased below the crystallization temperature. One strategy for solving this issue involves efforts to suppress PEO crystallization through the addition of inorganic nanoparticles and the introduction of PEO into confined media. Another strategy is the use of oligomeric ethylene oxide chains, since oligomeric ethylene oxide chains are essentially sufficient for complex formation with lithium ions. Thus, oligomeric ethylene oxide chains have been bound to flexible polymers, such as polysiloxanes, rigid mesogen structures, and inorganic nanoparticles such as SiO$_2$ and nanosheets. An advantage of this strategy is complete crystallization suppression.

Besides the addition of inorganic particles, cross-linked structures prepared by condensation between crosslinkers and compounds bearing oligomeric ethylene oxide chains have been utilized to improve mechanical properties of SPEs. Thus, immobilization of oligomeric ethylene oxide chains into inorganic networks should be an interesting approach to preparing inorganic-organic hybrids exhibiting both ionic-conductivity and better mechanical properties. Organophosphonic acids [R-PO(OH)$_2$; R:organic group] can form metal-oxygen-phosphorus networks with
various types of metals, and the use of organodiphosphonic acids \[(\text{HO})_2\text{OP}-\text{R-PO(OH)}_2; \text{R:organic group}\] enables immobilization of organic groups in metal-oxygen-phosphorus networks homogeneously.\(^{19-23}\) Crystallization of oligomeric ethylene oxide chains immobilized in inorganic networks can be expected to be suppressed irrespective of the temperature, moreover, leading to relatively high ionic conductivity, even at ambient temperatures.

This chapter describes the preparation of hybrids possessing oligomeric ethylene oxide chains and Ti-O-P networks \em via\ a non-hydrolytic sol-gel process,\(^{24}\) with Li\(^+\) ion conductivity estimated at ambient temperatures after LiClO\(_4\) doping.

### 5.2 Experimental Section

**Materials.** The reagents were used as received, and the solvents were purified by conventional procedures before use.

**Instruments.** Liquid-state \(^1\text{H}, \ ^{13}\text{C}\) and \(^{31}\text{P}\) NMR spectra were obtained on a JEOL JNM-EX500 spectrometer at 500.00 MHz, 125.65MHz, and 128.27 MHz, respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for \(^1\text{H}\) and \(^{13}\text{C}\) and to external 85\% H\(_3\)PO\(_4\) for \(^{31}\text{P}\) nuclei. Solid-state \(^{31}\text{P}\) magic-angle-spinning (MAS) NMR spectra were recorded with a JEOL ECX-400 spectrometer. Chemical shifts were referenced to external H\(_3\)PO\(_4\). The frequency was 128.27 MHz, and the pulse width was 3.3 \(\mu\)s. Fourier-transfer infrared (FT-IR) spectra were measured with a JASCO FT/IR-460 spectrometer. Raman spectra were recorded with a RENISHOW inVia spectrometer.
Preparation of 3,6,9-Trioxaundecane-1,11-diphosphonic acid ester (TDA ester).

All the manipulations were carried out under an inert atmosphere using standard Schrenk techniques or in a glove box filled with nitrogen. Organodiphosphonic acid bearing oligomeric ethylene oxide chains, 3,6,9-trioxaundecane-1,11-diphosphonic acid [(HO)₂OP(C₂H₄O)₃C₂H₄PO(OH)₂; TDA], was prepared via a hydrolysis reaction from TDA ester which was synthesized from 1,11-dibromo-3,6,9-trioxaundecane via a Michaelis-Arbuzov reaction.

Preparation of 1,11-dibromo-3,6,9-trioxaundecane was performed as reported previously. The characterization results of 1,11-dibromo-3,6,9-trioxaundecane were as follows: ¹H NMR (500 MHz, CDCl₃), δ(ppm): 3.43 (t, 4H, BrCH₂C₂H), 3.45 (t, 4H, BrCH₂C₂H), 3.68 (m, 8H, OCH₂C₂H); ¹³C NMR (125.65 MHz, CDCl₃), δ(ppm): 30.1 (BrCH₂), 70.7-70.9 (OCH₂C₂H₂), 71.3 (BrCH₂C₂H₂).

TDA ester was synthesized from 1,11-dibromo-3,6,9-trioxaundecane and triethylphosphite via a Michaelis-Arbuzov reaction under an inert atmosphere. The characterization results of 3,6,9-trioxaundecane-1,11-diphosphonic acid (TDA) ester were as follows: ¹H NMR (500 MHz, CDCl₃), δ(ppm): 1.33 (t, 12H, OCH₂C₂H₃), 2.13 (m, 4H, PCH₂), 3.61 (m, 8H, OCH₂C₂H₂O), 3.72 (m, 4H, PCH₂C₂H₂), 4.10 (m, 4H, OCH₂C₂H₃); ¹³C NMR (125.65 MHz, CDCl₃), δ(ppm): 16.4 (OCH₂C₂H₃), 27.5 (d, ¹J(¹³C-³¹P)=139 Hz, PCH₂), 61.6 (d, ²J(¹³C-³¹P)=6.2 Hz, PCH₂C₂H₂O), 65.2 (OCH₂C₂H₃), 70.5 (OCH₂C₂H₂O); ³¹P NMR (202.35 MHz, CDCl₃), δ(ppm): 30.2.

Preparation of 3,6,9-Trioxaundecane-1,11-diphosphonic acid (TDA).

TDA ester was further hydrolyzed with concentrated hydrochloric acid at 80°C for 48 h. The solution was then cooled down and concentrated to obtain a slightly
yellow transparent viscous liquid. TDA was dried in a vacuum before use. The characterization results of 3,6,9-trioxaundecane-1,11-diphosphonic acid (TDA) were as follows: $^1$H NMR (500 MHz, D$_2$O), $\delta$(ppm): 2.17 (m, 4H, PCH$_2$), 3.81 (m, 8H, OCH$_2$CH$_2$O), 3.82 (m, 4H, PCH$_2$CH$_2$); $^{13}$C NMR (125.65 MHz, D$_2$O), $\delta$(ppm): 28.0 (d, $^1$$J$($^{13}$C-$^{31}$P)=133 Hz, PCH$_2$), 65.7 (PCH$_2$CH$_2$O), 70.0-70.3 (OCH$_2$CH$_2$O); $^{31}$P NMR (202.35 MHz, CDCl$_3$), $\delta$(ppm): 31.4.

**Preparation of Ethylene-oxide-bridged TiOP hybrids.** All the manipulations were carried out under an inert atmosphere using standard Schrenk techniques or in a glove box filled with nitrogen.$^{25}$ An Ethylene-oxide-bridged TiOP hybrid (abbreviated as EO-TiOP) was synthesized from titanium tetrachloride (TiCl$_4$) and dried TDA in distilled dimethyl sulfoxide (DMSO) via the non-hydrolytic sol-gel process involving no water (Scheme 5.1).$^{19}$ In a typical preparation, half the total volume of DMSO was added slowly to TiCl$_4$ in CH$_2$Cl$_2$ (1.0 mol/L solution) dropwise with vigorous stirring, since dissolution of TiCl$_4$ in DMSO is highly exothermic.$^{28}$ After formation of a TiCl$_4$-DMSO complex, the CH$_2$Cl$_2$ was removed under reduced pressure. TDA was also dissolved in the other half volume of DMSO, and the molar concentration of the phosphonic acid group was fixed at 1.0 mol/L. The TiCl$_4$-DMSO solution was added to the TDA-DMSO solution under conditions of vigorous stirring to obtain a homogeneous solution, which was stirred for 5 minutes to form a transparent yellow gel. The gel was aged for 3 days, during which it became turbid and whitened gradually. After washing with CH$_2$Cl$_2$, distilled water, ethanol, distilled ethanol, and distilled acetonitrile, it was dried in a vacuum to obtain an EO-TiOP hybrid. The P/Ti ratio was fixed at 2.
LiClO$_4$ doping to EO-TiOP hybrids. Anhydrous lithium perchlorate (LiClO$_4$) was dissolved in dry acetonitrile, and EO-TiOP hybrid was added to the resultant solution. The [EO]:Li molar ratios were 5:1, 10:1 and 20:1, since it is generally accepted that Li$^+$ ions are typically coordinated by 4 ether oxygen atoms in Li-PEO complexes$^{29-31}$ and the maximum conductivity value was frequently observed at larger [EO]/Li ratios.$^1$ After refluxing for 24 h at 80$^\circ$C and vacuum drying, LiClO$_4$-doped EO-TiOP hybrids were obtained.

The ac impedance measurement. The LiClO$_4$-doped EO-TiOP hybrids were pressed into pellets, whose diameters and thicknesses were 1.1 cm and 0.1-0.45 cm, respectively. The pellets were placed between two Ni blocking electrodes at ambient temperatures. The ac impedance spectra were measured in the constant voltage mode at open circuit potential.$^{32}$ The frequency of all the measurements was in the range of 1MHz to 0.1 Hz with an ac amplitude of 10 mV at ambient temperatures.

5.3. Results and discussion

EO-TiOP hybrid possessing oligomeric ethylene oxide chains. A phosphorus environment of the EO-TiOP hybrid was investigated using solid-state $^{31}$P MAS NMR (Figure 5.1(a)). A $^{31}$P MAS NMR spectrum of the EO-TiOP hybrid exhibits three broad signals at 31, 23 and 12 ppm. Since $^{31}$P NMR signal of TDA was observed at 31.6 ppm and larger upfield shifts were reported for increasing numbers of Ti-O-P bonds,$^{19,20,33}$ the 31-ppm signal is assignable to $-PO(OH)_{2}$ environment and the 23- and 12-ppm signals are assignable to $-PO(OH)(OTi)$ and $-PO(OTi)_{2}$
environments, respectively. Since the main signal is observed at 23 ppm, a large portion of the phosphonic acid moieties forms one Ti-O-P bond.

The FT-IR spectrum of the EO-TiOP hybrid (Figure 5.2(b)) shows the disappearance of $\nu$(P-OH) (1040-940 cm$^{-1}$)$^{34}$ band originating from TDA (Figure 5.2(a)). New adsorption bands due to $\nu$(P-O) (1100-900 cm$^{-1}$) and $\nu$(Ti-O) (950-700 cm$^{-1}$ and 600-400 cm$^{-1}$) modes$^{35}$ on the contrary, are observed in the spectrum of the EO-TiOP hybrid, indicating the formation of Ti-O-P bonds.$^{22}$ Since adsorption bands due to $\nu$(C-H) (ca. 2950 cm$^{-1}$) and $\nu$(P=O) (1260-1240 cm$^{-1}$)$^{34}$ originating from TDA were observed in the spectrum of the EO-TiOP hybrid, ethylene oxide chains were clearly present in the EO-TiOP hybrid.

**LiClO$_4$-doping EO-TiOP hybrids.** The solid-state $^{31}$P MAS NMR spectra of all the LiClO$_4$-doped EO-TiOP hybrids [Figures 5.1(b)-5.1(d)] exhibit profiles similar to that of the EO-TiOP hybrid, indicating that LiClO$_4$ doping does not affect the Ti-O-P network structure. In the FT-IR spectra of the LiClO$_4$-doped EO-TiOP hybrids, new bands assignable to $\nu$(Cl-O) (636 cm$^{-1}$) appear in all the spectra, indicating the presence of ClO$_4^-$ ions [Figures 5.2(c)-5.2(e)].$^{34}$ It is generally accepted that the coordination of ether oxygen atoms to metal ions resulted in the shift of $\nu$(C-O-C) bands to lower frequencies,$^{36,37}$ and a new band for the Li$^+$-PEO complex appeared at 1089 cm$^{-1}$.$^{37}$ Thus, the appearance of a new band at 1090 cm$^{-1}$ in the spectrum of the LiClO$_4$-doped EO-TiOP hybrid with [EO]:Li=5:1 strongly suggests the coordination of the ether oxygen atoms to Li$^+$ ions.$^{37}$ The absence of an original $\nu$(C-O-C) band in the spectrum of the EO-TiOP hybrid appears to be due to overlapping with the $\nu$(P-O) band.
The Raman spectra of the LiClO$_4$-doped EO-TiOP hybrids are shown in Figures 5.3(c)-5.3(e). ClO$_4^-$ ion environments can be discussed on the basis of the position of the $v_1(A_1)$ band; the band at 933 cm$^{-1}$ is assignable to free ClO$_4^-$ ions, while the bands at 937 and 925 cm$^{-1}$ are due to contact ion pairs, Li$^+$-..ClO$_4^-$, and aggregates, respectively. In addition, the $v_1(A_1)$ bands of ClO$_4^-$ ions in LiClO$_4$ and LiClO$_4$-3H$_2$O are observed at 962 cm$^{-1}$ and 935 cm$^{-1}$, respectively [Figures 5.3(a) and 5.3(b)]. The $v_1(A_1)$ bands in the spectra of the LiClO$_4$-doped EO-TiOP hybrids with [EO]:Li=5:1, [EO]:Li=10:1 and [EO]:Li=20:1, on the contrary, are observed at 932 cm$^{-1}$, indicating the presence of free ClO$_4^-$ ions. These results strongly suggest that the isolation of ClO$_4^-$ ions is caused by the coordination of oxygen atoms of oligomeric ethylene oxide chains to Li$^+$ ions, results consistent with the IR observation. Based on these results and the typical Li$^+$ ion environment in PEO matrices, a typical local environment in the LiClO$_4$-doped EO-TiOP hybrids is proposed as shown in Figure 5.4.

The ionic conductivity values of the LiClO$_4$-doped EO-TiOP hybrids with [EO]:Li=5:1, [EO]:Li=10:1 and [EO]:Li=20:1 at ambient temperatures were 3.1×10$^{-5}$, 3.0×10$^{-5}$ and 1.9×10$^{-5}$ S cm$^{-1}$, respectively, listed in Table 5.1. The observed values are comparable to the following ionic conductivity values previously reported for Li$^+$-ion conductors possessing oligomeric ethylene oxide chains: 2.1×10$^{-8}$ S cm$^{-1}$ (10°C) and 1.1×10$^{-5}$ S cm$^{-1}$ (40°C) for oligomeric ethylene oxide chains grafted SiO$_2$ nanoparticles, up to the 10$^{-5}$ S cm$^{-1}$ range (ambient temperatures) for oligomeric ethylene oxide chains bound to layered zirconium phosphate, and up to the 10$^{-4}$ S cm$^{-1}$ range (ambient temperature) for oligomeric ethylene oxide chains connected to siloxane networks. The values in the present study are also comparable to the
ionic conductivity values of Li-doped cross-linked polymers possessing oligomeric ethylene oxide chains, up to the $10^{-4}$ S cm$^{-1}$ range at ambient temperatures.$^{40-42}$ Thus, these results indicate that oligomeric ethylene oxide chains immobilized in the Ti-O-P networks can be a medium for Li$^+$ ion transport to a degree comparable to that of other materials possessing oligomeric ethylene oxide chains.

### 5.4. Conclusions

This chapter exhibits that the Ti-O-P hybrids possessing oligomeric ethylene oxide chains were prepared from titanium tetrachloride and an organodiphosphonic acid possessing a $(C_2H_4O)_3$ group, 3,6,9-trioxaundecane-1,11-diphosphonic acid, via the non-hydrolytic sol-gel process, and that LiClO$_4$ was successfully doped to the Ti-O-P hybrid with [EO]:Li=5:1, 10:1, and 20:1. After doping of LiClO$_4$ to the hybrids, the Li$^+$ ions are likely to be solvated by the ether oxygen atoms, as shown by the presence of $\nu$(C-O-C) bands (at around 1090 cm$^{-1}$ for [EO]:Li=5:1) and the isolation of ClO$_4^-$ ions shown by Raman spectroscopy. Ionic conductivities at ambient temperatures were in the range of from $1.9\times10^{-5}$ to $3.1\times10^{-5}$ S cm$^{-1}$. These results clearly suggest that Ti-O-P hybrids possessing immobilized oligomeric ethylene oxide chains can be possible candidates for materials employable for solid polymer electrolytes.
References

5. B. Scrosati, F. Croce and S. Panero, J. Power Sources, 2001, 100, 93.


Scheme 5.1 Non-hydrolytic sol-gel processes for EO-TiOP hybrid.

Figure 5.1 $^{31}$P MAS NMR spectra of (a) EO-TiOP and (b)-(d) LiClO$_4$-doped EO-TiOP; (b) [EO]:Li=20:1, (c) [EO]:Li=10:1, and (d) [EO]:Li=5:1.
Figure 5.2 FT-IR spectra of (a) TDA and (b) EO-TiOP, (c)-(e) LiClO$_4$-doped TiOP; (c) [EO]:Li=20:1, (d) [EO]:Li=10:1, and (e) [EO]:Li=5:1.

Figure 5.3 Raman spectra of (a) LiClO$_4$, (b) EO-TiOP, and (c)-(e) LiClO$_4$-doped EO-TiOP; (c) [EO]:Li=20:1, (d) [EO]:Li=10:1, and (e) [EO]:Li=5:1.
Table 5.1  Ionic conductivity values of the LiClO₄-doped EO-TiOP hybrids.

<table>
<thead>
<tr>
<th>[EO]:Li ratio of EO-TiOP hybrid</th>
<th>$\sigma/10^{-5}$ S cm⁻¹</th>
</tr>
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<tbody>
<tr>
<td>5:1</td>
<td>3.1</td>
</tr>
<tr>
<td>10:1</td>
<td>3.0</td>
</tr>
<tr>
<td>20:1</td>
<td>1.9</td>
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</tbody>
</table>
Chapter 6

Conclusions
This thesis describes the preparation of inorganic-organic hybrids via a sol-gel process or a non-hydrolytic sol-gel process by using bridged-type precursors. The advantages of using bridged-type precursor are that the bridged-type precursors can be formed gel easier than non bridged-type precursors, and that the functional organic group is connected directly to inorganic network by covalent bonds, enable to prepare a variety of class-II inorganic-organic hybrids.

(1) The hydrolysis behavior of 1,4-bis(triethoxysilyl)benzene (BTB), a precursor of bridged polysilsesquioxane, was investigated with high-resolution $^{29}$Si nuclear magnetic resonance ($^{29}$Si NMR) spectroscopy at ambient temperature in a system with BTB:ethanol:water:HCl = 1:10:x:0.8×10^{-4} (x = 3, 6 or 9). Signals due to hydrolyzed triethoxysilyl groups as well as unhydrolyzed triethoxysilyl groups [-Si(OEt)$_3$, -Si(OEt)$_2$(OH), -Si(OEt)(OH)$_2$ and -Si(OH)$_3$ (OEt = OCH$_2$CH$_3$)] formed four sub-regions based on the number of hydroxyl groups bound to a silicon atom. In the initial stage of hydrolysis, one –Si(OEt)$_3$ group of BTB was preferentially hydrolyzed to –Si(OH)$_3$, which is opposite to the tendency predicted based on the inductive effect. It is assumed that one silicon environment affected the electron density of the other silicon environment by the compensation for the decrease in electron density of the silicon atom in the hydrolyzed group, –Si(OH)$_x$(OEt)$_{3-x}$, through an intra-molecular interaction such as the TS interaction and negative hyperconjugation. This unique hydrolysis behavior of BTB should affect the polycondensation process of BTB.
(2) Bridged polysilsesquioxane possessing dimanganese complex moiety, a model complex for catalase, was successfully prepared via the sol-gel process. The thermal stability of hydrogen peroxide decomposition catalysis of a dimanganese complex after 24-h treatment under acidic conditions at 80°C was drastically improved by immobilization in siloxane networks with no deactivation. The present results strongly suggest that bridged polysilsesquioxane bearing dimanganese complex moieties is a novel class II inorganic-organic hybrid with potential application for hydrogen peroxide decomposition catalyst in PEFC.

(3) Porous phenylene-bridged Ti-O-P hybrids have been synthesized from TiCl₄ and 1.4-bis(phosphono)benzene via the non-hydrolytic sol-gel process. The P/Ti ratio of the hybrid was fixed at 2, and the concentration of the phosphonic group was fixed to be 1.0 mol/L. A homogeneous gel was formed within short period at ambient temperature. The degree of the condensation of Ti-O-P bonds depends on the aging time at 80°C. The resultant hybrids can obtain high specific surface area (308 m² g⁻¹) possessing micro and mesopores with no use of any structure-directing reagent.

(4) The class II inorganic-organic hybrids possessing both oligomeric ethylene oxide chains and Ti-O-P networks were prepared from TiCl₄ and ethylene-oxide-bridged diphosphonic acid [(HO)₂OP(C₂H₄O)₃C₂H₄PO(OH)₂] via the non-hydrolytic sol-gel process, and LiClO₄ was successfully doped to the Ti-O-P hybrid with [EO]:Li=5:1, 10:1, and 20:1. After doping of LiClO₄ to EO-TiOP hybrids, the Li⁺ ions are likely to be
solvated by the ether oxygen atoms, as shown in FT-IR and Raman spectroscopies. Li$^+$ ion transport in the hybrids with ionic conductivity values in the $10^{-5}$ S cm$^{-1}$ range was observed at ambient temperatures, indicating that EO-TiOP hybrid can be applied for solid polymer electrolytes.

This thesis describes that the availability of the bridged-type precursors. The bridged polysilsesquioxane derived from the precursor containing of dimanganese complex moiety is a novel material to be applied to the hydrogen peroxide decomposition catalyst in PEFC. This thesis also demonstrates the availability of the bridged-type precursor to Ti-O-P hybrid via the non-hydrolytic sol-gel process. By using the robust phenylene group for the spacer, the resultant Ti-O-P hybrids can be possessed high specific surface area with no use of structure-directing reagent. In addition, the Ti-O-P hybrid derived from the precursor possessing oligomeric ethylene oxide chains shows the ionic conductivity after doping LiClO$_4$ at ambient temperature, indicating the employable candidates for SPEs. It is therefore concluded that the bridged-type precursor described in this thesis reveals the versatile availability for the class-II inorganic-organic hybrids.
List of Publications

The Publications Related to This Thesis

(1) “Preparation of LiClO₄-doped Titanium Organodiphosphonates Possessing Oligomeric Ethylene Oxide chains and Their Ionic Conductivity”, Chemistry Letters, accepted, Hitomi Saito, Masakata Dobashi, Hiroki Nara, Toshiyuki Momma, Tetsuya Osaka, and Yoshiyuki Sugahara.


(3) “Hydrolysis Behavior of the Precursor for the Bridged Polysilsesquioxane [1, 4-Bis(triethoxysilyl)benzene]: a ²⁹Si NMR study", Journal of Sol-Gel Science and Technology, 57, 51–56 (2011), Hitomi Saito, Yuki Nishio, Manabu Kobayashi, and Yoshiyuki Sugahara.

Other Publication

Review

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