Silicophosphate/silicophosphite hybrid materials prepared by solventless ethanol condensation

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We have developed organic–inorganic silicophosphate and silicophenylphosphite hybrid materials by means of alcohol condensation between organically modified alkoxysilane and anhydrous phosphoric or phosphonic acid under a solventless, catalyst-free, low-temperature, one-pot condition. The hybrid exhibits a low-melting property and is chemically more durable than that prepared by using a nonaqueous acid-base reaction between anhydrous phosphoric acid and organically modified chlorosilane. ²⁹Si and ³¹P NMR analyses have shown that the alcohol condensation yield was around 80%. Quantum chemical calculations have also performed in order to clarify the chemical durability improvement of the hybrids.

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1. Introduction

Organic–inorganic hybrid materials are potential candidates for use in the fabrication of electronic and photonic devices with high functionality because these materials can be processed easily and have a high solubility of functional molecules.¹⁾ Such materials are frequently prepared by using a sol–gel method because of their composition selectivity and low-temperature processibility. However, the sol–gel process is sometimes complicated, and it is difficult to obtain monolithic material because of crack formation during solvent evaporation.²⁾

Recently, an organic–inorganic silicophosphate hybrid has been obtained under a solventless, catalyst-free, low-temperature, one-pot condition^{3–6)} by using orthophosphoric acid and organically modified chlorosilane. The following acid-base reaction (metathesis) took place: $\text{Si-Cl} + \text{P-OH} \rightarrow \text{Si-O-P} + \text{HCl}\uparrow$. Here the reaction formula omitted the groups which do not participate in the reaction: $\text{Me}_2\text{SiCl}_2 + \text{H}_3\text{PO}_4 \rightarrow \text{Me}_2\text{ClSiOP(OH)}_2\text{O} + \text{HCl}\uparrow$ is abbreviated as $\text{Si-Cl} + \text{P-OH} \rightarrow \text{Si-O-P} + \text{HCl}\uparrow$. The starting materials were mixed and heat-treated at less than 300°C. The resultant viscous liquid was cooled down to an ambient temperature, producing a transparent monolithic hybrid material that contained an almost complete alternating polymer consisting of silicate and phosphate units and a high homogeneity in an inter-molecular scale. The crack-free monolithic hybrid material was easily obtained because of the absence of solvent evaporation.

One can easily introduce organic dyes into the abovementioned hybrid material as it melts at temperatures less than 100°C and possesses various organic groups.⁷⁾ Additionally, rare earth ions and Au nanoparticles can be easily dispersed in this hybrid material because the present material has copolymer structure consisting of silicate and phosphate units.⁸⁾ This high solubility of both the organic and the inorganic functional centers is one of the advantages of the optical host material application.

Another advantage of this organic–inorganic hybrid material is related to the low-temperature processibility of the material

because the melting temperature of the material is less than 100°C, the material can be used in a hot-emboss technique or photothermal fabrication in order to obtain photonic devices.⁹⁾ We have also fabricated a photograting structure with a sub-micron resolution in the silicophosphate hybrid.

The abovementioned reaction produces HCl gas, which is both toxic and caustic. Additionally, the residual HCl gas in the hybrid material may act as a catalyst for the hydrolysis of Si–O–P bonding, resulting in low durability. Thus, the silicophosphate hybrid prepared by the acid-base reaction is not durable.^{10–13)}

In this study, we will develop another class of low-melting silicophosphate hybrid formation reaction that is based on solventless alcohol condensation without HCl production: $\text{Si-OEt} + \text{P-OH} \rightarrow \text{Si-O-P} + \text{EtOH}\uparrow$.¹⁴⁾ Although this type of reaction is known as a nonhydrolytic sol–gel reaction, there are few reports on the silicophosphate network formation.¹⁵⁾ Therefore, the structure analyses have also been carried out using ²⁹Si and ³¹P nuclear magnetic resonance (NMR). The thermal property and the chemical durability of the hybrid material have also been investigated. Quantum chemical calculations have been performed in order to investigate the hydrolysis of the Si–O–P bonding in the silicophosphate hybrid.

2. Experimental

2.1 Preparation of organically modified silicophosphate and silicophenylphosphite hybrid

Anhydrous orthophosphoric acid (H₃PO₄) (Aldrich Co., Ltd.) and phenylphosphonic acid (PhH₂PO₃) (Aldrich Co., Ltd.) were used as the phosphoric and the phosphonic acids, respectively. Diphenyldiethoxysilane (Ph₂Si(OEt)₂) (Shin-Etsu Chemical Co., Ltd.) was used as the organosilane. Diphenyldichlorosilane (Ph₂SiCl₂) (Shin-Etsu Chemical Co., Ltd.) was also used for the sake of comparison. The compositions of the starting materials were H₃PO₄ : Ph₂SiX₂ = x : (1–x) (x = 0, 0.6) and Ph₂H₂PO₃ : Ph₂SiX₂ = y : (1–y) (y = 0, 0.5) (X = Cl or OEt), as shown in **Table 1**. The samples made from H₃PO₄ and Ph₂Si(OEt)₂ were designated as silicophosphate hybrid A, while silicophosphate hybrid B was made from H₃PO₄ and Ph₂SiCl₂. Silicophenylphosphite hybrids C and D were made from phenylpho-

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Table 1. Compositions of the Starting Reagents. The Values are Listed in mol% Unit

	Ph ₂ Si(OEt) ₂	Ph ₂ SiCl ₂	H ₃ PO ₄	PhH ₂ PO ₃
A	60	–	40	–
B	–	60	40	–
C	50	–	–	50
D	–	50	–	50

Fig. 1. Preparation scheme of organic-inorganic hybrid material from H₃PO₄, PhH₂PO₃ and Ph₂SiX₂ (X = Cl, OEt).

sphonic acid and Ph₂SiX₂ (X = OEt for C and X = Cl for D). The compositions of all the starting reagents were stoichiometric.

A mixture of the starting reagents was stirred and heat-treated at 180°C for 3 h, and quenched to room temperature. The resulting product was designated as the precursor. The precursor was melted again at 180°C for 1 h and 230–250°C for 3 h. Subsequently, the melt was quenched to room temperature. **Figure 1** shows the preparation scheme. The preparation process was carried out in an N₂ atmosphere.

2.2 Characterization of organically modified silicophosphate

The softening temperature, T_s , of the samples was measured by a thermal mechanical analysis using TMA 8310 (Rigaku Co.) under 1 g loading at a heating rate of 10 K/min.

The hybrid samples were prepared in glass cups (50 mL) in order to maintain a constant surface area exposed to the surrounding atmosphere at 8.2 cm². The durability of the materials was determined by the weight gain in saturated water vapor at 25°C. The hydrolysis of the hybrid provides the weight gain due to the water uptake: Si–O–P + H₂O → Si–OH + P–OH. A smaller weight gain corresponds to a higher durability.

The structure analyses were also performed using ²⁹Si and ³¹P magic angle spinning (MAS) NMR. The spinning rate for MAS was set to 3 kHz and 11–13 kHz for ²⁹Si and ³¹P, respectively. In order to assign the peak precisely, the static ²⁹Si NMR spectra were also obtained for the precursors A, B, and C dissolved in ethanol. The chemical shifts were presented in ppm with respect to tetramethylsilane for ²⁹Si (0 ppm) or phosphoric acid for ³¹P (0 ppm).

2.3 Quantum chemical calculations

In order to investigate the hydrolysis behavior of the Si–O–P bonding, the quantum chemical calculations were carried out on the model clusters as shown in **Fig. 2** using the Gaussian 03 program.¹⁶⁾ Models I and II simulated the hydrolysis in the silicophosphate and silicophenylphosphite hybrids, respectively. In order to reduce the computation time, we considered the methyl

Fig. 2. Transition state structures of the hydrolysis: (a) silicophosphate hybrid, (b) silicophenylphosphite hybrid. The geometry optimizations were performed at B3LYP/6-31G* level. The distance α , β and γ corresponds to the distance between O in water and Si, the Si–O length in the Si–O–P bonding, and the distance between O in Si–O–P bonding and H in H₃O⁺, respectively. We also calculated the total energy for the constant distance β in order to investigate the activation energy of hydrolysis.

groups on the Si atom instead of the phenyl groups for the simulations. Both the models had an oxonium ion as the catalyst and a hydrolyzing H₂O molecule. Additionally, the models without the oxonium ion and H₂O were also calculated. The geometry optimization and the Mulliken population analysis were carried out at B3LYP/6-31G* level with a constant distance between Si and the hydrolyzing H₂O. The transition state structures were also obtained by IRC calculation at the B3LYP/6-31G* level. The single point energy calculations were performed at the MP2/6-311+G** level. All the calculations were performed by using the supercomputer Origin 3800 at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

3. Results

The precursors were highly viscous and homogeneous transparent liquids. The final products were transparent, homogeneous, colorless, and crack-free solids.

The TMA curves of the products showed that T_s ranged from 50°C to 130°C (**Fig. 3**). The T_s values of the samples were found to be in the following order: B > A > D > C. Phosphoric acid provided a sample with higher T_s than phenylphosphonic acid did; A and B exhibited higher T_s than C and D did. It was also found that the acid-base reaction provided samples with higher T_s than the alcohol condensation reaction did; B and D exhibited higher T_s than A and C did, respectively.

In contrast to T_s , the durability of the samples was found to be in the following order: C > D > A > B (**Fig. 4**). The samples prepared by using solventless ethanol condensation (samples A and

Fig. 3. TMA curves of the silicophosphate and silicophenylphosphite hybrids.

Fig. 4. Weight gain in saturated water vapor at 25°C. The inset values are referred to the yields of P–O–Si bonding formation defined by the Eq. (1) in the article.

C) were chemically more durable than those prepared by using a nonaqueous acid-base reaction (samples B and D). We also found that the silicophenylphosphite hybrids C and D were more durable than silicophosphate hybrids A and B, respectively. The appearance of the hybrid C after exposed to water vapor was transparent, hybrids D, A translucent, and hybrid B opaque.

The ^{31}P MAS NMR spectra of the samples are shown in Fig. 5. For samples A and B, three peaks were observed around –11, –23, and –35 ppm, while for samples C and D, the peaks were observed around 15, 8, and –3 ppm. The areas obtained by a gaussian deconvolution are listed in Table 2.

In contrast to ^{31}P NMR spectra, the ^{29}Si MAS NMR spectra of all the samples exhibited a featureless peak only at –40 ppm, as shown in Fig. 6(d). The ^{29}Si chemical shifts of the precursors A, B and C dissolved in ethanol were –32, –37, –39, –43 and –46 ppm, as shown in Fig. 6(a)–(c).

The relative total energies of models I and II calculated by using the quantum chemical calculations were given in Fig. 7. The relative energy (closed circles), the distance between Si and H_2O (distance γ in Fig. 2, open squares), and that between silicon and oxygen (distance β , open triangles) for (a) model I and (b) model II were plotted against the distance between the Si–O–P bonding. This result indicated that when the distance

Fig. 5. ^{31}P MAS NMR spectra of the hybrid materials. Q^n and T^n are referred to P with n bridging oxygens and $(4-n)$ non-bridging oxygens and that with n bridging oxygens and $(3-n)$ non-bridging oxygens, respectively.

Table 2. Areas of Q^n and T^n units calculated from ^{31}P MAS NMR Spectra. The Yields of the P–O–Si Bonding Formation were also Calculated as $N(\text{P–OSi})/(N(\text{P–OH}) + N(\text{P–Si})) \times 100$

n	0	1	2	3	yield
A	0	7	41	51	81
B	0	9	29	63	85
C	20	48	32	–	56
D	11	44	45	–	67

Fig. 6. ^{29}Si NMR spectra of (a) precursor A, (b) precursor B, (c) precursor C, and (d) ^{29}Si MAS NMR spectra of hybrid A. The asterisks on the atomic symbols refer to the nuclei responsible for the chemical shift.

between Si and H_2O was decreased, the Si–O distance in Si–O–P bonding increased and the distance between the oxygen in Si–O–P bonding and the hydrogen in H_3O^+ decreased to 1.0 Å. As the total energies of model I first increased and then decreased with decreasing the distance α , the IRC calculation was per-

Fig. 7. Relative total energy (●), the distance β (Δ), and the distance γ (□) for (a) model I and (b) model II plotted against the distance α between Si-O-P bonding.

formed to obtain the transition state structure as shown in Fig. 2. This calculation succeeded and provided an activation energy of 1.9 kJ/mol. On the other hand, the model II provides no transition structure, as its total energy increased monotonously and IRC calculation failed. The Mulliken charges of the oxygen in Si-O-P bonding in the model I without the oxonium ion and H₂O were also calculated as -0.54, and -0.38 in the model II.

4. Discussion

The ³¹P MAS NMR peaks for samples A and B around -11, -23, and -35 ppm were assigned to P in PO(OSiPh₂)(OH)₂, PO(OSiPh₂)₂OH, and PO(OSiPh₂)₃, respectively; the P units were referred to as Q¹, Q², and Q³ because the ³¹P chemical shift in the P-O-Si bond provided a higher field shift than that in the P-OH bond.¹² Here, Qⁿ refers to P with *n* bridging oxygens and (4-*n*) nonbridging oxygens. The peaks for samples C and D around 15, 8, and -3 ppm were also assigned to ³¹P in PhH₂PO₃, PhPO(OSiPh₂)(OH), and PhPO(OSiPh₂)₂, respectively;¹¹ these P units were referred to as T⁰, T¹, and T², where Tⁿ refers to P with *n* bridging oxygens and (3-*n*) nonbridging oxygens. Table 2 lists the ratios of each structure unit and yield of P-O-Si bond formation calculated as follows:

$$\frac{N(\text{P}-\text{OSi})}{N(\text{P}-\text{OH}) + N(\text{P}-\text{OSi})} \times 100 (\%), \quad (1)$$

where N(P-OX) indicates the number of P atoms with P-OX bonding (X = Si or H). The ability to form a P-O-Si bond was found to be in the following order: B > A > D > C. The fact that the yields for the silicophosphate hybrids (samples A or B) were larger than those of the silicophenylphosphite hybrids (samples C or D) indicated that the use of H₃PO₄ as the starting reagent

resulted in a higher yield of the P-O-Si bond than that of PhH₂PO₃ did. Additionally, the yield for solventless alcohol condensation (samples A and C) was slightly lower than that of the nonaqueous acid-base reaction (samples B and D).

As mentioned in results section, the peak deconvolution is impossible for the ²⁹Si MAS NMR spectra because the peak at -40 ppm is featureless. Therefore, peak assignment was performed using the static NMR spectra of liquid samples because liquid NMR provided sharp spectra, although they did not provide quantitative information. Obviously the peaks at -37 and -43 ppm in Figs. 6 were also assigned to Si in Ph₂Si(OEt)(OP(OH)₂), and Ph₂Si(OP(OH)₂)₂, respectively; these Si units were referred to as D¹(Si*-O-P) and D²(P-O-Si*-O-P).^{11,12} Here, the asterisk refers to the nucleus that was responsible for the chemical shift. The peaks at -32, -39, and -46 ppm in Fig. 6(a)-(c) were assigned to Si in Ph₂Si(OEt)₂, Ph₂Si(OEt)(OSiPh₂(OH)), and Ph₂Si(OSiPh₂(OH))₂, respectively;^{17,18} these Si units were designated as D⁰, D¹(Si*-O-Si), and D²(Si-O-Si*-O-Si). On the basis of this assignment, the featureless peak at -40 ppm observed in the hybrids was mainly attributed to the Si in the D¹(Si*-O-P), D¹(Si*-O-Si), and D²(P-O-Si*-O-P) units. Ideally, there should be no Si-O-Si bonding when only alcohol condensation occurs. However, the system including phosphoric or phosphonic acid contained a little amount of water as impurity or the self-condensation reaction of the acids produced water, 2POH → P-O-P + H₂O. This water hydrolyzed the diphenyldiethoxysilane with the help of the phosphoric or phosphonic acid. Hence, Si-O-Si bonding was present in the products. As mentioned in the preceding discussion on ³¹P MAS NMR, Si-O-P bonds were mainly formed by the ethanol condensation reaction. Additionally, Si-O-Si bond was formed as a by-product.

In the case of the acid-base reaction, the formation of the by-product was negligible.^{11,13} The present authors have proposed the condensation mechanism as follows,^{11,12}

where X = Cl or OEt. The Lewis acidity of a cholro group is higher than that of an ethoxy group. This is because the reactivity of the acid-base reaction is higher than that of the ethanol condensation reaction.

It is obvious from Table 2 and Fig. 3 that the softening temperature depends on the yields of the network formation reaction. This result is in agreement with the previous report on silicophosphate hybrids.¹³

According to the quantum chemical calculations, the silicophenylphosphite hybrid was more durable than the silicophosphate hybrid because the hydrolysis activation energy was 1.9 kJ/mol in model I, while the relative energy increased monotonously in model II. Indeed, the oxygen charge on the Si-O-P bonding in model II is less than in model I due to the electrophobic phenyl group on P; this resulted in the suppression of the hydrolysis of Si-O-P bond. Additionally, the steric hindrance of the phenyl group improves the durability of the hybrids. The water durability observed, as shown in Fig. 3, agreed with that obtained by using the quantum chemical calculations: silicophenylphosphite hybrid (sample C) was more durable than silicophosphate hybrid (sample A).

The samples prepared by using diphenyldichlorosilane were less durable than those prepared by using diphenyldiethoxysilane, although the yields of network formation were high in the

former sample. We consider that the samples prepared by using diphenyldichlorosilane contained residual HCl, which assisted the hydrolysis of the hybrids in the presence of the water. Indeed, the appearance of the less durable hybrids was more opaque. This indicates that the following hydrolysis and gelation occurred in the hybrids.

As described in NMR result section, the yield of the Si-O-P bonding in the samples prepared by using diphenyldiethoxysilane was low. Nevertheless, the durability of these samples was high, indicating that these materials can be used as highly durable low-melting hybrids for optical host application.

5. Conclusions

We developed new class of the organic-inorganic silicophosphate and silicophosphite hybrids via the solventless alcohol condensation under the catalyst-free, low-temperature, one-pot condition. This reaction provided crack-free monolithic materials easily because of no solvent evaporation. The hybrid material shows low-melting property, as melting temperatures ranged from 50 to 110°C where the organic dyes do not degrade. We also investigated the local structure using ^{29}Si and ^{31}P NMR. The reaction provided alternating polymerization, i.e. Si-O-P formation, for the most parts, although the self-condensation, i.e. Si-O-Si or P-O-P formation, occurred. The functional centers such as the rare earth ions will disperse homogeneously in the alternating copolymer of silicate and phosphate as reported previously. Additionally, the chemical durability was much higher than that of the hybrids prepared by the acid-base reaction. Therefore, the present hybrid material is a good candidate of the optical host material for the organic and/or inorganic functional centers.

The quantum chemical calculations were revealed that the improvement in water durability was due to the suppression of the hydrolysis of the Si-O-P bonding because the phenyl group on P decreases the oxygen charge on the Si-O-P bonding.

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