Salt Catalysts Containing Basic Anions and Acidic Cations for the Sol−Gel Process of Titanium Alkoxide: Controlling the Kinetics and Dimensionality of the Resultant Titanium Oxide

Yasushi Murakami,* Taki Matsumoto, and Yoshio Takasu

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan

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The sol−gel process from titanium alkoxide monomer to titanium oxide polymer was remarkably enhanced by salt catalysts containing basic anions and acidic cations. An ammonium carbonate catalyst promoted the precipitation of spherical titanium oxide particles at low concentrations of titanium alkoxide and water at room temperature. Dehydrative polycondensation in the sol−gel process involves both deprotonation and dehydroxylation, and the carbonate anion enhanced the deprotonation as a base catalyst while the ammonium cation enhanced the dehydroxylation as an acid catalyst. If the ammonium acetate catalyst was added, the monolithic titanium oxide gel which consists of sheetlike titanium oxide particles was formed. The acetate anion acted not only as the catalyst for the dehydrative polycondensation but also as a ligand coordinating to titanium for capping the polycondensation sites, resulting in planar titanium oxide particles.

Introduction

The sol−gel processes from titanium alkoxides to titanium oxide polymer have been widely studied as a preparation method for ultrafine particles[1−3] and monolithic gel[4,5] of titanium dioxide under mild conditions. The sol−gel process consists of the hydrolysis of titanium alkoxides and subsequent polycondensation.

Barringer and Bowen[1] have obtained fine spherical particles (340−500 nm) of TiO$_2$ with narrow distribution of the particle size from 0.1−0.2 M titanium ethoxide and 0.3−0.7 M H$_2$O (H$_2$O/Ti > 2.5). Xu and Anderson[2] have prepared colloidal particles of TiO$_2$ with fine diameters less than 3 nm from 0.2 M titanium amiloxide and 1.2 M nitric acid at pH 2. The particle sizes depend on the concentrations of titanium alkoxide and H$_2$O. The size of alkoxy groups in alkoxides also plays an important role in determining the particle size, and the titanium alkoxide containing bulky alkoxy groups such as titanium amiloxide reduces the hydrolysis rate, which is advantageous for the preparation of fine colloidal particles.[6]

Yoldas[4] has prepared monolithic gels by reacting titanium tetraethoxide (0.2−0.5 M) with H$_2$O (H$_2$O/Ti = 2) under acidic conditions with HCl or HNO$_3$ for a few days. Kamiya et al.[7] obtained highly viscous sols from 1.7−2.8 M titanium tetraisopropoxide and 1.0−9.0 M H$_2$O added with HCl. They also reported that the low concentration (0.1 M) of titanium ethoxide is insufficient to grow the monolithic gel or the high-viscosity sol.

Doeuff et al.[5] have added acetic acid to titanium butoxide solutions to shorten the gelation time (91 min for 0.2 M titanium butoxide) and allow the formation of the monolithic gel at low concentration (0.15 M) titanium butoxide (the gelation time,

900 min). Acetic acid is more effective to produce the monolithic gel than other acids such as HCl and HNO$_3$.

We have found that the salt catalysts accelerated the sol−gel process[8] and were more effective for the polycondensation than conventional catalysts such as an acid catalyst (e.g. HCl, HNO$_3$, or CH$_3$COOH), and a base catalyst (e.g. aqueous ammonia). The dehydrative polycondensation of two M-OH species needs both deprotonation of one hydroxy species and dehydroxylation of the other to form M−O−M oxo species and water:

$$-\overset{|}{\underset{|}{M}}-OH+-\overset{|}{\underset{|}{M}}-OH \longrightarrow -\overset{|}{\underset{|}{M}}-O-\overset{|}{\underset{|}{M}}-+H_2O \qquad (1)$$
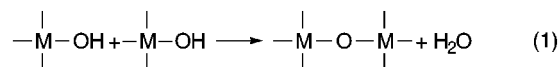
In organic chemistry, it has been known that deprotonation is accelerated by a basic catalyst while dehydroxylation is accelerated by an acid catalyst. An acid−base pair catalyst is expected to accelerate the overall polycondensation. If a strong acid and a strong base were mixed, they neutralize each other and the resulting salt does not act as an acid−base pair catalyst. However, the salt neutralized from a weak acid and a weak base is expected to act as an acid−base pair catalyst: an anion acts as a base while a cation acts as an acid. The salt catalyst containing a basic anion and an acidic cation will effectively accelerate the overall polycondensation. By using a polycondensation catalyst such as a salt catalyst, it may be possible to accelerate the polycondensation independently under the control of the hydrolysis and thereby obtain a monolithic gel which is difficult to achieve from a low concentration of titanium alkoxide in solution.

Experimental Section

All water used in this study was deionized by AQUARIUS GS-200 System (Advantec). Titanium tetra-*n*-butoxide (Kanto

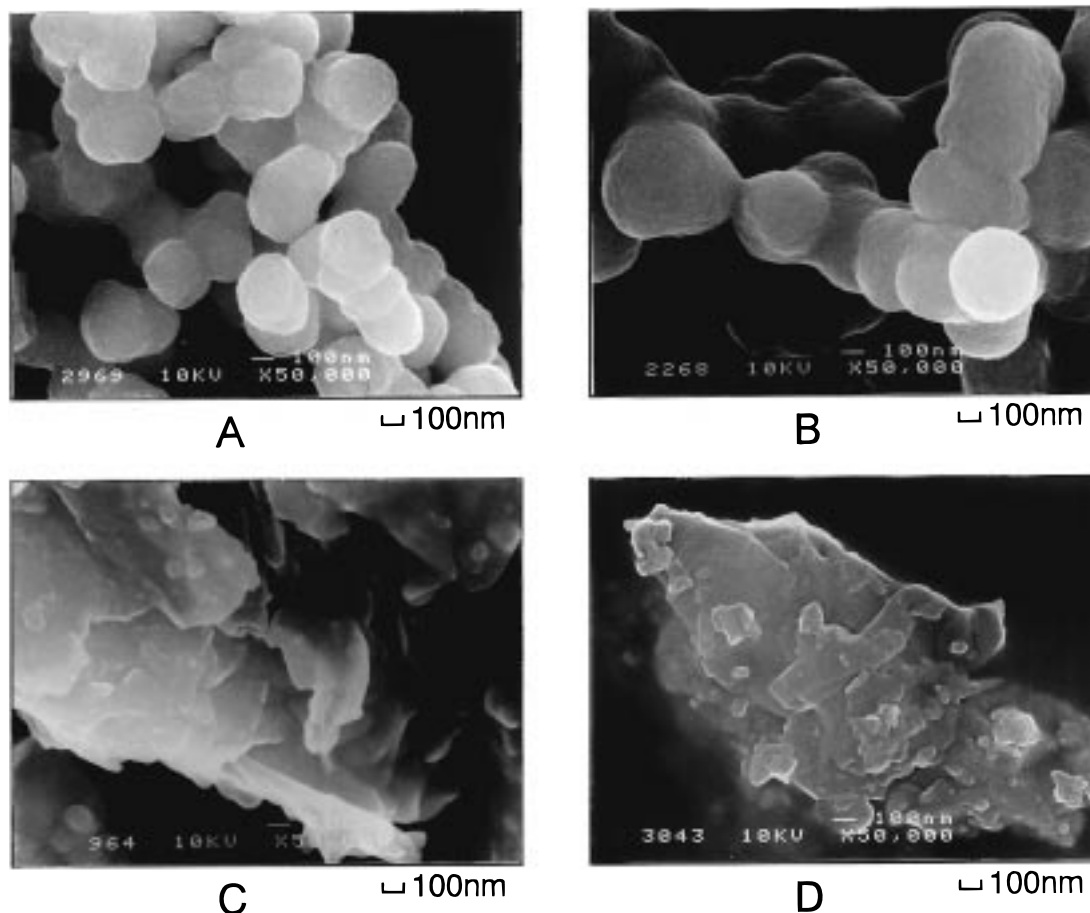* Corresponding author. Fax: +81-268-22-9048. E-mail: yasmura@giptc.shinshu-u.ac.jp.

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Figure 1. High-resolution scanning electron micrographs of titanium oxide prepared with (A) excess water (1.5 M), (B) ammonium carbonate (0.05 M), (C) ammonium acetate (0.05 M), and (D) ammonium acetate (0.05 M) and diethylene glycol (0.5 M). Samples were dried under vacuum at room temperature.

Chemical Co., Inc., >97%), ammonium carbonate (Kanto Chemical Co., Inc., special grade reagent), and ammonium acetate (Kanto Chemical Co., Inc., special grade reagent), diethylene glycol (Wako Pure Chemical Industries, Ltd., special grade reagent), and 1-butanol (Wako Pure Chemical Industries, Ltd., special grade reagent) were used without further purification.

In a nitrogen atmosphere, 10 mL of the butanol solution containing 1.25 mmol of tetra-*n*-butoxide, and 15 mL of another butanol solution containing 1.25 mmol of ammonium carbonate or ammonium acetate as a salt catalyst and 12.5 mmol of water, were prepared. The sol−gel reaction started when the two butanol solutions were mixed to be a total of 25 mL of the solution (tetra-*n*-butoxide 0.05 M, H_2O 0.5 M, and a salt catalyst 0.05 M). The reaction temperature was kept at 25 °C with a circulated water bath. The reaction process was followed by measuring the solution viscosity[8] (Yamaichi Electronic, Viscomate VM-1A-L).

The resulting precipitates and gels were dispersed with methanol and dropped on smooth plates of a cleaved highly oriented pyrolytic graphite, dried under vacuum for 4 h and observed in morphology with a high-resolution scanning electron microscope (HR-SEM, JEOL JMS-6100F). They were also dried at 90 °C in air and ground to powder and their infrared (IR) and the ultraviolet−visible (UV−vis) absorption spectra were measured. The IR absorption spectra of the sample powders diluted with KBr were obtained with the spectrometer (Perkin-Elmer 1650FTIR) by the transmission method. The UV−vis absorption spectra were obtained using the spectrometer (Shimadzu UV-2500PC) in the reflection mode.

Results

Catalytic Effects of Ammonium Carbonate. Neither precipitation nor increase in the solution viscosity was observed when no catalyst was added to the butanol solution containing titanium tetra-*n*-butoxide (0.05 M) and water (0.5 M). No apparent change in the solution suggested that the reaction from titanium alkoxide to titanium oxide species scarcely proceeded. When the concentration of water was increased to 1.5 M, aggregates of spherical particles were precipitated. The precipitate was observed to consist of aggregates of spherical particles by HR-SEM (Figure 1A). Thus, the large amount of water enhanced the hydrolysis of titanium tetra-*n*-butoxide and then increased the concentration of hydroxy groups bonded to the titanium species which are reactants for the polycondensation.

Neither precipitation nor an increase in the solution viscosity was observed when hydrochloric acid, nitric acid, acetic acid, or aqueous ammonia was added to be 0.05 M as a conventional catalyst. Either, the acid catalyst or the base catalyst alone was insufficient for the overall sol−gel process to proceed.

When 0.05 M ammonium carbonate was added to the butanol solution containing 0.05 M titanium tetra-*n*-butoxide and 0.5 M water, the titanium oxide was precipitated. The precipitate consists of aggregates of spherical particles (Figure 1B). Their shape was similar to that of particles obtained by the addition of excess water without any catalyst (Figure 1A). However, with the ammonium carbonate catalyst, a much lower concentration of water caused titanium oxide to precipitate, compared to the case without the catalyst. Thus, the ammonium carbonate

TABLE 1: Dependence of the Induction Time of the Particle Formation on the Concentration of Ammonium Carbonate[a]

concn of ammonium carbonate/M	t/min
0.005	300
0.020	15
0.035	8
0.050	5

[a] Concentration of water: 0.5 M.

TABLE 2: Dependence of the Induction Time of the Particle Formation on the Concentration of Water

	t/min	
concn of water/M	with ammonium carbonate[a]	without ammonium carbonate
0.05	300	c
0.25	15	c
0.50	8	c
1.00	5	8
1.50	0[b]	2

[a] Concentration of ammonium carbonate: 0.05 M. [b] Quickly. [c] No apparent change in 10 h.

catalyst was found to accelerate sol−gel reaction and then enhance the precipitation.

Table 1 gives the induction time for the particle formation, t, as a function of the concentration of ammonium carbonate. The induction time for the particle nucleation was determined from the time when the solution become turbid. The induction time is seen to decrease remarkably with an increase in the concentration of ammonium carbonate.

Table 2 gives the induction time for the particle formation, t, as a function of the concentration of water in the 0.05 M titanium tetra-*n*-butoxide butanol solution in which 0.05 M ammonium carbonate was present or not. No apparent change was observed in 10 h for the solution containing the low concentration of water (<1.0 M) without ammonium carbonate. With 0.05 M ammonium carbonate, the low concentration of water leads to the formation of the precipitate in 5 h and the induction time decreased with an increase in the concentration of water. Consequently, ammonium carbonate plays a role as a catalyst for the sol−gel process of titanium alkoxide monomer to form titanium oxide polymer.

Catalytic and Coordinative Effects of Ammonium Acetate. When ammonium acetate was added as salt catalyst, the solution viscosity increased with reaction time as shown in Figure 2. Finally, a homogeneous gel state was attained after 250 min. The solution viscosity increased more extensively at the higher concentration of ammonium acetate. The results suggest that ammonium acetate also plays a role as the catalyst for the sol−gel process.

Doeuff et al.[5] have reported that the titanium oxide gel was obtained from titanium tetra-*n*-butoxide at the concentration of more than 0.15 M in the presence of acetic acid. In our experiments, ammonium acetate enabled the transformation of 0.05 M titanium tetra-*n*-butoxide into the gel. To obtain a gel from 0.15 M titanium tetra-*n*-butoxide solution without ammonium acetate, it took about 900 min for the gelation as in the study of Doeuff et al.[5] This implies that ammonium acetate also accelerated the sol−gel process.

As shown in Figure 1C, stacks of sheetlike particles were observed in the alkoxy-derived titanium oxide. The shape of titanium oxide particles in the gel is quite different from that in the precipitates. The sheetlike particles were homogeneously
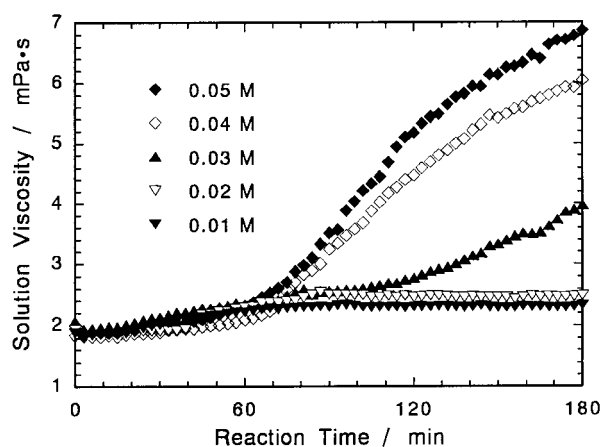
Figure 2. Time course of the solution viscosity and its dependence on the ammonium acetate content. [Titanium tetra-*n*-butoxide] = 0.05 M and [H_2O] = 0.5 M in the solution. The ammonium acetate contents are shown in this figure.
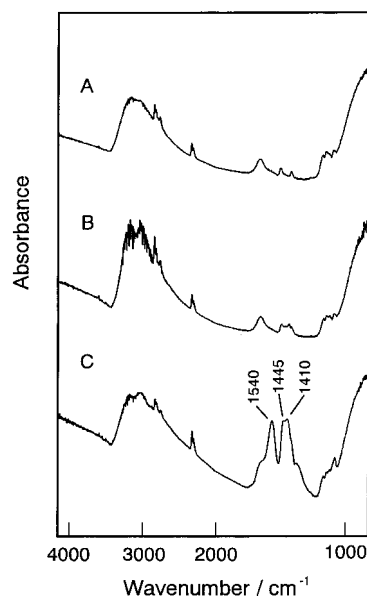
Figure 3. IR adsorption spectra of titanium oxides prepared by the sol−gel process with (A) excess water (1.5 M), (B) ammonium carbonate (0.05 M), and (C) ammonium acetate (0.05 M). Samples were dried at 90 °C.

present in the butanol solution to form a gel while the spherical particles were precipitated in the butanol solution. Therefore, the surface of the sheetlike particle seems to have more affinity to butanol than that of the spherical particle.

Even with the ammonium carbonate catalyst, the solution viscosity increased without precipitation when diethylene glycol was added to be 0.5 M as a hydrolysis inhibitor.[9,10] The shape of titanium oxide particles in the gel was sheetlike (Figure 1D) and similar to that observed in the ammonium acetate catalyst system. Even for the ammonium carbonate system, sheetlike titanium oxide particles were obtained by the addition of diethylene glycol as an inhibitor for the hydrolysis of the alkoxide. Thus, it was considered that ammonium acetate acts not only as a catalyst for the sol−gel process but also as an inhibitor for hydrolysis in the sol−gel process.

IR spectra of the titanium oxide products are shown in Figure 3. The IR spectrum of titanium oxide prepared using ammonium carbonate as catalyst is almost the same as that of titanium oxide

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TABLE 3: IR Absorption Bands Corresponding to COO Stretching in Various Acetates

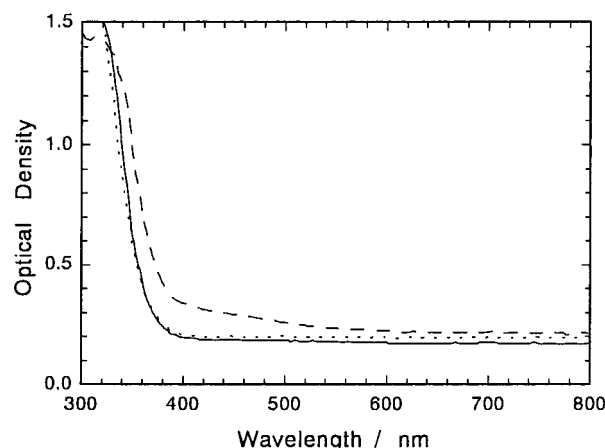|	coordination	$\nu_{sym}(COO)/cm^{-1}$	$\nu_{asym}(COO)/cm^{-1}$	$\Delta\nu/cm^{-1}$	ref
this work		1410, 1445	1540	130, 95	
Ti(OCOCH₃)₄	monodentate	1300	1725	425	11
	bidentate	1435	1565	130	11
Ti(IV)−acetate complexes	monodentate	1295	1720	425	5
	bidentate chelating	1470	1550	80	5
	bidentate bridging	1430	1590	160	5
CH₃COONH₄		1410	1582	172	12

Figure 4. UV−vis adsorption spectra of titanium oxides prepared by the sol−gel process with excess water (- - -), ammonium carbonate (——) and ammonium acetate (− − −). Samples were dried at 90 °C.

prepared only with excess water (1.5 M). On the other hand, the IR spectrum of titanium oxides prepared with ammonium acetate was different from those spectra. The characteristic absorption bands were observed at 1410, 1446, and 1540 cm⁻¹, which are attributed to COO stretching.
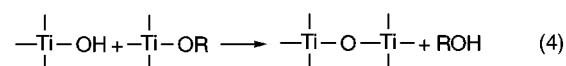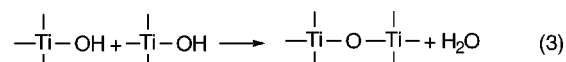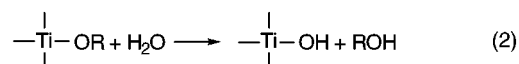
IR absorption bands corresponding to COO stretching on various acetates are summarized[5,11,12] in Table 3. The characteristic absorption bands observed in the present work (Figure 3C) are quite different from those for monodentate in Ti(IV)−acetate complexes observed at 1295 (symmetric) and 1720 cm⁻¹ (antisymmetric), but similar to those for bidentate of Ti(IV)−acetate complexes observed at 1430−1470 (symmetric) and 1550−1590 cm⁻¹ (antisymmetric). The observed bands are therefore attributable to COO stretching bands for bidentate of the titanium oxide-acetate complex. The affinity of the sheetlike particle to butanol should result from the bidentate coordination of the acetate ion to titanium oxide. This coordination should restrict the dimension of the titanium oxide growth so that the sheetlike particles were formed by the lower dimensional growth.

UV−Visible Absorption. UV−visible spectra of the titanium oxides dried at 90 °C are shown in Figure 4. For the spherical particles of titanium oxides prepared with excess water (1.5 M) and no catalyst, and with ammonium carbonate catalyst, the absorption bands were observed below 360 nm. For the sheetlike titanium oxide prepared using ammonium acetate as a catalyst, the absorption edge was shifted to longer wavelengths (ca. 380 nm) and a new absorption was observed around 450 nm. Kamato[13] and Holding et al.[14] proposed that the appearance of a new absorption band which is assignable to new charge transfer bands resulted from surface complexation of titanium oxide with surface modifiers. In the present study, the absorption band of the sheetlike titanium oxide was different from that of the spherical one. The sheetlike titanium oxide had surface

complexation with the bidentates of acetate ions, which may change the band gap of the titanium oxide surface.

Discussion

The sol−gel process of a titanium alkoxide to form a titanium oxide polymer consists of hydrolysis and polycondensation:[1,15]

$$-Ti-OR + H_2O \longrightarrow -Ti-OH + ROH \qquad (2)$$

$$-Ti-OH + -Ti-OH \longrightarrow -Ti-O-Ti- + H_2O \qquad (3)$$

$$-Ti-OH + -Ti-OR \longrightarrow -Ti-O-Ti- + ROH \qquad (4)$$

where OR is an alkoxy group and ROH is the corresponding alcohol.

The initial step (2) is hydrolysis in which an alkoxy group is replaced with a hydroxy group. Since a metal ion has several coordination sites, replacements of hydroxy groups for alkoxy groups occur successively.[16] The following steps, (3) and (4), are dehydrative polycondensation and dealcoholic polycondensation, respectively.

One approach of the enhancement of the sol−gel process is the use of a high concentration of the reactants. If the excess water is used, the hydrolysis (2) is accelerated. The acceleration of the hydrolysis increases the hydroxy species which are reactants for the polycondensations (3) and (4). Although the increase in the hydroxy species accelerated the polycondensations, the number of hydroxy groups coordinated to a titanium ion should be three or more to achieve the high branching growth of the titanium oxide. In such a case, it may be impossible to obtain the titanium oxide that has fiberlike or sheetlike structure with low branching.

Another approach is to raise the reaction temperature. Ligands coordinated to the metal ion are removed at higher temperatures. Higher reaction temperatures enhanced not only polycondensations but also hydrolysis. This approach would not make it possible to obtain the titanium oxide with low branching.

A third way of changing the reaction pathway is to use catalysts. The catalyst for polycondensations should act differently for hydrolysis, and vice versa. Acid catalysts such as HCl, HNO₃, and CH₃COOH, and base catalysts such as aqueous ammonia, have been reported to be effective for hydrolysis.[16,17] To our knowledge, there have been no research on a catalyst for polycondensation.

Either acid catalysts or base catalysts would not be effective to accelerate the overall polycondensations. The dehydrative polycondensation requires both deprotonation of one hydroxy species and dehydroxylation of the other to form M−O−M oxo species and water. In a similar manner, dealcoholic polycondensation is required for both deprotonation of a hydroxy species and dealkoxylation of an alkoxy group to form M−O−M oxo

species and the corresponding alcohol. The deprotonation is accelerated by the base catalyst while the dehydroxylation and the dealcoholation are accelerated by the acid catalyst. Thus, the presence of the acid catalyst and the base catalyst is required for acceleration of the overall polycondensations.

If a strong acid and a strong base were mixed, they neutralize each other and the resulting salt does not act as an acid–base pair catalyst. However, the salt neutralized from a weak acid and a weak base contains a basic anion and an acidic cation. For example, ammonium acetate decomposed to an ammonium cation and an acetate anion in the solution

$$CH_3COONH_4 \rightarrow NH_4^+ + CH_3COO^- \qquad (5)$$
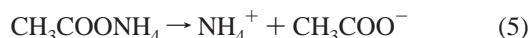
The ammonium cation reacts with a hydroxy anion to form ammonia and water:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (6)$$
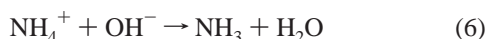
which is the reverse reaction of the base dissociation. Equation 6 proceeds because ammonia is a weak base, indicating that the ammonium cation acts as an acid catalyst. The acetate anion accepts a proton to form acetic acid:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH \qquad (7)$$

which is the reverse reaction of the acid dissociation. Reaction 7 proceeds because acetic acid is a weak acid, indicating that the carbonate anion acts as a base catalyst. The resultant ammonia and acetic acid immediately react to reproduce an ammonium cation and an acetate anion:

$$NH_3 + CH_3COOH \rightarrow NH_4^+ + CH_3COO^- \qquad (8)$$

Therefore, the salt neutralized from the weak acid and the weak base such as ammonium carbonate or ammonium acetate acts as an acid–base pair catalyst. It is expected to accelerate the overall polycondensation reaction.

If the catalyst for polycondensations is used, polycondensations can be accelerated independently from the hydrolysis reaction. The titanium oxide can be obtained from low concentrations of the titanium alkoxide and water. Moreover, the polycondensation proceeds even if the hydrolysis was inhibited to decrease the fraction of hydroxy groups. Therefore, the catalyst for polycondensations makes it possible to obtain a titanium oxide with low branching.

When ammonium acetate is used, the acetate anion is coordinated to the titanium ion more strongly than the alkoxy group. The coordination of the acetate anion decreases the fraction of the hydroxy species. Since polycondensation is accelerated by the salt catalyst, a small amount of the hydroxy

species is polycondensed, and consequently a low-dimensional network is formed.

Conclusion

Salt-catalyzed sol–gel process of titanium-*n*-butoxide was examined. Polycondensations were found to be enhanced by salt catalysts which contain basic anions and acidic cations. The catalysts for polycondensation make kinetic control of the sol–gel process possible and enable one to synthesize the metal oxide at low temperature and to inhibit the hydrolysis for the dimensional control of the titanium oxide growth.

Since a large number of salt catalysts are available, it is expected that the salt-catalyzed sol–gel process of metal alkoxides will provide a general strategy for inorganic chemistry on the metal oxide network bonding. The development of such a synthetic approach should allow to control kinetics in the sol–gel process and morphology of the resultant products.

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