Design of Catalysts for Low-Temperature Synthesis of Highly Polymerized Titanium Oxides

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Reactions of a titanium alkoxide to a titanium oxide in a sol-gel process were significantly accelarated by adding hydrazine monohydrochloride and acetamidine hydrochloride as catalysts. By using hydrazine monohydrochloride, the solution exhibited an extremely high maximum viscosity with spinnability although the solution viscosity increased slowly. These solution changes suggest that particle creation sites are restricted and the particle number decreases. Consequently each particle grow slowly to a particle with a high polymerization degree. Using acetamidine hydrochloride, the solution increased in viscosity faster and changed from a sol to a translucent gel before reaching a high viscosity. Because of the larger number of particles, each particle grew quickly but not to a particle with a high polymerization degree. Particle creation sites decreased accoridng to the concentration ratio of an acid to a base in an acid-base pair catalyst. The concentration ratio of acid to base was determined by the acid dissociation.
Key words: titanium oxide, synthesis, sol-gel, salt catalyst, spinnability

1. INTRODUCTION

The sol-gel process of converting titanium alkoxides to titanium oxide polymer have been widely studied as a preparation method for ultrafine particles[1-6] and monolithic gels[7,8] of titanium dioxide under mild conditions. We have found that salt catalysts accelerated reactions in a sol-gel process more effectively than conventional catalysts such as acid catalysts (e. g. HCl, HNO_3 or CH_3COOH), or base catalysts (e. g. aqueous ammonia).[9] The sol-gel process consists of hydrolysis of titanium alkoxides and the subsequent polycondensation. The dehydrative polycondensation of two M-OH species proceeds between deprotonation of one hydroxy species and dehydroxylation of the other to form M-O-M oxo species and water:

$$-M\text{-}OH + -M\text{-}OH \rightarrow -M\text{-}O\text{-}M\text{-} + H_2O \quad (1)$$
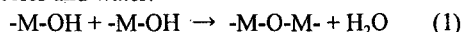
In organic chemistry, the deprotonation is accelerated by base catalysts while the dehydroxylation is accelerated by an acid catalyst. An acid-base pair catalyst is expected to accelerate the overall polycondensation.

If a strong acid and a strong base are 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. For example, ammonium acetate decomposes to an ammonium ion and an acetate ion in the solution:

$$CH_3COONH_4 \rightarrow NH_4^+ + CH_3COO^- \quad (2)$$
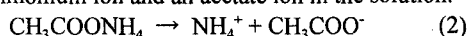
The ammonium ion reacts with a hydroxy ion to form ammonia and water:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \quad (3)$$
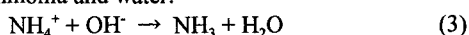
which is the reverse reaction of a base dissociation. Reation (3) proceeds because ammonia is a weak base, while an ammonium ion acts as an acid catalyst. The acetate ion accepts a proton to form acetic acid:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH \quad (4)$$
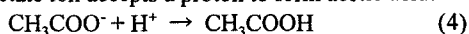
which is the reverse reaction of an acid dissociation.

Reaction (4) proceeds because acetic acid is a weak acid, while an acetate ion acts as a base catalyst.

In this study, hydrazine monohydrochloride and acetamidine hydrocloride were used as catalysts in the sol-gel process. A protonated hydrazine ion and a protonated acetamidine ion act as acids similar to an ammonium ion:

$$[NH_2NH_3]^+ \rightarrow NH_2NH_2 + H^+ \quad (5)$$
$$[CH_3C(=NH)NH_2]^+ \rightarrow CH_3C(=NH)NH_2 + H^+ \quad (6)$$
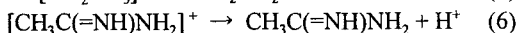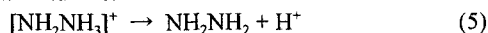
However, a chloride ion is not a base like an acetate ion because hydrochloric acid is a strong acid. Instead of a chloride ion, hydrazine and acetamidine, which are formed by reactions (5) and (6) act as bases:

$$NH_2NH_2 + H^+ \rightarrow [NH_2NH_3]^+ \quad (7)$$
$$CH_3C(=NH)NH_2 + H^+ \rightarrow [CH_3C(=NH)NH_2]^+ \quad (8)$$
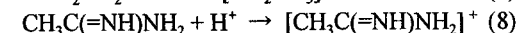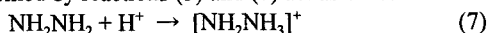
These reactions (7) and (8) are the reverse reactions of (5) and (6), respectively. Instead of a salt which contains acidic cation and basic anion, a conjugated acid-base pair was found to be an active catalyst in the sol-gel process as well.

In this study, reactions of a titanium alkoxide to a titanium oxide in a sol-gel process were examined using hydrazine monohydrochloride and acetamidine hydrochloride as a conjugated acid-base pair to control the creation and growth of a titanium oxide. Synthesis of a titanium oxide with a high polymerization degree and high spinnability was found by both restricting the number of particles created and accelerating their growth.

2. EXPRIMENTAL SECTION

Reagent. All water used in this study was deionized by AQUARIUS GS-200 System (ADVANTECH). Titanium tetra-isopropoxide (KANTO CHEMICAL CO., INC., 97%), acetamidine hydrochloride (TOKYO KASEI CO., INC., 94%), hydrazine monohydrochloride (TOKYO KASEI CO., INC., special grade reagent), diethylene glycol (Wako Pure Chemical Industries, Ltd., special grade reagent),

n-butylamine (TOKYO KASEI CO., INC., 99%) and 1-butanol (Wako Pure Chemical Industries, Ltd., special grade reagent). They were used without further purification.

Procedures. In nitrogen atmosphere, 10 ml of the butanol solution containing 12.5 mmol of a titanium tetra-isopropoxide and 25 mmol of diethylene glycol, and 15 ml of another butanol solution containing 0.125 mmol of acetamidine hydrochloride or hydrazine monohydrochloride as a catalyst and 25 mmol of water were prepared. The sol-gel reaction started when the two butanol solutions were mixed to a total of 25 ml (titanium tetra-isopropoxide: 0.5 M, diethylene glycol: 1.0 M, the catalyst: 0.005 M and H_2O: 1.0 M). Reaction temperature was kept at constant of 25°C with a circulated water bath. The reaction process was followed by measuring the solution viscosity (Yamaichi Electronic, VISCOMATE VM-1A-L).

3. RESULTS

Figure 1 shows the time course of the solution viscosity during the reaction of titanium isopropoxide with the catalysts hydrazine monohydrochloride and acetamidine hydrochloride as a catalyst.

Viscosity in the solution containing hydrazine monohydrochloride slowly increased, and finally reached about 160 mPa s, followed by a transformation from a sol to a gel. The sol with a high viscosity exhibited both a high transparency and a high spinnability, suggesting a low branching of the titanium oxide at the molecular level and a high degree of polymerization. Using acetamidine hydrochloride, the solution viscosity increased quickly. The transformation from a sol to a gel in the solution was observed at the low solution viscosity of about 30 mPa s. The gel is opaque, suggesting a high branching of titanium oxide.

In order to grow each particle with a high polymerization degree, the number of particle was restricted since the concentration of reactant monomers was constant. At a high polymerization degree, the number of particles prepared using hydrazine monohydrochloride is smaller than that of particles prepared using acetamidine hydrochloride. That is, the
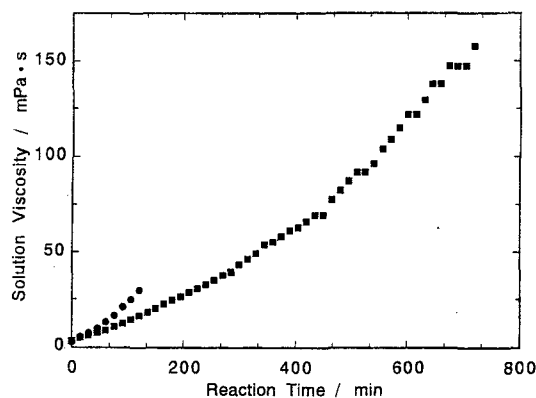
reaction rate decreased with the decrease in the number of particles.

Using hydrazine monohydrochloride, the viscosity of the solution increased much more slowly than when using acetamidine hydrochloride (Fig. 2a). It also increased siginificantly with the addtion of n-butylamine as a base (Fig. 2b). That is, the reaction rate increased with a base. On the contrary, the maximum viscosity significantly decreased. The number of particles also increased with a base.

In the case of acetamidine hydrochloride, only a little increase in the reaction rate was observed with the addition of n-butylamine. The experimental reactions with acetamidine hydrochloride suggested the presence of a base. It is likely that a part of protonated acetamidine ion in acetamidine hydrochloride was dissociated into acetamidine and proton as described in reaction (6) and a resulting acetamidene acted as a base.

4. DISCUSION

The particle creation and growth. The sol-gel process of converting a metal alkoxide to a metal oxide polymer consists of hydrolysis and polycondensation. The condensation reactions by oxolation in an $S_N 2$ mechanism were described in Pierre's review:[10]

$$\text{M-OH} + \text{M-X} + \text{B} \rightarrow \overset{\text{H-B}}{\underset{|}{\text{M-O-M-X}}}$$
$$\rightarrow [\text{M-O-M-X}]^- + [\text{H-B}]^+ \quad (9)$$
$$[\text{M-O-M-X}]^- + [\text{H-B}]^+ \rightarrow \overset{\text{H-B}}{\underset{|}{\text{M-O-M-X}}}$$
$$\rightarrow \text{M-O-M} + \text{HX} + \text{B} \quad (10)$$

Fig. 1.   Time course of solution viscosity in the case of salt catalysts acetamedine hydrochloride (●) and hydrazine monochloride (■). $[\text{Ti}(OC_4H_9)_4] = 0.5$ M, $[H_2O] = 1.0$ M, [diethylene glycol] = 1.0 M and [catalyst] = 0.005M.
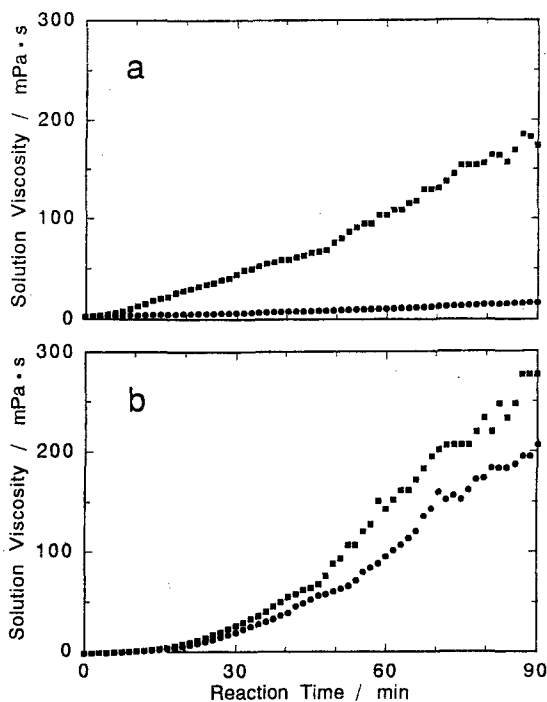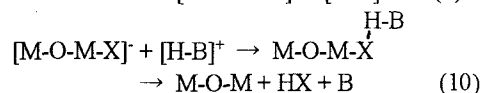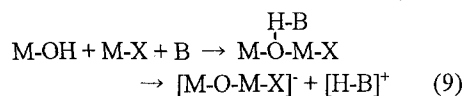
Fig. 2.   Time course of solution viscosity in the case of salt catalysts acetamedine hydrochloride (■) and hydrazine monochloride (●) when without any base (a) and when with n-butylamine (b). $[\text{Ti}(OC_4H_9)_4] = 0.2$ M, $[H_2O]$ = (a) 1.25 and (b) 1.0 M, [diethylene glycol] = 0.5 M, [catalyst] = 0.005M and [n-butylamine] = 0.5 M.

In this formula, M is a metal species such as Ti. B is a base. $[H-B]^+$ is the conjugate acid and X is a hydroxy OH or alkoxy OR group. During the basic catalysis of a formation of oxo bridges (9), a base catalyst, B, binds a partially charged hydrogen atom, H^{d+}, of an hydroxy group belonging to the M-OH structure. This increases a negative partial charge of an oxygen atom of this hydroxy group. The resulting nucleophilic oxygen binds to a metal belonging to the M-X structure.

Similarly, during the acidic catalysis of condensation (10), a proton H^+ binding to a base catalyst binds the oxygen atom of a hydroxy or alkoxy group belonging to the M-X structure.

When the concentration of a base is higher than that of an acid, reaction (9) is faster than reaction (10). An intermediate species, $[M-O-M-X]^-$, is formed by reaction (9) before a total polycondensation is completed by reaction (10). That is, a polymerization start easily in reaction (9) with a base but completes slowly. Therefore, a lot of particles of metal oxide were created. On the other hand, when the concentration of an acid is larger than that of a base, reaction (10) is faster than reaction (9). Reaction (2) occurs more rapidly due to the relatively high concentration of $[H-B]^+$. Therefore, particle growth in (10) proceeds more quickly than particle creation.

A concentration ratio of an acid to a base in a conjugate acid-base pair catalyst. A conjugate acid-base pair, $[H-B]^+$ and B, transforms both ways:

$$[H-B]^+ \rightleftarrows B + H^+ \qquad (11)$$
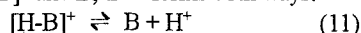
$[H-B]^+$ is an acid and B is a base. If the reaction (11) is fast and reaches a state of equilibrium, concentrations of $[H-B]^+$ and B are determined by the equilibrium constant K_a of the acid dissociation.

When the pH value is higher such as in the case of a protonated hydrazine ion in this study ($pK_a=7.94$), the concentration of $[H-B]^+$ is higher than that of B, i.e. the concentration of the acid is higher than that of the base. Therefore, using hydrazine monohydrochloride, a particle growth proceeded rather than a particle creation. On the other hand, when the pH value is lower such as in the case of a protonated acetamidine ion in this study ($pK_a=1.60$), the concentration of B was higher than that of $[H-B]^+$, i.e. the concentration of the base is higher than that of the acid. Therefore, using acetamidine hydroxide, a particle creation was observed rather than a particle growth.

An active catalyst of a conjugate acid-base pair. If the conjugate acid-base pair is to be used as a catalyst for a metal oxide synthesis, reaction (11) needs to be fast. The rate of reaction (11) is independent of the equilibrium constant of the acid dissociation, but increases with a decrease of an activation energy of reaction (11). In order to lower the activation energy of reaction (11), it is necessary that an appropriate conjugate acid-base pair, such a $[H-B]^+$ and B is used. It appears that the free energy of $[H-B]^+$ is higher than that of B because $[H-B]^+$ is positively charged. The potential curve of a charged species is broadened by the delocalization of the positive charge as in $[H-B]^+$. When the potential curve of $[H-B]^+$ is broadened, the activation energy of reaction (11) is lowered.

Acetamidine hydrochloride and hydrazine hydrochloride are catalytically active in the synthesis of titanium oxides. The symmetrical structure of protonated acetamidine and protonated hydrazine ions allows the positive charge of a protonated ion to be delocalized, and therefore the activation energy of reaction (11) is lowered.

5. CONCLUSION

The particle creation and the particle growth of titanium oxide by a sol-gel process were controlled using a conjugate acid-base pair catalyst, in this case hydrazine monohydrochloride or acetamidine hydrochloride. Particle creation increased according to the concentration of base while particle growth increased according to the concentration of acid. The concentration ratio of acid to base (the molarity) in the conjugate acid-base pair catalyst was controlled by the addition of acid or base. A conjugate acid-base pair catalyst which has the symmetric structure of a protonated species exhibited the high catalytic activities.

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