

아세트산과 티타늄 이소프로폭시드의 반응기구에 관한 연구

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The study on the reaction mechanism of titanium isopropoxide with acetic acid

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Introduction

In the recent decades, sol-gel process has received increased attention due to the ability to produce high quality ceramic raw materials from which dense ceramic bodies are fabricated. The technological importance of titania based materials has been well known for a long time. These materials can be used as pigments, as powders for catalytic or photo catalytic applications, as colloids and thin films for electro luminescence devices [1, 2]. Direct addition of water to TMA leads to the formation of disordered precipitates. Therefore, their high reactivity should be controlled to obtain a desired range of uniform spherical powders and homogeneous gels. Chemical modification of TMA with alcohols, chlorides, acids or bases, chelating ligands, etc is commonly employed to retard the hydrolysis and condensation reaction rates in order to control the condensation pathway of the evolving polymer [3, 4, 5]. Acetic acid is one of the chemical additives commonly used in sol-gel processing of transition metal alkoxide. Hydrolysis and condensation reaction of TIP are strongly modified in the presence of acetic acid (AcOH). This is due to the complexing ability of acetate ligands. Although modification reactions have been documented in literature, it has been rarely attempted to elucidate the reaction mechanism of TIP with AcOH. The study on the modification reaction of TIP by AcOH had been only reported by Sanchez and co-workers.

This paper investigated on the reaction mechanism in a mixture of TIP and AcOH by the FT-IR analysis for several solutions. A new model for the reaction mechanism is proposed, based on the variation of the relative intensity ratios of FT-IR spectra for isopropyl alcohol and isopropyl acetate ester with reaction time. We have compared our result and that of Sanchez which is known much. We have also investigated the effect of starting alkoxides on the molecular structure of trimer and/or dimer which are generated at early stage of reaction and on the reaction rate. Because of the importance of the esterification reaction, its evolution with time was another focus of this paper.

Experiments

When glacial acetic acid (J. T. Baker) is added to pure titanium isopropoxide (TIP, Aldrich), an exothermic reaction takes place leading to a clear solution. IPOH and IPOAcE are produced during the reaction. After intimate mixing, the clear solution is left to stand in a closed vessel in order to avoid evaporation of AcOH, IPOH, and IPOAcE. It was found that the aging process strongly depend on the concentration of TIP and AcOH at a given temperature (45°C). We thus tried to check the influence of [AcOH]/[TIP] ratio (0.025~8) on the modifying process of TIP. In addition to the solutions of direct interest, the FT-IR absorption analysis were performed for the pure TIP, IPOH (Aldrich), AcOH, IPOAcE (Yakuri) as well as mixtures of IPOH-AcOH, IPOH-IPOAcE, H₂O-IPOAcE and AcOH-IPOAcE. No gel was obtained when the [AcOH]/ [TIP] ratio was smaller than 1.5. When the [AcOH]/[TIP] ratio was greater than 2, the gelation time quickly decrease with increasing the AcOH concentration.

To investigate the effect of precursors on the reaction mechanism, the FT-IR absorption band were measured for the mixture of AcOH and titanium tetra-butoxide (TTB, Ti(OBun)₄, Aldrich) with time. n-butyl alcohol (NBOH) and butyl acetate ester (BOAcE) are generated during the reaction of AcOH and TTB. The FT-IR absorption band for pure n-butyl alcohol (Junsei) and butyl acetate ester (Aldrich) were also measured. FT-IR spectra were recorded on a BIO-RAD spectrometer in the 4000-350 cm⁻¹ frequency range. Spectra of solutions were measured by putting a droplet between two KRS5 windows.

Result and discussion

Fig. 1 shows FT-IR spectra for the mixtures of IPOH/IPOAcE, AcOH/IPOAcE, AcOH /IPOH/IPOAcE, AcOH/IPOH and H₂O/IPOAcE. An absorption band at 1247 cm⁻¹, which is main absorption band of IPOAcE, is clearly shown to be in IPOH/IPOAcE, AcOH/ IPOAcE and AcOH/ IPOH/ IPOAcE solution, but it did not appear in AcOH/ IPOH solution with reaction time of an hour. The absorption bands at 1294 and 1714cm⁻¹, which are main absorption bands of AcOH, were not observed in H₂O/IPOAcE solution with reaction time of an hour. In sol-gel process, the direct esterification reaction of AcOH and alcohol generated by the chemical modification reaction of metal alkoxides with AcOH has been reported for the first time by JADA as shown in eq.(1)



However, JADA added concentrated HCl in a mixture of TEOS with AcOH. Therefore, hydronium ion[H⁺] that acts as a catalyst of reaction (1) exists very much in the reaction solution. Many studies reported that a direct esterification reaction between the propanol and acetic acid is possible in a mixture of titanium alkoxides and acetic acid. But, there is no report on the formation mechanism of hydronium ion in alkoxide/AcOH solution so far. Therefore, it is thought that generation of IPOAcE and water by direct esterification reaction might be possible theoretically, their influence is negligible in the entire process.

Figs. 2 and 3 show the FT-IR spectra for pure IPOH, IPOAcE and IPOH/IPOAcE mixtures ($0.1 = [\text{IPOH}]/[\text{IPOAcE}] \leq 0.9$) and the variation of FT-IR spectra with reaction time when a $[\text{AcOH}]/[\text{TIP}]$ ratio of 0.5, respectively. Two absorption bands at 1721 and 1270 cm^{-1} appeared in all of Figs. 2 and 3. In Fig. 2, they are not associated with the pure starting solution and increases in intensity with increasing the IPOH concentration. Absorption bands at 1721 cm^{-1} and around 1280 cm^{-1} (from 1260 to 1300 cm^{-1}) were assigned to the stretching vibration $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively, of acetate group (AcO^-) coordinated to the titanium atoms by monodentate mode ($\Delta\nu > 425 \text{cm}^{-1}$) so far. When acetic acid is added in large excess ($[\text{AcOH}]/[\text{TIP}] = 10$), Doeuff et al. assigned two bands at 1718 and 1270 cm^{-1} to the monodentate acetate ligand due to the large frequency separation ($\Delta\nu = 450 \text{cm}^{-1}$). This result agrees correctly with two bands that appear newly in IPOH and IPOAcE mixture, and an absorption band due to acetate groups bonded to titanium by monodentate mode does not appear in the Nakamoto's book that is quoted by several investigators. Therefore, it can be concluded that two absorption bands at 1721 and 1270 cm^{-1} in Fig.3 are due to the interaction of IPOH and IPOAcE that is generated by the reaction of TIP and AcOH. In Fig. 3, an absorption band at 660 cm^{-1} appearing since 2 min after is attributed to stretching vibration of the $\nu(\text{Ti-O-Ti})$ bond because its appearance also in the pure TiO_2 (rutile) particles. In early stage of reaction, the formation of Ti-O-Ti bonds means that condensation reaction is gone fast in the TIP and AcOH solution. Variations of the relative intensity ratio of absorption bands at 1741, 1721, and 1440 cm^{-1} in Fig. 3 are shown in Fig. 4 as a function of reaction time. Relative intensity ratios of IPOH at 1721 cm^{-1} and IPOAcE at 1741 cm^{-1} (hereafter denoted as RI $[\text{IPOH}]/[\text{IPOAcE}]$) decreased for 1 h, and increase until next 6 h, and thereafter, decreased continuously with increasing reaction time (Fig.4 (A)). On the contrary, RI $[\text{IPOAcE}]/[\text{Ti-OAc}]$ increased for 2 h, and decrease until next 9 h, and thereafter, increased continuously with increasing reaction time (Fig.4 (B)). RI $[\text{IPOH}]/[\text{Ti-OAc}]$ increased dramatically at the beginning of the process for 2 h, then become almost constant. At early reaction for 1h, decrease of RI $[\text{IPOH}]/[\text{IPOAcE}]$ and increase of RI $[\text{IPOAcE}]/[\text{Ti-OAc}]$ and RI $[\text{IPOH}]/[\text{Ti-OAc}]$ arise from the formation of IPOAcE by the esterification reaction. However, because the role of AcOH is the generation of metal alkoxo-acetates ($\text{Ti}(\text{OR})_{4-x}(\text{OAc})_x$) by modification reaction with TIP and this reaction is very fast, we had come to the conclusion that direct modification reaction is negligible in the entire process. After the reaction time of 6 h, RI $[\text{IPOH}]/[\text{IPOAcE}]$ decrease, while RI $[\text{IPOAcE}]/[\text{Ti-OAc}]$ increases monotonically. These results can be attributed to the formation of IPOAcE by esterification reaction between IPO and AcO in oligomer. After the reaction time of 1 h, increase of RI $[\text{IPOH}]/[\text{IPOAcE}]$ is caused by increase of IPOH concentration that is generated by the alcohol forming condensation between unreacted Ti-OPI and Ti-OH

Conclusion

Chelating acetate ligands were generated first by reaction between TIP and AcOH, and then bridging acetate ligands were created. Acetic acid reacted very fast with titanium isopropoxide than titanium tetra-butoxide. We could know that the molecular structure of dimer and/or trimer that Sanchez presents can be created by the reaction

of titanium tetra butoxide and acetic acid rather than that of titanium isopropoxide and acetic acid. Esterification reaction of molecular level and of in oligomer occurred sequentially with increasing reaction time.

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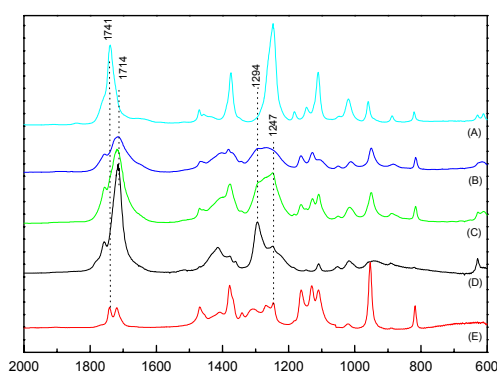


Fig.1. FT-IR spectra of : (A) $H_2O:IPOAcE=1:1$, (B) $AcOH:IPOH = 1:1$ (C) $AcOH:IPOH:IPOAcE = 4.5:4.5:1$, (D) $AcOH:IPOAcE=9:1$ (E) $IPOH:IPOAcE = 9:1$. (reaction time of (A) and (B) : 1h).

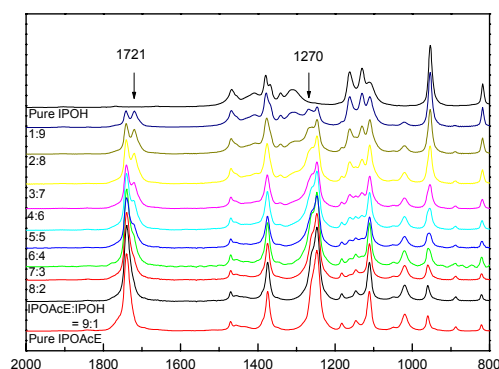


Fig.2. FT-IR spectra of pure isopropyl acetate ester, pure isopropanol and mixtures of pure isopropyl acetate ester and pure isopropanol.

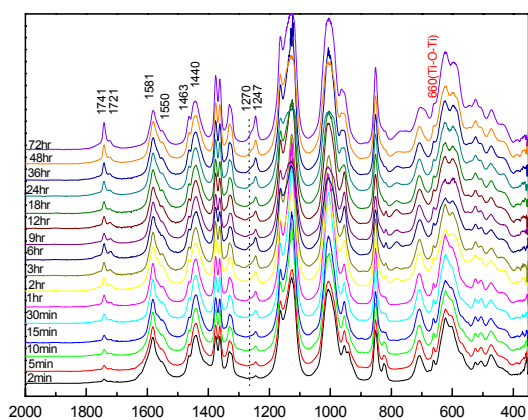


Fig.3. FT-IR spectra of mixtures of acetic acid and titanium isopropoxide as a function of reaction time ($[AcOH] / [TIP] = 0.5$).

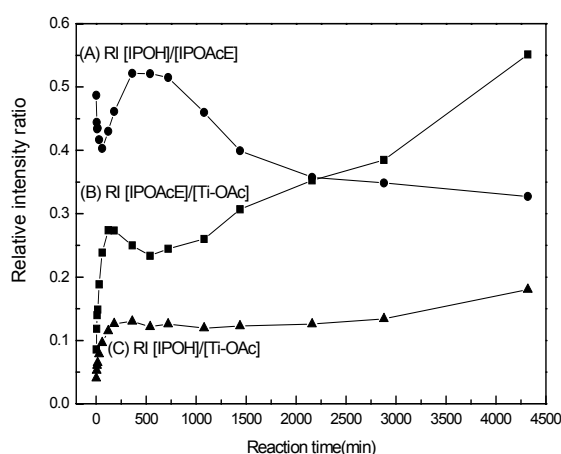


Fig.4. Variations of the absorption bands intensity ratios as a function of reaction time.