Articles

Structural Investigation of the Hydrolysis-Condensation Process of Modified Titanium Isopropoxide

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The structures of modified $Ti(OPr^i)_4$ with chelating ligands (L) such as ethylacetoacetate (Etac), acetylacetone (Acac) and methylacetoacetate (Mtac) were identified by using IR, ^1H NMR and ^{13}C NMR spectroscopies, and the octahedral structure was confirmed after modification. The pre-edge peaks of XANES spectra of modified metal alkoxides also denoted the mixture of five-fold and six-fold structures. The EXAFS fitting results showed the local structure around Ti atom after alkoxide modification. The hydrolysis-condensation rates of modified Ti alkoxide with organic additives were investigated by ^1H NMR spectroscopy. The $Ti(OPr^i)_4$ modified by Acac was less reactive toward hydrolysis-condensation reaction than those modified by the other alkoxides, which can be attributed to the stable ligand structure between $Ti(OPr^i)_4$ and Acac. The small particle size of modified $Ti(OPr^i)_4$ sol was obtained when Acac was employed.

Introduction

The chemical modification of metal alkoxide with alcohols, chlorides, acids/bases, and chelating ligands is commonly used to retard the hydrolysis and condensation reaction rates. These modification of metal alkoxides with chelating ligands results in the control of condensation pathway to evolve the inorganic polymer. Therefore, the particle size, morphology, and properties of the prepared gels are greatly affected by the types of precursors. Many results have been reported to describe the role of chelating ligand in the modification of metal alkoxide. Babonneau and Livage *et al.*[1] had reported the structure of $Al(OBu)_3$ with ethylacetoacetate (Etac). The Etac groups modified the $Al(OBu)_3$ with the formation of bidentate ligand structure which was much less susceptible to hydrolysis reaction than $Al(OBu)_3$. Nass *et al.*[2] had reported the modification of Al alkoxide with acetylacetone and ethylacetoacetate. This modification resulted in the small particle size of alumina sols in the range of 1 to 15 nm. The particle size of alumina sols strongly depended on the types of chelating ligands as well as on the molar ratio of $Al(OBu)_3$ to chelating ligands. Shul et al. had reported that chelating ligand of hexylene glycol was used in the rutilent phase of TiO_2.[3] This low temperature transformation of rutilent phase could be due to the stable bidentate ligand structure of modified Ti alkoxide with hexylene glycol. Yang *et al.*[4] had reported that stable bidentate ligand structure between $Al(OBu)_3$ and ethylene glycol affected the phase transformation behaviour of Ru/Al_2O_3 as well as particle size of Ru after oxidation and reduction. These results reported the importance of alkoxide modification with chelating ligands and the effects of chelating agent on the properties of prepared gels. However, few systematic studies have been reported about the quantitative hydrolysis-condensation rate and stability of modified metal alkoxides. In the present study, the structure of modified Ti alkoxides with organic additives such as acetylacetone, methylacetoacetate and ethylacetoacetate was characterized using by ^1H NMR, ^{13}C NMR, FT-IR, and XANES/EXAFS spectroscopies. The hydrolysis and condensation rates of these modified metal alkoxides were obtained by ^1H NMR spectroscopy. The effects of organic additives on the properties of prepared sol/gel were also disscussed.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded by using a Varian Gemini 200 spectrometer with the signals of the $CDCl_3$ solvent as an internal standard. FT-IR Spectra was obtained from a Nicolet Impact 410 spectrometer in the 4000-400 cm^{-1} frequency range. Solutions were studied by putting a droplet between two KBr windows. TiO_2 powder dispersed in a KBr pellet was studied. Dynamic light scattering for the particle size measurement was recorded with a Brookhaven Zeta plus device. Elemental analysis was done by the Gmbh Vario Elemental Analysensysteme. Freshly distilled chemicals were purchased and used from the Aldrich Chemical Company. The reactions were carried out in dried solvents and under nitrogen gas. The volatile components were removed by vacuum distillation. X-ray absorption (XANES/EXAFS) at the K-edge (4968 eV) was performed the thickness of the cells was 0.1 mm, and the windows were made of X-ray-transparent kapton.

Modified $Ti(OPr^i)_{4-x}(L)_x$. The compounds of acetylacetone, methylacetoacetate and ethylacetoacetate were individually added to $Ti(OPr^i)_4$ in isopropanol solvent in the following molar ratios: 1 : 1, 2 : 1, 3 : 1. The resulting pale-yellow solution was purified by vacuum distillation.

Hydrolysis-condensation reaction. $Ti(OPr^i)_{4-x}(L)_x$ was hydrolyzed with two equivalents of D_2O containing $CDCl_3$ solvent. ^1H NMR spectra on these sol solutions were recorded at 10 minutes intervals. TiO_2 powder was obtained after drying these sol solutions in a vacuum oven (80 °C, 5 hours).

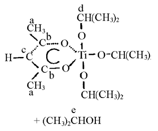
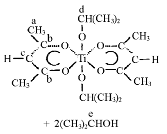
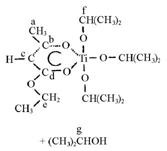
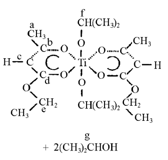
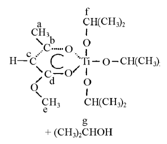
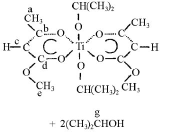
Results and Discussion

The modified titanium alkoxides. In our study, a stoichiometric reaction for the production of the modified titanium alkoxide complexes take place as following.

$$Ti(OPr^i)_4 + x(\text{Acac, Etac, Mtac: L}) \rightarrow Ti(OPr^i)_{4-x}(L)_x + x\ {}^iPrOH$$

The NMR peak assignments of various titanium complexes obtained from different molar ratios are indicated in Table 1. Firstly we examined the 1 : 1 molar ratio of $Ti(OPr^i)_4$ and ethylacetoacetate in detail. Two kinds of peaks corresponding to methine position of the isopropoxide attached to titanium are shown in Figure 1 (a) and (b) and also labelled as (c) in Table 1. We know that the above reaction took place due to the appearance of the new peak (δ_H = 4.77 ppm) while maintaining the expected peak (δ_H = 4.49 ppm) from $Ti(OPr^i)_4$. The above reaction is verified by the appearance of another peak at δ_H = 4.03 ppm which clearly indicates that isopropanol is released from the reaction. The CH_3 peak (δ_H = 1.94 ppm) and the two CO peaks (δ_{C1} = 172.5 ppm, δ_{C2} = 184.8 ppm) indicate the existance of a asymmetrical Ti-O bonding of the Etac. The ratio of the released CH peak of isopropanol (δ_H = 4.03 ppm) and the sum of the isopropoxide (δ_H = 4.77 ppm, δ_H = 4.49 ppm) attached to titanium was 1 : 3. We estimated that roughly 67 percent of the unreacted isopropoxide group remained in this reaction.

Table 1. ^1H and ^{13}C NMR data of modified Ti alkoxides in $CDCl_3$

$Ti(OPr^i)_4$: Organic additive		^1H NMR δ (ppm)	^1H NMR Assignment	^{13}C NMR δ (ppm)	^{13}C NMR Assignment	Structure suggested
Acetyl-acetone	1:1	5.51	c	191.3	b	
		4.78, 4.49	d	102.7	c	
		4.03	e	78.7, 76.2	d	
		2.03, 1.92	a	64.2	e	
	1:2	5.51	c	191.3, 187.3	b	
		4.78	d	102.7	c	
		4.02	e	78.7	d	
		2.03, 1.92	a	64.4	e	
Ethyl-aceto-acetate	1:1	4.95	c	184.8	b	
		4.77, 4.49	f	172.5	d	
		4.03	e, g	88.3	c	
		1.94	a	79.1, 76.3	f	
				64.3	g	
	1:2	4.95	c	184.8	b	
		4.77	f	172.5	d	
		4.03	e, g	88.3	c	
		1.94	a	79.1	f	
				64.3	g	
Methyl-aceto-acetate	1:1	4.94	c	185.1	b	
		4.75, 4.49	f	172.9	d	
		4.03	g	87.9	c	
		3.55	e	79.3, 76.3	f	
		1.92	a	64.4	g	
	1:2	4.94	c	185.1	b	
		4.75	f	172.9	d	
		4.03	g	87.9	c	
		3.55	e	79.3	f	
		1.92	a	64.4	g	

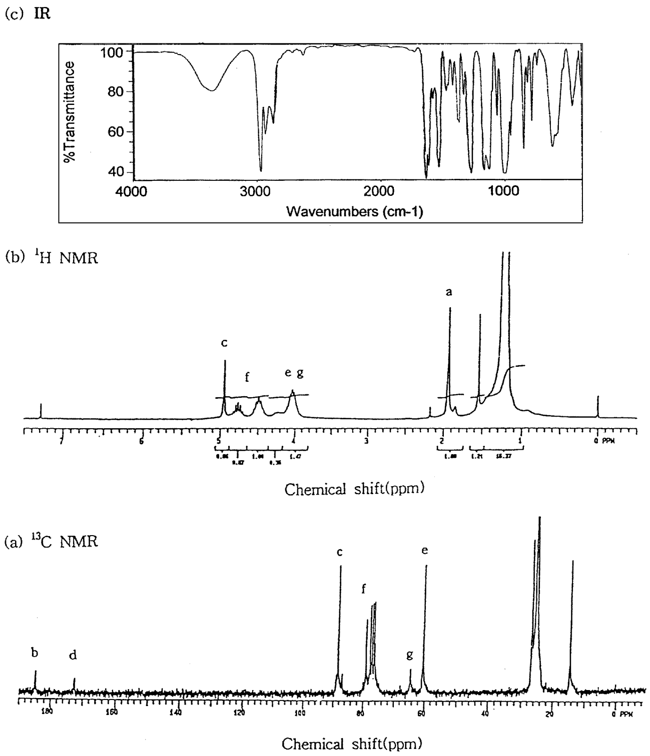


Figure 1. IR, ^1H and ^{13}C NMR spectra of $Ti(OPr^i)_3(Etac)$.

The broad absorption bands around 1096 cm^{-1} (C-O) and 627 cm^{-1}[ν(Ti-O)] in a IR spectrum of this complex suggest that isopropoxide groups are still bonded to titanium. The absorption bands around 2900 cm^{-1}[ν(C-H)], 1630 cm^{-1} (C=O), 1531 cm^{-1} (C-C) and lower frequency at 470 cm^{-1} [ν(Ti-O) are evidence of Etac groups being bonded to titanium. The spectral data of this modified complex were different from $Ti(OPr^i)_4$ which has equivalent isopropoxide groups.[5] Another evidence of the above reaction is that the XANES/EXAFS spectra of this complex shown in Figure 2 shows a single pre-peak and the intensity of this peak become smaller due to the chemical modification, this results suggesting that the coordination around titanium is changed from four to five or six.[6]

The XANES (X-ray absorption Near Edge Spectrum) of Ti is sensitive to the coordination structure and valence state of Ti atom. In the octahedral TiO_2 had small triplet pre-edge peaks, which associated with the $A_{1g} \rightarrow T_{2g}$ and $A_{1g} \rightarrow E_g$

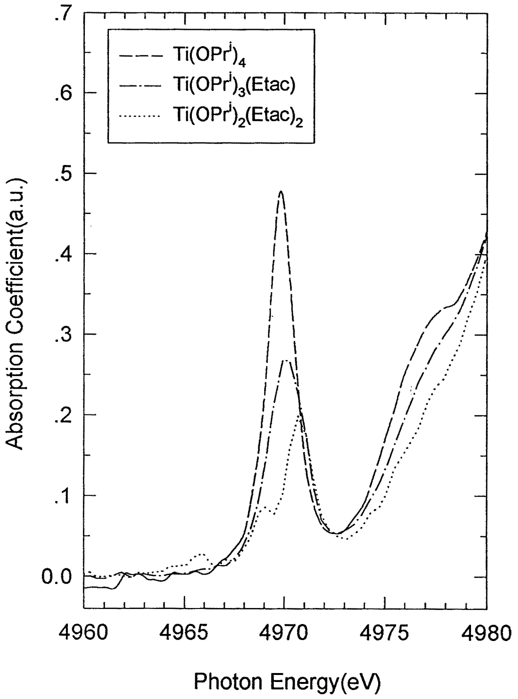
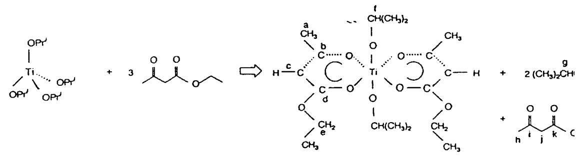


Figure 2. Pre-edge of XANES (X-ray Absorption Near Edge Structure) spcetra of Ti(OPr^i)$_4$ and the modified with ethylacetoacetate at Ti K-edge.



Scheme 3

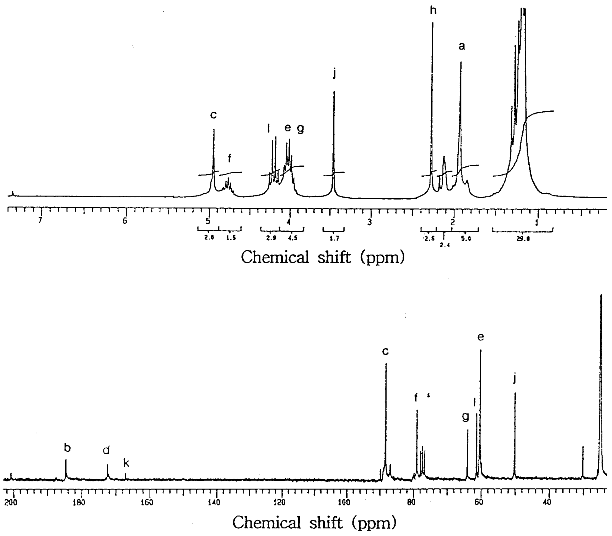


Figure 3. ^{1}H NMR spectra of modified Ti alkoxides with ethyl acetoacetate. [Ti(OPr^i)$_4$: Etac = 1 : 3]

transition. In tetrahedral symmetry, the final states were T_2 and E (A1T2, A1E), and only one strong pre-edge peak near 4968eV can be observed. In the XANES of Ti(OPr^i)$_4$, one strong pre-edge peak is observed near 4969 eV and the height of pre-edge peak at *ca*. 4970 eV is 0.47, which shows the tetrahedral symmetry of Ti(OPr^i)$_4$. In the case of Ti(OPr^i)$_3$(Etac)$_2$, the small new peak at 4969 eV is observed and the intensity of pre-edge peak at 4970 eV is decreased into 0.198. It implies the existence of octahedral symmetry of Ti atom in Ti(OPr^i)$_2$(Etac)$_2$. However, the XANES spectra of Ti(OPr^i)$_2$(Etac)$_2$ is not completely similar to that of six-fold TiO_2, anatase or rutile, which implies the mixture of five-fold and six fold octahedral structure in Ti(OPr^i)$_2$(Etac)$_2$.

In a case when two or more moles of Etac were used for the reaction, ^{1}H and ^{13}C NMR signals of the $\delta_H = 4.49$ ppm and $\delta_C = 76.3$ ppm disappeared and others still remained. The ratio of the released CH peaks of isopropanol ($\delta_H = 4.03$ ppm) and the isopropoxide ($\delta_H = 4.77$ ppm) attached to titanium was equal. In the reaction of 1 : 2 or even excess molar ratio, two moles of isopropoxide was removed, replaced by two moles of Etac in Figure 3. The pre-edge peaks of XANES spectra of modified titanium-Etac complex has reduced intensity with two peaks shown. Where the above results denote the mixture of five-fold and six-fold octahedral structures of Ti(OPr^i)$_2$(Etac)$_2$.

Modified titanium(IV) acetylacetone and methylacetoacetate complexes were also identified using the same method. The shape, position, and intensity of spectral data on these complexes are very simliar to what has been discussed above (Table 1).

Hydrolysis-condensation reaction. Ti(OPr^i)$_{4-x}$(L)$_x$ was hydrolyzed with two equivalents of D_2O containing $CDCl_3$ solvent. The rate of this reaction on the Ti(OPr^i)$_2$(Etac)$_2$ was observed by NMR spectroscopy progressing time and shown as representative example. Upon comparison of the three spectra, new signals appeared and also the signal intensity had changed. The multiplet peaks at 4.77 ppm corresponding to the -CH- part of the isopropoxy group bonded to titanium are removed by addition of D_2O (Figure 4). The free isopropanol becomes clearly visible at a new peak position ($\delta_H = 3.96$ ppm). The chemical shift of -OCH_2- part of the ethylacetoacetate attached to titanium complex at 4.02 ppm is moved toward peak at 4.18 ppm corresponding to free ethylacetoacetate ligand during hydrolysis reaction. This peak at 4.18 ppm keeps on growing as time progresses. Furthermore, the -CH- peak of isopropyl group at 4.77 ppm rapidly disappeared. However methyl peak of Etac bonded to titanium at 1.92 ppm slowly hydrolyzed, but still reminants were shown in ^{1}H NMR spectra.

Ti(OPr^i)$_3$(Etac) was also hydrolyzed by the same condition and observed hydrolysis rate was faster than that of Ti(OPr^i)$_2$(Etac)$_2$ in Figure 5. The rate of hydrolysis-condensation reaction was inversely proprotional to the amount of ligand added: this was inclusive of all the ligands tested. It is postulated that the hydrolysis rate of the more stable six-fold structured Ti(OPr^i)$_2$(Etac)$_2$ is slower than the less stable five-fold structured Ti(OPr^i)$_3$(Etac).[7]

Upon comparison of the ligands, the rate of these reactions increased in the following order (Figure 6): Ti-Mtac > Ti-Etac > Ti-Acac bond. One could calculate rate constant in a direct way and the rates of these reaction are dependent on

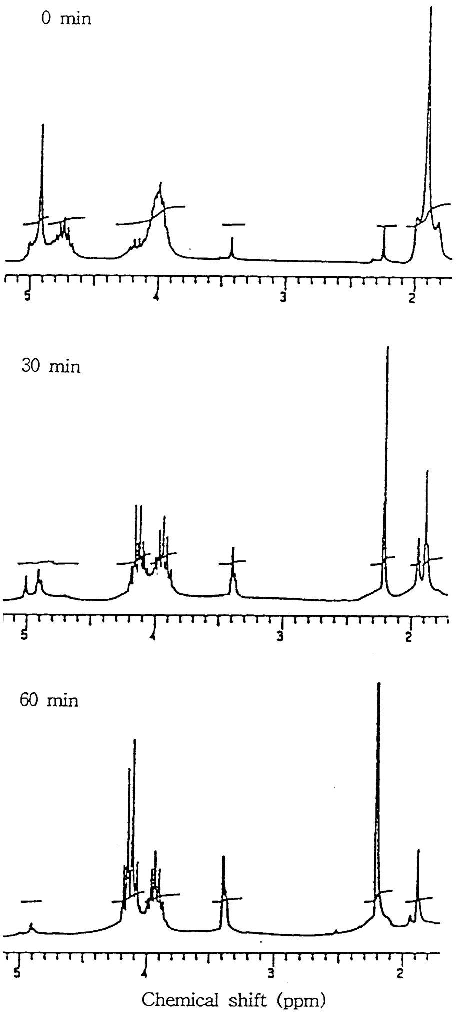


Figure 4. ^1H NMR spectra of $Ti(OPr^i)_2(Etac)_2$ obtained at different time intervals in hydrolysis-condensation reaction.

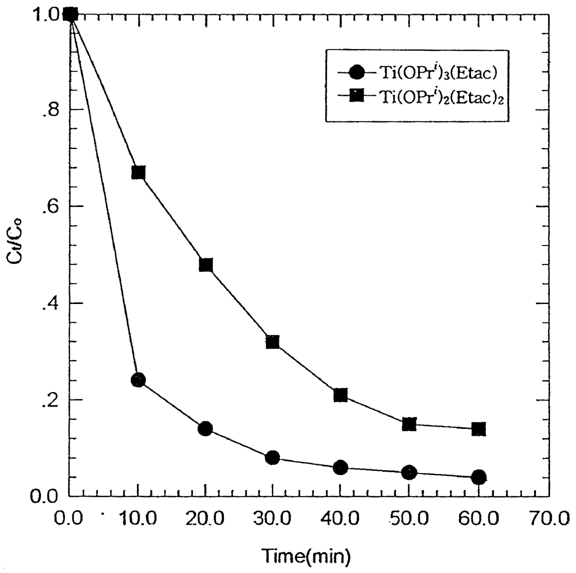


Figure 5. Rates of hydrolysis-condensation of $Ti(OPr^i)_{4-x}(Etac)_x$ in $CDCl_3$. C_t: concentration of $Ti(OPr^i)_{4-x}(Etac)_x$ at t hours. C_o: initial concentration of $Ti(OPr^i)_{4-x}(Etac)_x$.

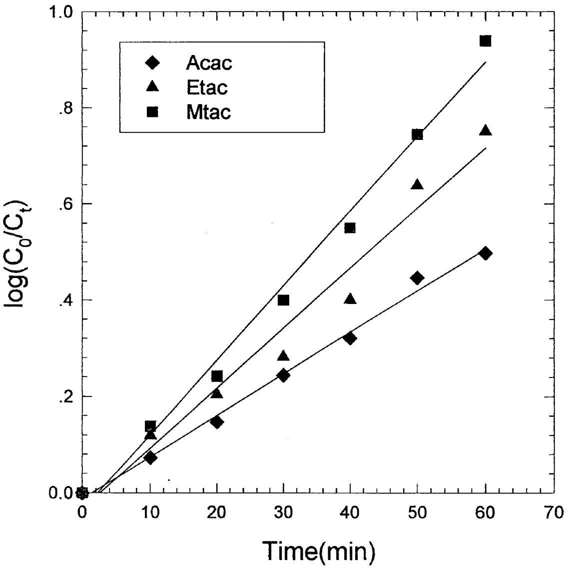


Figure 6. Rates of hydrolysis-condensation reaction of $Ti(OPr^i)_2(L)_2$ in $CDCl_3$. (L: Etac, Acac, and Mtac). C_t: concentration of $Ti(OPr^i)_2(L)_2$ at t hours. C_o: initial concentration of $Ti(OPr^i)_2(L)_2$.

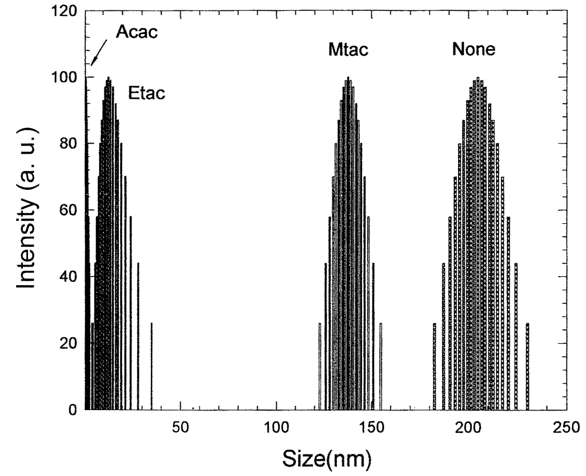


Figure 7. Particle size distributions of Ti alkoxide sol and modified Ti alkoxide sols with organic additives.

the type of ligand added.

The particle size of these hydrolyzed sol were measured on $Ti(OPr^i)_2(OR)_2$ (Figure 7). The size of TiO_2 sol without ligand was not homogeneous, the largest is approximately 205 nm. The particle size of modified TiO_2 sol with Mtac was 140 nm. The value of the smaller particle size with Etac was 13 nm and the smallest one obtained from the reaction with Acac was about 5 nm of homogeneous composition. The rate of hydrolysis-condensation reaction was related to the size of the particle of the resulting TiO_2 sol. Homogeneous thin TiO_2 could be obtained by controlling hydrolysis-condensation rate which in turn is dependent on the type of ligand used.[8] Analyzing Data were obtained from the TiO_2 powder dried in a vacuum oven, the organic additives bonded to titanium was still identified as remaining. The strong absorption bands around 1630 cm^{-1} [ν(C=O)], 1531 cm^{-1} [ν(C-C)], 1270 cm^{-1} [ν(C-O)] and 470 cm^{-1} [ν(Ti-

OEtac)] indicated the existence of these ligands in IR spectra. Elemental analysis data on TiO_2 powder with Etac ligand were obtained (O: 8.98 ± 0.45%, C: 10.47 ± 0.11%, H: 2.53 ± 0.07%).

Conclusion

The modified titanium alkoxides with organic additives (chelating ligand) such as β-diketone and β-keto-ester such as acetylacetone, ethylacetoacetate, and methylacetoacetate have been described. The rate of the hydrolysis-condensation reaction is inversely proportional to the amount of ligand. Furthermore, the reaction decreases in the following order of Ti-Mtac, Ti-Etac, and Ti-Acac. The particle size in the TiO_2 sol are dependent upon the properties of the ligand used and the ratio of additives. The trace of ligand used in the final product, TiO_2 power, was also detected as existing bound to titanium.

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References

1. Bonhomme-Coury, L.; Babonnearu, F.; Livage, J. J. *Sol-Gel Sci. & Tech.* **1994**, *3*, 157.
2. Nass, R.; Schmidt, J. H. *Non-Crystalline Solids* **1990**, *121*, 329.
3. Shul, Y. G.; Oh, K. S.; Yang, J. C.; Jung, J. K. T. *Sol-Gel Sci. & Tech.* **1997**, *8*, 255.
4. Yang, J. C.; Shul, Y. G. *Catal. Lett.* **1996**, *36*, 41.
5. Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.
6. Livage, J.; Henry, M. *Ultrastructure Process of Advanced Materials*; Mackenzie, J. *et al.*, Eds.; John Wiley and Sons: New York, 1998; p 78.
7. Sedlar, M.; Sayer, J. M. *Sol-Gel Sci. & Tech.* **1995**, *5*, 27.
8. Babonneau, F.; Coury, L.; Livage, J. J. *Non-Crystalline Solids* **1990**, *121*, 153.