parallel to the *c* axis are present with a distorted octahedral site at $^{1}/_{2},0,0$ and a distorted tetrahedral site at $^{1}/_{2},0,^{1}/_{4}$. In the three materials studied the Ti has been partially replaced by Nb and either Zn, Al, or Li. The cell volumes and Ti–O bond lengths observed in the three structures reflect the degree of Ti substitution in the particular material. In the Li- and Zn-substituted materials where much of the Ti has been replaced by the larger Nb, Zn, and Li atoms, the bond lengths and cell volumes are larger than those observed in rutile itself, for which $V = 62.45$ Å^3 and Ti–O = 1.945 × 4, 1.986 × 2 Å. In $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ titanium is replaced by equal amounts of slightly larger Nb and considerably smaller Al cations, and consequently, the bond lengths and cell volume are somewhat smaller than in rutile.

The structure of $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$ closely resembles that of rutile itself with occupation of the rutile octahedral cation site only. The Zn–O bond lengths of 1.9848 (1) and 2.0023 (2) Å are slightly shorter than the average bond lengths observed for octahedral Zn in $Zn_2Mo_3O_8$[8] of about 2.1 Å but reflect the average bond lengths for the Nb/Ti/Zn site.

Like the Zn-substituted material, $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ differs little from the basic rutile framework. The bond lengths of 1.9757 (4) × 2 and 1.9478 (2) Å are within the range quoted for octahedral Al–O distances of 1.85–1.98 Å.[9]

The structure of $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ shows finite occupation of both the channel and framework sites by Li ions, demonstrating once again that lithium ions are stable in both distorted and regular oxygen environments. The intercation distances suggest that Li(2) and Li(3) are unlikely to be simultaneously occupied. The distorted octahedral Li(2) site shares faces with two Li(1)/Ti/Nb octahedral sites, with Ti–Li(2) distances of 2.34 Å. The distorted tetrahedral Li(3) does not share a face with the Li(1)/Ti/Nb site, the closest Ti–Li(3) distance being 2.462 Å. The Li–Ti distances are similar to the shortest distance of Ti–Li = 2.33 Å seen in $Li_2Ti_3O_7$.[10] The site occupancy of Li(2) is apparently double that of Li(3), in which case it is not the Ti–Li contact distances that significantly affect the distribution, but the coordination, the octahedral coordination being preferred over that of tetrahedral coordination. The average Li–O values of 2.076 and 1.85 Å in Li(2) and Li(3) sites are typical for octahedrally and tetrahedrally coordinated Li, respectively.[9]

When powder refinement is carried out on a solid in which a given ion may be distributed over several sites and with a low occupancy of each site, it is generally necessary to tie the *B* factors of all the sites together in order to continue the refinement; this inevitably reduces the precision with which the highly correlated occupancies and *B* factors are determined.

Powder neutron diffraction at ISIS has proved a useful tool for determining the structure of materials; in particular the very high resolution of the data and the low *d*-spacing limit of 0.4 Å have permitted very accurate structure parameters to be obtained.

Acknowledgment. We thank W. A. T. Harrison and R. M. Ibberson at the Neutron Division, Rutherford-Appleton Laboratory, UK, for their help in this work; the computer center at Heriot-Watt University for the provision of computing facilities for profile refinement, and the SERC for financial support.

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Structural Investigation of the Hydrolysis–Condensation Process of Titanium Alkoxides $Ti(OR)_4$ (OR = OPr^i, OEt) Modified by Acetylacetone. 1. Study of the Alkoxide Modification

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Chemical modifications of alkoxides have been extensively used in sol–gel processing for a better control of the hydrolysis–condensation process. In this paper, the modification of titanium alkoxides ($Ti(OPr^i)_4$, $Ti(OEt)_4$) with acetylacetone is investigated by using infrared, ^1H and ^{13}C NMR, and X-ray absorption (XANES–EXAFS) spectroscopies. The reaction with titanium isopropoxide leads to a unique species, $Ti(OPr^i)_3acac$ (acac = acetylacetonate), whose structure is precisely described. It appears to be a monomer with titanium in 5-fold coordination. The reaction between acetylacetone and titanium ethoxide leads to the existence of several species in equilibrium, monomers in 5-fold coordination and oligomers in 6-fold coordination. These structural differences are related to the ability of the alkoxy groups to behave as bridging ligands. A study of the dilution of the modified precursor $Ti(OPr^i)_3acac$ in ethanol is also presented. Substitution of isopropoxy groups by ethoxy groups occurs and leads to the formation of new monomeric and oligomeric species. These products were characterized by ^1H NMR spectroscopy.

Introduction

Sol–gel processing has been widely investigated, especially for the manufacture of glasses and ceramics.[1,2] It requires the use of molecular precursors, mainly metal alkoxides from which a solid network is obtained through

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(1) *Ultrastructure processing of advanced ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988.

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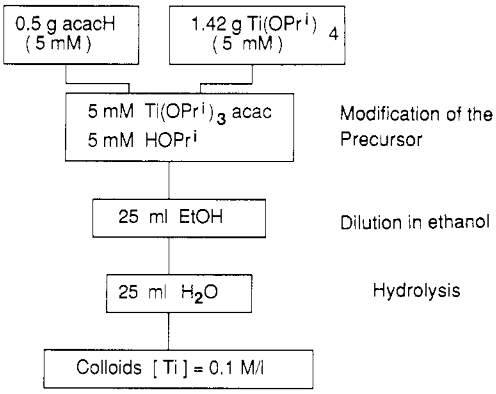

Figure 1. Preparation of TiO_2-based colloids from modified titanium alkoxides.

a hydrolysis–condensation process.[3] Polycondensation can be highly influenced by modification of the precursor, by using some chemical additives.[4,5] Stable colloidal solutions, monolithic gels, or precipitates can be prepared depending on these additives.[6,7] Some properties of the final product, such as optical absorption, can also be modified simply by choosing a convenient additive.[8] Consequently, a considerable effort is currently being directed toward the understanding of the inorganic polymerization reactions.

Acetylacetone has often been used in sol–gel processing as a chemical additive to reduce the reactivity of metallic alkoxides.[5,9–12] Stable TiO_2-based colloids have been prepared by using a new precursor, $Ti(OPr^i)_3acac$, derived from the modification of titanium isopropoxide by acetylacetone.[6] The preparation of these colloids is summarized in Figure 1. The purpose of this work was to investigate all the steps of this process. In this first paper, a study of the modification of titanium alkoxides with acetylacetone as well as the effect of the dilution of the precursors in alcohol is presented. In the following paper, the hydrolysis process leading to the formation of colloids will be investigated.

Prior reports have already mentioned the reaction that occurs between alkoxide and acetylacetone,[13,14] but very little is known about the structure of the new species. This paper presents a structural investigation of the modification of titanium alkoxides with acetylacetone. Two different alkoxides have been chosen, $Ti(OPr^i)_4$ and $Ti(OEt)_4$. Structural data concerning titanium alkoxides have already been published from use of different techniques: cryoscopy[15] and infrared,[16] light scattering,[17] X-ray absorption,[18] ^1H NMR,[15,19] and also ^{47}Ti and ^{49}Ti NMR[20] spectroscopies. Titanium ethoxide $Ti(OEt)_4$ clearly appears as an oligomeric species, a trimer in liquid state, while titanium isopropoxide $Ti(OPr^i)_4$ is a monomer. This difference is mainly due to the ability of alkoxy groups to behave as bridging ligands between titanium ions. Thus it should be quite interesting to compare the structures of the two modified precursors prepared from the reaction of acetylacetone on titanium isopropoxide and ethoxide. The dilution of the modified isopropoxide in ethanol, one of the preparative steps of the colloids, has also been studied to determine whether exchange of alkoxy groups could occur and therefore influence the structure of the modified precursors. All the studied samples were liquid, and the structural investigations were done by using infrared, ^1H and ^{13}C NMR, and X-ray absorption spectroscopies.

Experimental Section

The preparations of several $Ti(OR)_3acac$ compounds with OR = OMe, OEt, OPr^n, OBu^n, and OBu^s have already been described in literature.[13,14] Titanium isopropoxide $Ti(OPr^i)_4$ (Fluka) was used as received. Acetylacetone (acacH, Prolabo) was distilled before use. Acetylacetone (0.5 g, 5 mM) was mixed with 1.42 g (5 mM) of $Ti(OPr^i)_4$ by using magnetic stirring. The reaction produced was exothermic and resulted in a yellow solution, while both precursors were colorless liquids. The new compound was assumed to be the modified alkoxide $Ti(OPr^i)_3acac$, according to the following reaction:

$$\mathrm{Ti(OPr^i)_4 + acacH \rightarrow Ti(OPr^i)_3acac + Pr^iOH} \qquad (1)$$

The excess of isopropyl alcohol can be distilled, and the remaining compound appears as a yellow liquid. If the solution is exposed in air, after a few minutes, some needle-shaped crystals appeared which were quite sensitive to moisture. Attempts to isolate crystals for X-ray analysis were not successful due to a poor quality of the crystals. These crystals are certainly hydrolysis products from the precursor.

The synthesis of the $Ti(OEt)_4$-derived precursor is similar to that of $Ti(OPr^i)_3acac$. Acetylacetone (0.5 g, 5 mM) was mixed with 1.14 g (5 mM) of $Ti(OEt)_4$ (Fluka). Again, the reaction was exothermic, and the resulting solution became yellow. The new compound was assumed to be $Ti(OEt)_3acac$ according to a reaction similar to (1). The final $Ti(OEt)_3acac$ solution is stable.

The purpose of this work was to study these precursors under conditions similar to those used in sol–gel processing. It is known that the degree of condensation alkoxides and their derivatives and thus their structure can be influenced by factors such as concentration, nature of the solvent, etc. For these reasons, the excess of alcohol produced during the preparations was generally not removed, and characterizations were mainly performed in alcoholic solutions.

Infrared absorption spectra were taken with a 580 Perkin-Elmer spectrometer over the 4000–200-cm^{-1} region, by using two KRS5 disks. NMR spectra (^1H and ^{13}C) were recorded on an AM 250 Bruker spectrometer. The samples were diluted in a $CCl_4/CDCl_3$ mixture. Room-temperature X-ray absorption experiments (XANES-EXAFS) were performed at the titanium K edge. Measurements were done at LURE, the French synchrotron facility, by using the EXAFS III spectrometer. The solutions were introduced into 0.1-mm-thick cells with X-ray transparent kapton windows. The experimental conditions and data analysis were

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Table I. Infrared Data of the Modified Alkoxide $Ti(OPr^i)_3acac$ in Isopropyl Alcohol (1/1 Ratio)

ν, cm^{-1}	assignment
3360	ν(O–H):Pr^{i}OH
2980	ν(C–H):Pr^{i}OH, Pr^{i}O, acac
2940	ν(C–H):Pr^{i}OH, Pr^{i}O, acac
2870	ν(C–H):Pr^{i}OH, Pr^{i}O, acac
1610	ν(C–C) + ν(C–O):acac
1590	ν(C–C) + ν(C–O):acac
1530	ν(C–C) + ν(C–O):acac
1470	δ(CH$_3$):Pr^{i}OH, Pr^{i}O, acac
1430	δ(CH$_3$):Pr^{i}OH, Pr^{i}O, acac
1380	δ(CH$_3$):Pr^{i}OH, Pr^{i}O, acac
1330	ν(C–CH$_3$):Pr^{i}OH, Pr^{i}O
1280	ν(C–CH$_3$):acac
1165	γ_s(CH$_3$):Pr^{i}OH, Pr^{i}O
1130	γ_s(CH$_3$):Pr^{i}OH, Pr^{i}O
1015	ν(C–O):Pr^{i}O
995	ν(C–O):Pr^{i}O
955	ν(C–O):Pr^{i}O
930	ν(C–O):Pr^{i}OH + n(C–CH$_3$) acac
850	γ_a(CH$_3$):Pr^{i}O
820	γ_a(CH$_3$):Pr^{i}OH
770	
665	γ(CH$_3$–CO–C):acac
620	ν(Ti–O):Pr^{i}O
550	
440	ν(Ti–O):acac
355	ν(Ti–O):acac

described in a previous paper.[18]

Results and Discussion

$Ti(OPr^i)_4$ Modified with Acetylacetone. The yellow solution obtained after the mixing of acetylacetone with titanium isopropoxide in a 1/1 ratio has been characterized by infrared, ^{1}H and ^{13}C NMR, and X-ray absorption spectroscopies (XANES–EXAFS). Preliminary results have already been published;[6] a more complete study is now presented.

The infrared spectrum of the solution was recorded, and absorption bands have been tentatively assigned in Table I, according to infrared spectra of pure titanium isopropoxide and acetylacetone as well as published data on acetylacetonato complexes.[21-23] Several bands correspond to methyl groups present in both isopropoxy and acetylacetonato groups. The band around 1000 cm^{-1} is due to the ν(C–O) stretching vibration of isopropoxy groups bonded to titanium, while the broad band centered about 620 cm^{-1} is associated with the ν(Ti–O(Pr^i)) stretching vibration. These bands show that some isopropoxy groups remain bound to titanium. No bands appear around 1700 cm^{-1} which could be attributed to ν(C–O) vibration of free acetylacetone (ketone form). Apparently, the acetylacetone was completely consumed in the reaction. Moreover, the broad band centered at 1610 cm^{-1} corresponding to the ν(C–O) and ν(C–C) stretching modes of the enol form is now split into two bands centered at 1590 and 1530 cm^{-1}. These bands have been assigned to the ν(C–O) and ν(C–C) vibrations of acetylacetonato groups bound to titanium. These new Ti–O bonds are responsible for the appearance of two bands at 440 and 355 cm^{-1}, corresponding to the ν(Ti–O(acac)) stretching vibrations.

For the NMR study, free isopropyl alcohol was removed from the solution by simple evaporation. Both ^{1}H and ^{13}C NMR spectra were recorded, and peak assignments were done by comparison with the spectra of titanium isopropoxide and acetylacetone (Table II). The ^{1}H NMR spectrum reveals many features characteristic of isopropoxy groups; several peaks appear at around 1.2 ppm due to C*H*$_3$ protons as well as two septuplets (J_{H-H} = 6.1 Hz) at 4.48 and 4.76 ppm due to the C*H* protons. Acetylacetonato groups give rise to two peaks at 1.92 and 2.03 ppm indicative of C*H*$_3$ protons and one peak at 5.48 ppm due to the C*H* proton. The ^{13}C NMR spectrum is in good agreement with the ^{1}H NMR spectrum. The peaks around 25 ppm correspond to methyl groups of both isopropoxy and acetylacetonato groups. The two peaks at 76.4 and 78.5 ppm are assigned to the *C*H carbon of the isopropoxy groups, while the peak at 102.3 ppm is due to the *C*H carbon of the acetylacetonato groups. This spectrum also exhibits two peaks at 187 and 191 ppm, which have been assigned to the *C*O carbon atoms of the acac groups.

Table II. ^{1}H and ^{13}C NMR Data of the Modified Alkoxide $Ti(OPr^i)_3acac$

^{1}H NMR		^{13}C NMR	
δ, ppm	assignment	δ, ppm	assignment
1.15	CH$_3$ (OPr^i)	25.1	CH$_3$(acac) + CH$_3$(OPr^i)
1.19	CH$_3$ (OPr^i)	25.7	CH$_3$(acac) + CH$_3$(OPr^i)
1.24	CH$_3$ (OPr^i)	26.5	CH$_3$(acac) + CH$_3$(OPr^i)
1.91	CH$_3$ (acac)	76.4	CH (OPr$^i_1$)
2.02	CH$_3$ (acac)	78.5	CH (OPr$^i_2$)
4.48 sp[a]	CH (OPr$^i_1$)	102	CH (acac)
4.76 sp	CH (OPr$^i_2$)	187	CO (acac)
5.48	CH (acac)	191	CO (acac)

[a] sp: septuplet.

The spectra show that isopropoxy and acetylacetonato groups are all bound to titanium. Moreover, the integration of the proton spectrum confirms the presence of three isopropoxy groups per acetylacetonato group. Two of the isopropoxy groups appear magnetically equivalent (OPr$^i_2$: δ_{CH} = 4.76 ppm; δ_{CH} = 78.5 ppm) while the third is nonequivalent (OPr$^i_1$: δ_{CH} = 4.48 ppm; δ_{CH} = 76.4 ppm). Another interesting feature concerns the acetylacetonato group. The single peak due to the CH group in both ^{1}H and ^{13}C spectra seems to show that only one species is present. In that case, the two C*H*$_3$ peaks in the ^{1}H spectrum and the two *C*O peaks in the ^{13}C spectrum could be due to a nonsymmetric bonding of the bidentate acac group to titanium. This assumption is in good agreement with published data on aluminum alkoxides substituted by acetylacetone.[24,25] The dimeric compound $[Al(OPr^i)_2(acac)]_2$ exhibits two C*H*$_3$(acac) peaks in the ^{1}H NMR spectrum as well as two *C*O(acac) peaks in the ^{13}C NMR spectrum. This dimer transforms with time into a crystallized trimer, $[Al(OPr^i)_2(acac)]_3$, whose structure has previously been determined by X-ray diffraction. The acac groups are unsymmetrically bound to the aluminum atoms with two Al–O distances of 1.907 and 1.919 Å.

The ^{1}H NMR spectrum of the starting solution in isopropyl alcohol was also recorded. When compared to the previous NMR experiment, some new peaks appear due to the presence of free isopropyl alcohol, at 2.24 ppm (O*H*) and at 4.03 ppm (C*H*). This last signal should exhibit a septuplet structure instead of the observed broad band. This is also related to the broadening of the OPr$^i_1$ peaks at 4.48 ppm. The OPr$^i_2$ peaks remain resolved. It clearly indicates that the OPr$^i_1$ group is more labile than the OPr$^i_2$ groups and thus can exchange more easily with molecules of free isopropyl alcohol.

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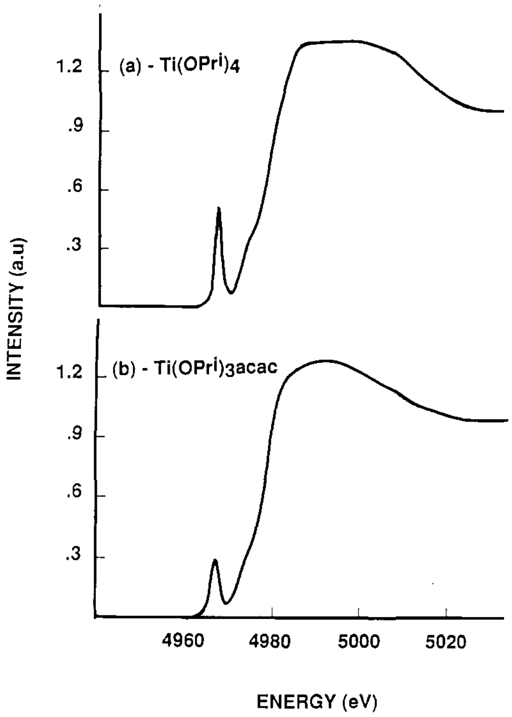

Figure 2. Ti K-edge XANES spectra of (a) Ti(OPr^i)$_4$ and (b) Ti(OPr^i)$_3$acac.

A XANES–EXAFS study of the modified precursor has been performed. X-ray absorption techniques provide a convenient way to obtain structural information on liquid samples. XANES and EXAFS results have been previously reported on titanium alkoxides[18] and have shown that the nature of the precursor, monomer or oligomer, can be determined by using complementary data from XANES (coordination number) and EXAFS (Ti–Ti distances). Figure 2 shows the titanium K-edge spectrum of the modified precursor Ti(OPr^i)$_3$acac in isopropyl alcohol (1/1 ratio) as well as the spectrum of Ti(OPr^i)$_4$. It exhibits a single preedge peak centered on 4967.4 eV with an intensity of 0.30. A small triplet would be expected for 6-fold coordinated Ti^{4+} ion, while a more intense singlet should correspond to 4- or 5-fold coordination. In the case of titanium isopropoxide, the single prepeak centered at 4967.2 eV with an intensity of 0.50 was previously assigned to a monomeric species in 4-fold coordination.[18] The decrease in intensity from Ti(OPr^i)$_4$ to Ti(OPr^i)$_3$acac suggests a higher coordination number for the modified alkoxide. The absence of a triplet feature characteristic of a species with octahedral symmetry suggests 5-fold coordination of the titanium ion. Thus Ti(OPr^i)$_3$acac should be a monomeric species with the titanium ion surrounded by one bidentate acac group and three terminal isopropoxy groups.

The EXAFS results are in agreement with this assumption. The radial distribution function of the EXAFS signal and the k-space filtered EXAFS spectrum of Ti(OPr^i)$_3$acac are represented in Figure 3. The EXAFS curve was fitted with the conventional single-scattering formalism of the EXAFS effect,[26] and the fitting results are summarized in Table III. Ti(OPr^i)$_4$ data are given in Table III as well. The fitted parameters are the following: the edge E_0, the absorbing atom–neighbor distance R, the number of neighboring atoms N, a factor related to both thermal and static disorder σ, and the agreement factor ρ. The electron mean path $\lambda(k)$ was approximated by $\lambda = k/\Gamma$, and Γ was fitted.

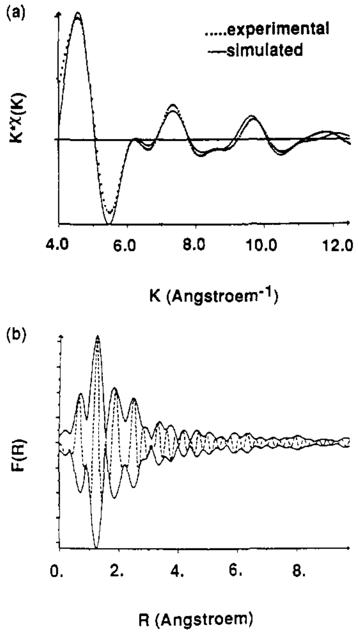

Figure 3. (a) Ti K-edge filtered EXAFS spectrum of Ti(OPr^i)$_3$acac. (b) Radial distribution function of Ti(OPr^i)$_3$acac.

Table III. Fitted EXAFS Parameters of Titanium Isopropoxide Ti(OPr^i)$_4$ and Modified Alkoxide Ti(OPr^i)$_3$acac

compd	N	R, Å	σ, Å	E_0, eV	Γ, Å^{-2}	ρ, %
Ti(OPr^i)$_4$						
Ti–O	3.0	1.76	0.077	4981	0.8	3
Ti–C	6.0	2.95	0.059	4977	0.8	
Ti–C	3.8	3.24	0.059	4977	0.8	
Ti(OPr^i)$_3$acac						
Ti–O	3.1	1.79	0.088	4986	1.5	6.2
Ti–O	2.4	2.02	0.088	4986	1.5	
Ti–C	9.7	3.04	0.098	4979	1.5	

Only one Ti–O distance (R = 1.77 Å) was previously found for Ti(OPr^i)$_4$ corresponding to terminal isopropoxy groups.[18] The modified precursor now exhibits two different Ti–O distances. The shorter one (R = 1.79 Å) corresponds to terminal isopropoxy groups while the longer one (R = 2.02 Å) could be assigned either to bridging isopropoxy groups or to acetylacetonato groups. The XANES results have ruled out the possibility of an oligomeric species so that this distance can correspond only to acetylacetonato groups. The relative ratio of both distances is in agreement with the Ti(OPr^i)$_3$acac stoichiometry, i.e., three long Ti–O distances and two short ones. The determination of distances by EXAFS techniques is not accurate enough to show whether two different long Ti–O distances exist, which would correspond to the unsymmetric bonding of acac groups. Likewise, it is not possible to determine whether two different Ti–O short bond lengths occur, which would indicate the presence of two kinds of OPr^i groups, as revealed by NMR. The fitted Ti–C distance (R = 3.04 Å) is related to a high σ factor. This reveals a distribution in distances for carbon atoms of both acac ($CH_3COCHCOCH_3$) and isopropoxy groups ($CH(CH_3)_2O$), as well as a large mobility of these terminal isopropoxy groups.

Taken together, these results show that the reaction of acetylacetone on titanium isopropoxide in a 1/1 molar ratio give rise to a new modified precursor, Ti(OPr^i)$_3$acac, according to reaction 1. This new compound is a monomeric species in which the Ti^{4+} ion in 5-fold coordination is

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(26) Teo, B. K. *EXAFS: Basic principles and data analysis*; Springer-Verlag: Berlin, 1986.

Table IV. ^{1}H and ^{13}C NMR Data of the Modified Alkoxide $\mathrm{Ti(OEt)_3acac}$

^{1}H NMR		^{13}C NMR	
δ, ppm	assignment	δ, ppm	assignment
1.17	CH_3 (OEt)	18.6	CH_3 (acac) + CH_3 (OEt)
1.19	CH_3 (OEt)	25.2	CH_3 (acac) + CH_3 (OEt)
1.22	CH_3 (OEt)	25.5	CH_3 (acac) + CH_3 (OEt)
1.93	CH_3 (acac)	26.5	CH_3 (acac) + CH_3 (OEt)
1.99	CH_3 (acac)	71.6	CH_2 (OEt)
2.04	CH_3 (acac)	72.2	CH_2 (OEt)
4.43 q[a]	CH_2 (OEt)	102.2	CH (acac)
5.52	CH (acac)	102.5	CH (acac)
5.54	CH (acac)	102.9	CH (acac)
5.55	CH (acac)	188.0	CO (acac)
		191.0	CO (acac)

[a] q: quartet.

surrounded by a bidentate acac group and three terminal $\mathrm{OPr^i}$ groups. The acac group is bound to titanium in a nonsymmetric way. This can easily be explained if one consider that β-dicarbonyl compounds exist in two forms, the so-called keto and enol. The relative percentage of each forms was calculated by integrating the ^{1}H NMR spectrum of the pure acetylacetone and was found to be 5% for the keto form and 95% for the enol one. Thus the OH group of the enol form can react with the OR group of the alkoxide to create a Ti–O(acac) bond after the removal of an alcohol molecule. The second oxygen atom of the enol form can be bound to titanium via a dative bond.[14] Two different kinds of isopropoxy groups were identified by NMR: the two equivalent ones could be assigned to groups in a cis position toward the acac group, while the last one should occupy the trans position. This characteristic position could explain why this group is more labile than the other two.

$\mathrm{Ti(OEt)_4}$ Modified with Acetylacetone. The structural investigation performed on the product of the modification of titanium ethoxide with acetylacetone is similar to the previous one concerning titanium isopropoxide. The infrared spectrum of $\mathrm{Ti(OEt)_3acac}$ in ethanol (1/1 ratio) was recorded, and bands have been assigned by comparing with the spectra of $\mathrm{Ti(OEt)_4}$ and $\mathrm{Ti(OPr^i)_3acac}$. Two points should be emphasized: (i) The broad bands centered around 1100 cm^{-1} show the presence of ethoxy groups bonded to titanium. (ii) The bands at 1530, 1590, and 1610 cm^{-1} assigned to the ν(C–O) and ν(C–C) coupled vibrations of acac groups in $\mathrm{Ti(OPr^i)_3acac}$ are also seen in this spectrum, slightly shifted to 1525, 1595, and 1605 cm^{-1}, respectively. This clearly confirms that acac groups are also bound to titanium in this new compound.

As previously, ethanol was evaporated from $\mathrm{Ti(OEt)_3acac}$ before the NMR study. Peaks at 2.9 ppm (O*H*) and 3.8 ppm (C*H*$_2$OH) on the ^{1}H NMR spectrum show, however, that some ethanol still remains in the product. The spectra are more complicated and peak assignments are more difficult than those of $\mathrm{Ti(OPr^i)_3acac}$. Assignments have been done by comparing with the spectrum of $\mathrm{Ti(OEt)_4}$ and $\mathrm{Ti(OPr^i)_3acac}$ and are summarized in Table IV. These results are in agreement with the infrared study in that ethoxy and acetylacetonato groups are bound to titanium. NMR spectra, however, clearly show that both compounds $\mathrm{Ti(OPr^i)_3acac}$ and $\mathrm{Ti(OEt)_3acac}$ are in some ways very different. The following can be noted: (i) The multiplicity of the peaks assigned to the CH group of acac shows that several species exist in this sample. (ii) Three peaks are assigned to the C*H*$_3$ protons of acac groups. The two peaks at 1.93 and 2.04 ppm are similar to those found in the isopropoxide-derived product. They could be due to acetylacetonato groups nonsymmetrically bound to titanium. This can also be related to the two *C*O peaks on the ^{13}C NMR spectrum. But the ^{1}H NMR spectrum clearly exhibits another peak due to some CH_3 protons of acac groups. The chemical shift corresponding to this peak is intermediate between the two previously described chemical shifts. This shift could be due to the presence of acac groups symmetrically bound to titanium, but that seems unlikely in the context of the results obtained for the $\mathrm{Ti(OPr^i)_3acac}$ compound. Chemical exchange between several species would seem to be more plausible and could explain the presence of a single peak.

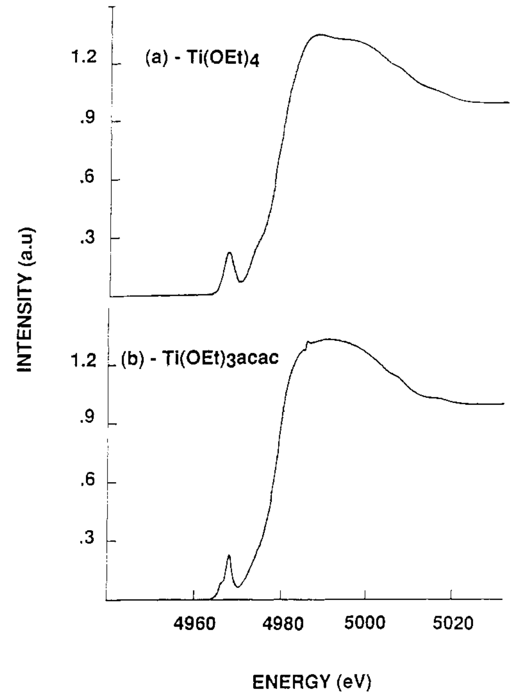

Figure 4. Ti K-edge XANES spectra of (a) $\mathrm{Ti(OEt)_4}$ and (b) $\mathrm{Ti(OEt)_3acac}$.

Table V. Fitted EXAFS Parameters of Titanium Ethoxide $\mathrm{Ti(OEt)_4}$ and Modified Alkoxide $\mathrm{Ti(OEt)_3acac}$

compd	*N*	*R*, Å	σ, Å	E_0, eV	Γ, Å^{-2}	ρ, %
$\mathrm{Ti(OEt)_4}$						
Ti–O	3.4	1.82	0.072	4995	1.5	5.9
Ti–O	1.8	2.05	0.072	4995	1.5	
Ti–Ti	1.2	3.12	0.056	5013	1.5	
$\mathrm{Ti(OEt)_3acac}$						
Ti–O	2.9	1.81	0.085	4989	1.3	7.8
Ti–O	3.6	2.04	0.085	4989	1.3	
Ti–C	9.9	2.98	0.125	4978	1.3	

The titanium K-edge XANES spectrum of the $\mathrm{Ti(OEt)_3acac}$ compound is represented in Figure 4 together with that of $\mathrm{Ti(OEt)_4}$. It exhibits a prepeak centered at 4968.1 eV (intensity 0.25) with a shoulder at 4966.1 eV. $\mathrm{Ti(OEt)_4}$ shows a single prepeak at 4967.6 eV (intensity 0.32). This peak has previously been assigned to a titanium ion in 5-fold coordination.[18] The decrease in intensity and the presence of a shoulder seem to imply that the reaction between acetylacetone and titanium ethoxide leads to a mixture of 5- and 6-fold coordinated species. The former should correspond to monomers, while the latter should correspond to oligomers.

The EXAFS results are given in Figure 5 and Table V. The first peak of the radial distribution function is apparently due to noise. The other two intense peaks correspond to two Ti–O distances of 1.79 and 2.03 Å. The spectrum also reveals some Ti–C distances at 2.98 Å. The comparison with the EXAFS results on $\mathrm{Ti(OEt)_4}$ and on

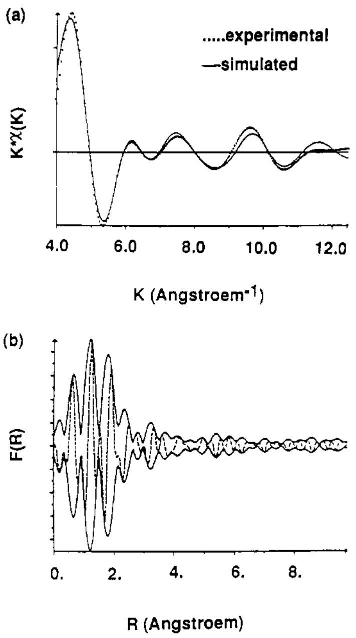

Figure 5. (a) Ti K-edge filtered EXAFS spectrum of Ti(OEt)$_3$acac. (b) Radial distribution function of Ti(OEt)$_3$acac.

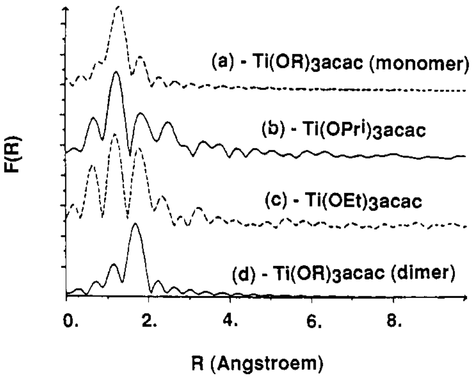

Figure 6. Simulated radial distribution functions of Ti(OR)$_3$acac species [monomer and dimer] compared to experimental radial distribution functions of Ti(OPr^i)$_3$acac and Ti(OEt)$_3$acac.

Ti(OPr^i)$_3$acac are interesting. The short Ti–O distance corresponds to terminal ethoxy groups, while the long one is due either to bridging ethoxy groups or to acetylacetonato groups. Compared to the starting precursor Ti(OEt)$_4$, the Ti–Ti distances seem to have disappeared. This could show that Ti(OEt)$_3$acac is only a monomeric species like Ti(OPr^i)$_3$acac. In fact, oligomeric species can be present, and the absence of peaks due to Ti–Ti correlations could correspond to a large disorder in the Ti neighboring atoms of the absorber. This could be the case if an exchange between monomers and oligomers was to occur. The monomeric species could be similar to Ti(OPr^i)$_3$acac with two long Ti–O distances and three short Ti–O distances. The simplest oligomeric species would be a dimer containing one acetylacetonato group and two terminal and two bridging ethoxy groups surrounding titanium in 6-fold coordination. In such a case, four long Ti–O distances and two short Ti–O distances are expected. Each assumption (monomer and dimer) has been simulated with two Ti–O distances, at 1.79 and 2.02 Å. The results are summarized in Figure 6, together with the experimental radial structure function of Ti(OPr^i)$_3$acac and Ti(OEt)$_3$acac. The isopropoxide-derived precursor clearly appears to be a monomer, while the ethoxide-derived precursor is an intermediate form between the monomeric and the dimeric species.

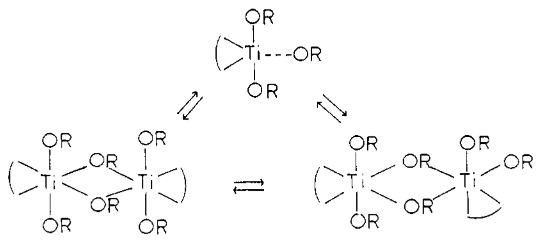

Figure 7. Proposed structure for the different Ti(OEt)$_3$acac species (OR = OEt).

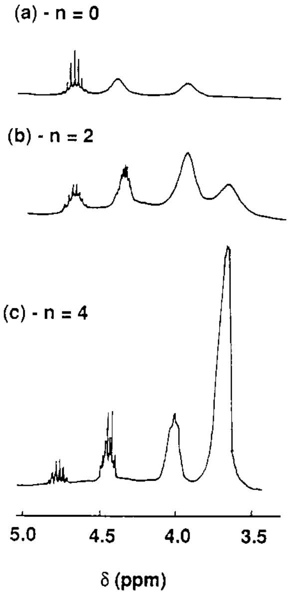

Figure 8. Influence of the dilution of Ti(OPr^i)$_3$acac in ethanol on the ^{1}H NMR CH_3 peaks (a) and CH peaks (b, c) of acac groups (n = EtOH/Ti).

All the spectroscopic techniques used to investigate the structure of the modified alkoxide Ti(OEt)$_3$acac clearly show an equilibrium of monomeric (5-fold coordinated) and oligomeric (6-fold coordinated) species. The difference in structure with Ti(OPr^i)$_3$acac is due to the greater ability of ethoxy groups to bridge titanium ions. A possible representation of these species is given in Figure 7. The monomeric species could be associated with the ^{1}H NMR peaks at 1.93 and 2.04 ppm (CH_3: acac) and at 5.55 ppm (CH: acac), while the oligomeric species should correspond to the peaks at 1.99 ppm (CH_3: acac) and at 5.52 and 5.54 ppm (CH: acac).

Influence of Dilution of Ti(OPr^i)$_3$acac in Ethanol. The dilution of Ti(OPr^i)$_3$acac modified precursor in ethanol has been studied to determine whether exchange between alkoxy groups could occur. Ti(OPr^i)$_3$acac in isopropyl alcohol (1/1 ratio) was diluted with ethanol (1/3 ratio), and the infrared spectrum was recorded. The comparison with the spectrum of the starting compound (Ti(OPr^i)$_3$acac + Pr^{i}OH) shows several new bands at 1100, 1050, 910, 875, and 600 cm^{-1}. The bands at 1050 and 875 cm^{-1} are due to free ethanol, while the other three bands are characteristic of ethoxy groups bound to titanium, ν(C–C) at 1100 cm^{-1}, ν(C–O) at 910 cm^{-1}, and ν(Ti–O) at 600 cm^{-1}. This last band in fact includes two contributions, that of Ti-O(Pr^i) and Ti-O(Et) stretching vibrations. The shape of the band and the position of its maximum seems to show that ethoxy groups bound to titanium are in the majority.

^{1}H NMR spectra were recorded for a solution of Ti(OPr^i)$_3$acac in isopropyl alcohol (1/1 ratio) diluted in ethanol. The ratio between the precursor and ethanol, n, ranges from 1 to 6. Figure 8a represents the evolution of

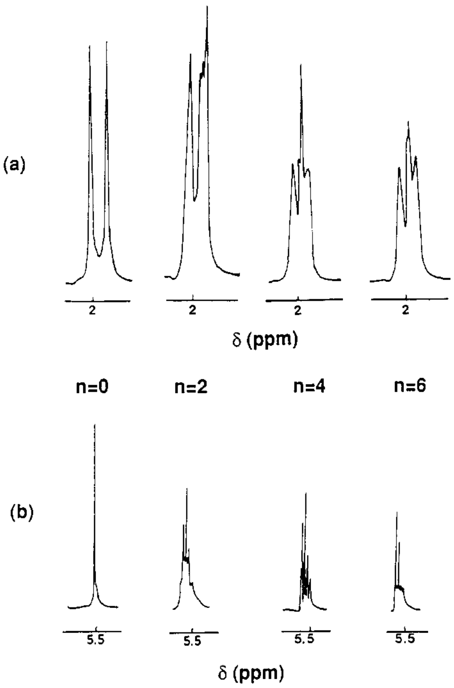

Figure 9. Influence of the dilution of $Ti(OPr^i)_3acac$ in ethanol on the ^1H NMR CH and CH_2 peaks of bound isopropoxy and ethoxy groups (n = EtOH/Ti).

the CH_3 peaks of the acetylacetonato groups. The two peaks at 1.93 and 2.04 ppm previously described for the monomeric $Ti(OPr^i)_3acac$ species still remain. However, they broaden as n increases. Upon addition of ethanol, two new peaks appear at 1.97 ppm for $n > 1$ and at 1.99 ppm for $n > 3$. This last peak was noted earlier in the ^1H NMR spectrum of $Ti(OEt)_3acac$. The CH peak of the acac groups was unique in the $Ti(OPr^i)_3acac$ spectrum (δ = 5.50 ppm). Several new peaks at 5.52, 5.54, and 5.56 ppm appear with the addition of ethanol, their relative intensities depending upon the value of n (Figure 8b). An increase in the amount of ethanol caused a decrease in the peak at 5.52 ppm, an increase of the peak at 5.54 ppm for $2 < n < 4$, and an increase of the peak at 5.56 ppm.

Four groups of peaks generally appear in the 3.5–5 ppm range (Figure 9). There are usually two well-resolved multiplets due to isopropoxy groups (δ = 4.75 ppm) and ethoxy groups (δ = 4.44 ppm) bonded to titanium. There are also two other more or less resolved multiplets, whose chemical shifts depend on the amount of ethanol. They could correspond to isopropoxy ($3.95 < \delta < 4.05$ ppm) and ethoxy ($3.70 < \delta < 3.85$ ppm) groups bonded to titanium undergoing exchange with free alcohol molecules. These peaks cannot be resolved for $n < 3$. The isopropoxy multiplet can be resolved for $n = 4$ and the ethoxy multiplet for $n = 5$. The chemical shift of the peaks corresponding to the most tightly bonded isopropoxy groups is similar to that of OPr^i_2 groups, which are the less labile isopropoxy groups of $Ti(OPr^i)_3acac$. The new peaks due to bound ethoxy groups correspond to those found in $Ti(OEt)_3acac$. It also seems interesting to note that each peak due to bonded alkoxy groups splits into two components when the amount of ethanol is increased.

These different spectra show that isopropoxy groups are easily substituted by ethoxy groups when $Ti(OPr^i)_3acac$ is diluted with ethanol. The spectrum tends to be similar to that of $Ti(OEt)_3acac$ for a large amount of ethanol. A more detailed analysis of the spectra has been done to get some quantitative results regarding this substitution. The number of isopropoxy (δ = 4.75 ppm) and ethoxy (δ = 4.44 ppm) groups corresponding to the well-resolved multiplets is reported in Table VI. The peak due to the six methyl protons of the acac group was taken as a reference for the integration. The accuracy of the measurements is relatively poor, especially when the number of protons is less than one. Nevertheless a decrease in the isopropoxy groups and an increase in the ethoxy groups are clearly visible. The previous study has shown that the monomeric $Ti(OPr^i)_3acac$ species has two types of OR positions. One, OR_1, is more labile than the second, OR_2. The resolved multiplets could therefore correspond to alkoxy groups in the OR_2 position. Thus, there are three possibilities for the two OR_2 existing positions: (i) two isopropoxy groups, (ii) one isopropoxy and one ethoxy groups, or (iii) two ethoxy groups. The first species present in $Ti(OPr^i)_3acac$ should correspond to a peak at 5.51 ppm while the third species present in $Ti(OEt)_3acac$ should produce one peak at 5.55 ppm and a broad second peak at 5.50 ppm due to the oligomeric species in exchange. A possible assignment of the CH peaks of the acac groups could be as follows: the peak at 5.52 ppm results from the $Ti(OPr^i)_2(OR)acac$ species, the peak at 5.54 ppm is due to the $Ti(OPr^i)(OEt)(OR)acac$ species, and the peak at 5.56 ppm arises from the $Ti(OEt)_2(OR)acac$ species. OR represents the labile (OR_2) position that should be occupied by either an isopropoxy group or an ethoxy group in exchange with alcohol molecules. According to this assumption, the protons of these OR groups should not contribute to the resolved multiplets.

Table VI. Influence of the Dilution of the Modified Alkoxide $Ti(OPr^i)_3acac$ in Ethanol: Number of Tightly Bound Isopropoxy and Ethoxy Groups per Titanium According to NMR Data

	exptl		calcd	
n(EtOH)	$n(OPr^i)$	n(OEt)	$n(OPr^i)$	n(OEt)
1	1.0	0.3	1.5	0.4
2	0.7	0.4	1.1	0.5
3	0.6	0.5	1.0	0.8
4	0.8	1.0	0.9	0.9
5	0.8	1.1	0.6	1.4
6	0.4	0.8	0.6	1.2

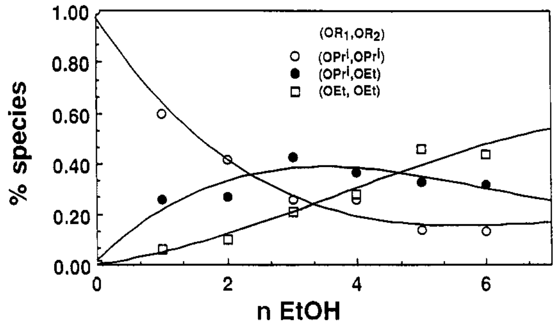

Figure 10. Percentage of the various species present in a $Ti(OPr^i)_3acac/Pr^iOH/EtOH$ solution ($1/1/n$ ratio).

The percentage of each species (i, ii, iii) was evaluated simply by considering the height of each CH peak. The results are summarized in Figure 10. The numbers of tightly bound isopropoxy and ethoxy groups were calculated according to these percentages and compared to the experimental data (Table VI). The agreement is rather good. Three species seem to be present when $Ti(OPr^i)_3acac$ is diluted in ethanol. $Ti(OPr^i)_2(OR)acac$ is most prevalent for $n < 2$, $Ti(OPr^i)(OEt)(OR)acac$ for n = 3 and 4, and $Ti(OEt)_2(OR)acac$ for $n > 5$.

The peak at 5.50 ppm could be assigned to oligomeric species in exchange if a comparison is done with the Ti-

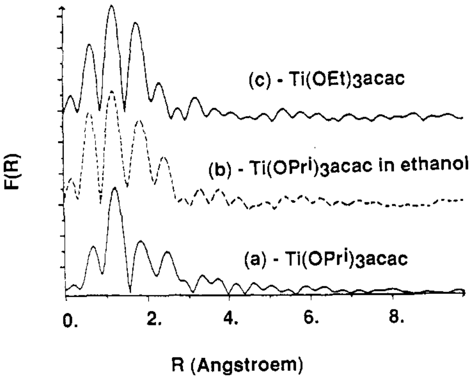

Figure 11. Radial distribution function of the EXAFS spectra of (a) Ti(OPr^i)$_3$acac, (b) Ti(OPr^i)$_3$acac in ethanol (1/3 ratio), and (c) Ti(OEt)$_3$acac.

(OEt)$_3$acac precursor. Its intensity is always rather low. This peak should be related to the two peaks at 1.97 and 1.99 ppm due to methyl protons of acac groups. The peak at 1.99 ppm was already mentioned for Ti(OEt)$_3$acac and assigned to oligomeric species. The peak at 1.97 ppm could also be assigned to oligomers with bonded isopropoxy groups instead of ethoxy groups. This peak appears just after the dilution while the peak at 1.99 ppm becomes visible for $n > 4$. A final point seems to confirm our assignment concerning the existence of three species, the splitting of the multiplets due to tightly bound alkoxy groups. The two groups of isopropoxy peaks could correspond to the Ti(OPr^i)$_2$(OR)acac and Ti(OPr^i)(OEt)(OR)acac species, while the two groups of ethoxy peaks could correspond to the Ti(OPr^i)(OEt)(OR)acac and Ti(OEt)$_2$(OR)acac species.

Both XANES and EXAFS spectra at the Ti K edge were recorded for a solution of Ti(OPr^i)$_3$acac/Pr^{i}OH/EtOH in a 1/1/3 ratio. XANES exhibits a prepeak at 4968.0 eV (intensity 0.22) with a shoulder at 4966.2 eV. It is different from the spectrum of Ti(OPr^i)$_3$acac but rather similar to that corresponding to Ti(OEt)$_3$acac. Species in both 5- and 6-fold coordination may be present in this solution. The radial distribution function of the EXAFS spectrum is represented in Figure 11 with those of Ti(OPr^i)$_3$acac and Ti(OEt)$_3$acac. It appears to be intermediate between those of the two modified precursors. The relative ratio between the long and short Ti–O distances seems to be more important than for Ti(OPr^i)$_3$acac. The increase in the longer bond distances could be explained by the substitution of isopropoxy groups by ethoxy groups, thus the formation of bridges between titanium ions. The NMR study has previously shown that the substitution is not complete for EtOH/Ti = 3. This explains why the relative ratio between long and short Ti–O distances is less than for the precursor Ti(OEt)$_3$acac.

This study clearly shows that the ethanol is not only a solvent for the Ti(OPr^i)$_3$acac precursor. Some substitution of isopropoxy groups by ethoxy groups occurs, depending upon the amount of ethanol. This leads to the equilibrium formation of oligomeric species in 6-fold coordination and monomeric species in 5-fold coordination.

Conclusion

Titanium alkoxides have been modified with acetylacetone to get stable TiO_2-based colloids via a hydrolysis–condensation process. The modification of two alkoxides, Ti(OPr^i)$_4$ and Ti(OEt)$_4$, as well as their dilution in alcohol, have been investigated as the first step of the preparation process. Structural information on these liquid samples have been provided by using several spectroscopies: infrared, ^{1}H and ^{13}C NMR, and X-ray absorption (XANES–EXAFS).

The monomeric Ti(OPr^i)$_4$ alkoxide reacts with acetylacetone to form a new precursor, Ti(OPr^i)$_3$acac. This compound exists as a monomer in 5-fold coordination. The acac group is unsymmetrically bound to titanium with an average distance of 2.02 Å. Two isopropoxy groups are equivalent to one another, while the third isopropoxy group, more labile, is nonequivalent. The average Ti–O distance is 1.79 Å. The oligomeric Ti(OEt)$_4$ alkoxide also reacts with acetylacetone, but the final product is a mixture rather than a unique species. Monomeric species similar to Ti(OPr^i)$_3$acac exist in equilibrium with oligomeric species having the titanium ion in 6-fold coordination. In this case, the titanium ion is presumably surrounded by one acac group, two terminal (R = 1.82 Å) and two bridging (R = 2.05 Å) ethoxy groups.

The differences between the modified precursors depend upon the ability of the alkoxy groups to behave as bridging ligands. Previous studies have shown that primary alkoxy groups (OMe, OEt, OPr^n, OBu^n) prefer to occupy bridging sites between titanium ions while secondary (OPr^i) or tertiary (OBu^t, OAm^t) groups prefer terminal positions. The dilution of the monomeric Ti(OPr^i)$_3$acac species in ethanol leads to the substitution of isopropoxy groups by ethoxy groups, leading to the formation of oligomeric species. The solvent, therefore, can greatly influence the structure of the species in solution and thus the relative reactivity.

The hydrolysis process of these modified precursors is investigated in part 2.

Acknowledgment. We gratefully acknowledge Dr. C. Cartier and Prof. M. Verdaguer for their helpful contribution in the X-ray absorption experiments. Y. Besace is also acknowledged for his technical assistance in the NMR experiments.

Registry No. Ti(OPr^i)$_4$, 546-68-9; Ti(OEt)$_4$, 3087-36-3; Ti(OPr^i)$_3$acac, 15701-48-1; Ti(OEt)$_3$acac, 53479-21-3.