ELECTRONIC STRUCTURE INDUCED BY THE TRANS-TO-GAUCHE CONFORMATIONAL CHANGE IN THE BUTOXYL GROUP OF POLYMERIZED *n*-BUTYL-*o*-TITANATE STUDIED BY DV-Xα CLUSTER CALCULATIONS

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The change in the electronic structure of pol-Ti(OBu)₄ due to the conversion from trans to gauche of butoxyl groups is investigated by DV-X α cluster calculations. The effect of gauche-conformation of β -carbon in OBu introduces a characteristic level in the energy region near the Fermi level. This level might play a crucial role in the catalytic process which is found in the photolysis of water over pol-Ti(OBu)₄/SiG, as well as the L level of the clusters A₁ and A₂ of [Ti(OBu)(OMe)(OH)₄]²⁻. As for the increase of the coordination number from four to six during the process of polymerization, the electronic structures of the tetrahedral cluster [Ti(OBu)₂(OH)₂] and the molecule monomer-Ti(OBu)₄ are calculated and compared with that of the octahedral cluster B₁ of [Ti(OBu)₂(OH)₄]²⁻.

1. Introduction

It was found previously [1] that the [polymerized *n*-butyl-o-titanate (pol-Ti(OBu)₄) + methanol(CH₃OH)] complex shows a remarkable photocatalytic activity for water decomposition. As a result of the study on its electronic structure by DV-X α cluster calculations, we concluded in the previous paper [2] that substitution of a methoxyl ligand for a butoxyl ligand introduces a characteristic localized state close to the Fermi level, whose state might play a crucial role in the photocatalytic process. The solid which is obtained from a mixture of silica gel and an Ti(OBu)₄(monomer)-benzene solution by evaporating the solvent, is unstable itself. However, in a recent series of experiments using pol-Ti(OBu)₄/silica gel which was prepared by a special method, we have found its photocatalytic activity on the decomposition of water in spite of no addition of methanol. Unusual line intensities in the CH

0039-6028/88/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) stretching region for butoxyl groups were observed sometimes in Raman spectra of catalysts during the process of preparation. From these facts it might be concluded that a change in the conformation of butoxyl groups induces a peculiar feature of the electronic state of the $[Ti(OBu)_2O_4]$ unit in solid pol-Ti(OBu)_4. In order to find a preparation method to obtain a catalyst with higher activity, the knowledge of the electronic states around the active center is indispensable. In this paper we reveal by DV-X α cluster calculations the electronic structure of $[Ti(OBu)_2(OH)_4]$ and $[Ti(OBu)(OMe)(OH)_4]$ clusters when the trans-gauche conformation change of butoxyl groups is introduced. The changes in the electronic structure of Ti and each ligand, and the changes in the bond character during polymerization of $Ti(OBu)_4$ (monomer) are clarified with an increasing Ti coordination number from 4 to 6.

2. Experimental

The catalyst, $[\text{pol-Ti}(OBu)_4 + CH_3OH]/SiG$ was prepared by the same method as used in the previous measurement [1]. A-type of silica gel (Fuji-Davison Chemical Ltd.) was heated at 180 °C for 2 h and then cooled down to room temperature in a desiccator, which was kept under vacuum by a rotary pump, directly before preparation. Ti(OBu)_4(monomer) was obtained from Nippon Soda Co., Ltd. 0.5 g of Ti(OBu)_4(monomer) was polymerized in parts ten times (not at one time) at room temperature. The whole procedure of the polymerization took about a month. A non-aqueous reaction was established by using Davison molecular sieves 3A during preparation.

The photochemical reaction apparatus and method were the same as those used in the previous experiments [3]. The reaction tube was illuminated using a Toshiba mercury lamp H400-P (400 W) covered with a hard glass tube to filter light of wavelength longer than about 350 nm.

Raman spectra were measured for a bulk sample, using the 514.5 nm line of a CR-8 argon ion laser as an exciting source with a JASCO R-800 spectrometer.

3. DV-X α method for cluster models

In the previous calculations [2], we assumed that butoxyl groups are conjugated by α -, β -, γ -methylene and δ -methyl carbons in all trans-forms. From the experimental results which will be described in section 4.1, it might be considered that some changes in the electronic structure are induced due to transformations of butoxyl groups in solid pol-Ti(OBu)₄. The net work structure of pol-Ti(OBu)₄ is supposed to be the same as that mentioned in the previous paper [2], but the change appears only in the butoxyl group. Normal

pol-Ti(OBu)₄ includes the local cluster unit B₁, which was calculated in the previous work [2], or B₂ (shown in fig. 4), whose geometry is given by rotating the two butoxyl groups in cluster B_1 by 180° around the z-axis (see fig. 3 of ref. [2]). As a result of the calculations, there is no interesting difference in electronic structure between B_1 and B_2 . The probable and effective conformational changes of butoxyl groups on the electronic structure of pol-Ti(OBu)4 may be considered to be transformations from trans to gauche of α -, β -, γ -methylene and δ -methyl carbons. For convenience, the normal (all transforms) and transformed butoxyl groups are designated as OBu and OBu', respectively, hereafter. We focus, in the present work, our attention on the effects on the electronic properties of the local structure units, the $[Ti(OBu)_2O_4]$ unit in pol-Ti(OBu)₄ and the [Ti(OBu)(OMe)O₄] unit in the [pol-Ti(OBu)₄ + CH₃OH] complex, induced by transformations of OBu. The bond lengths and bond angles which are not concerned with the trans-gauche conformation change, are taken equal to those in the previous paper [2]. The $[Ti(OBu)(OBu')(OH)_4]^{2-}$, $[Ti(OBu')_{2}(OH)_{4}]^{2-}$ and [Ti(OBu')(OMe)(OH)₄]²⁻ clusters are obtained by conformational changes of OBu in the $[Ti(OBu)_2(OH)_4]^{2-}(B_2)$ and $[Ti(OBu)(OMe)(OH)_4]^{2-}(A_2)$ (shown in fig. 5) clusters.

Rotational isomers, whose geometries are shown in figs. 1a-1h, are obtained by the transformations from trans to gauche for y-methylene and δ -methyl groups of OBu in cluster B₂. The results of the DV-X α cluster calculations for those clusters do not reveal any significant difference in the electronic structure as compared with the case of B₂. Therefore, the electronic structures which can explain the experimental facts are investigated by application of the DV-X α method to the cluster models shown in figs. 2, 3 and 4 in the case of trans-to-gauche conformational changes of the β -methylene group. The clusters B_3 -1-1, B_3 -2-1, B_4 -1-1 represent the $[Ti(OBu)(OBu')(OH)_4]^{2-}$ unit which is obtained by trans to gauche conversion of β -carbon (fig. 2). The cluster B_3 -2-1 is established when the OBu' in the cluster B_3 -1-1 is rotated 20° around the z-axis, and the cluster B_4 -1-1 is obtained when rotated -50° around the z-axis. By those axial rotations, the δ -hydrogen H(32) comes near the O ion labeled 3 in fig. 2 until the O(3)-H(32) distance is equal to 1.860 a.u. in the case of the B₃-2-1 cluster, and the β -hydrogen H(21) comes near the O(3) until the O(3)-H(21) distance is equal to 1.875 a.u. in the case of the B_4 -1-1 cluster, as shown in fig. 2. The clusters B_5 -1-2, B_5 -2-2 which are shown in fig. 3, represent the other [Ti(OBu)(OBu')(OH)₄]²⁻ unit which is established by another trans-to-gauche conversion of β -carbon. The cluster B₅-2-2 is obtained when the OBu' of the cluster B_{s} -1-2 is rotated 50° around the z-axis and then the β -hydrogen H(21) comes near the O(2) ion until the O(2)-H(21) distance is equal 1.875 a.u.. The clusters B₃-3, B₄-2, B₅-3 represent the $[Ti(OBu')_2(OH)_4]^{2-}$ unit which is obtained when the β -carbon of two OBu' is transformed from trans to gauche in cluster B_2 . The O(2)-H(17) distance is



Fig. 1. Structures of eight rotational isomers owing to transformations from trans to gauche of γ and δ -carbons of a butoxyl group, the [Ti(OBu)(OBu')(OH)_4]²⁻ clusters: Bu: T-T-T-T; Bu': (a) T-T-T-G, (b) T-T-T-G', (c) T-T-G-T, (d) T-T-G'-T, (e) T-T-G-G, (f) T-T-G-G', (g) T-T-G'-G, (h) T-T-G'-G'.



Fig. 2. Structures of the clusters B_3 -1-1, B_3 -2-1, B_4 -1-1 for the $[Ti(OBu)(OBu')(OH)_4]^{2-}$ unit.



Fig. 3. Structures of the clusters B_5 -2-2, B_5 -1-2 for the $[Ti(OBu)(OBu')(OH)_4]^{2-}$ unit.



Fig. 4. Structures of the cluster B_2 for the $[Ti(OBu)_2(OH)_4]^{2-}$ unit, and of the clusters B_3 -3, B_4 -2, B_5 -3 for the $[Ti(OBu')_2(OH)_4]^{2-}$ unit.



Fig. 5. Structures of the cluster A_2 for the $[Ti(OBu)(OMe)(OH)_4]^{2-}$ unit, and of the cluster A_5 for the $[Ti(OBu')(OMe)(OH)_4]^{2-}$ unit.

1.860 a.u. in cluster B_3 -3, and the O(2)-H(12) distance is 1.875 a.u. in the clusters B_4 -2 and B_5 -3.

Cluster A_5 shown in fig. 5 represents the $[Ti(OBu')(OMe)(OH)_4]^{2-}$ unit which is obtained by a trans-to-gauche conversion of OBu in cluster A_2 for the $[Ti(OBu)(OMe)(OH)_4]^{2-}$ unit which was calculated previously [2]. The O(3)-H(24) distance is equal to 1.860 a.u. in cluster A_5 . Though there has been no experimental evidence in the solid $[pol-Ti(OBu)_4 + CH_3OH]$ complex, we calculate the electronic structure of cluster A_5 for the sake of comparison.

The application of the DV-X α cluster method is the same as that used in the previous work and the parameter α of the local exchange-correlation potential is chosen as 0.7, which was used in the previous calculations [2]. The total number of electrons is taken as 142 in $[\text{Ti}(\text{OBu})_2(\text{OH})_4]^2^-$, $[\text{Ti}(\text{OBu}')_2(\text{OH})_4]^{2-}$ and $[\text{Ti}(\text{OBu})(\text{OBu}')(\text{OH})_4]^{2-}$ clusters, and 118 in $[\text{Ti}(\text{OBu}')(\text{OH})_4]^{2-}$ (A₅) cluster.

4. Results and discussion

4.1. Experimental results

The results of the photolysis of water over $[pol-Ti(OBu)_4 + CH_3OH]/SiG$ (1) and over $pol-Ti(OBu)_4/SiG$ (I') were compared in a flow system by



Fig. 6. Relation between the hydrogen yield and the time of illumination for I (over [pol-Ti(OBu)₄ + CH₃OH]/SiG) and I' (over pol-Ti(OBu)₄/SiG): (\bigcirc) I; (\bigcirc) I'.

continuous irradiation for five hours. Fig. 6 shows the changes in the hydrogen concentration in the exit gas against time of illumination for I and I'. In figs. 7 and 8, the changes in yields of O_3 , which is one of the oxidising products, and of CH₄, which is present in a very small amount and may be a decomposing product of catalyst or solvent, are plotted against time of illumination for I and I', respectively. The hydrogen yield amounts to the same stationary value about 40 minutes after illumination and then is nearly constant for 1.5 hours for both I and I'. However, though the yield for I is nearly kept constant during all illumination times, it starts to decrease about 1.5 hours after illumination with a rapid drop for I', as shown in fig. 6. The hydrogen yield momentarily corresponds to its catalytic activity, and therefore the yield change reflects directly the change of the catalytic activity. The O₃ yield increases with the time of illumination for I and begins to decrease gradually at about 2 hours after the illumination for I', without a rapid drop like the hydrogen yield. The ratios of the (mean) H_2 and O_3 yields for I to those for I' are 1.41 and 2.27, respectively. The CH4 yield increases linearly with illumination time for I. The yield of CH_4 for I' increases only slightly about 3 hours after illumination and is kept almost constant for further illumination time (fig. 8). The ratio of the (mean) CH_4 yield for I to that for I' is 3.8_8 , and is larger than the ratio of the (mean) H_2 yield. This fact suggests that the rapid drop of H₂ yield in photolysis catalysed by pol-Ti(OBu)₄/SiG might not be



Fig. 7. Relation between O₃ yield and the time of illumination for I (over [pol-Ti(OBu)₄ + CH₃OH]/SiG) and I' (over pol-Ti(OBu)₄/SiG): (\odot) I; (\odot) I'.

due to a decomposition of the catalyst itself. It can be considered that a conformational change induces an electronic structure of the pol-Ti(OBu)₄, which shows a photocatalytic activity for water decomposition, and then comes back to the stable conformation without photocatalytic activity by using a part of the light energy.



Fig. 8. Relation between CH_4 yield and the time of illumination for I (over [pol-Ti(OBu)₄ + CH_3OH]/SiG) and I' (over pol-Ti(OBu)₄/SiG): (\bigcirc) I; (\bigcirc) I'.

Fig. 9 shows unusual Raman line intensities in the CH stretching region of butoxyl groups, which were observed sometimes in Raman spectra for pol- $Ti(OBu)_4$ during the process of polymerization. For the *n*-C₄H₉OH molecule (fig. 10a), we calculated the CH stretching frequencies of the butyl group by the ab initio MO method (Gaussian 82) with the 4-31G basis set. The normal modes of the CH stretching vibration found in this calculation are shown in fig. 10. In our previous study [4], we showed that the calculated vibrational frequencies using the 4-31G basis set are almost uniformly greater by 8% than the observed fundamental frequencies. Therefore, the Raman line at 2967 cm^{-1} with unusual intensity as shown in fig. 9a is assigned to the CH₃ asymmetric stretch, β -CH₂ antisymmetric stretch (36A"). An antisymmetric Raman line for the CH stretching mode of aliphatic groups is known to be more sensitive than a symmetric one to the surrounding environments. The unusual raman line observed at 2650 cm⁻¹ (fig. 9b) suggests that Fermi resonance interaction occurs between the CH stretching fundamentals of a molecule (unit) and those of conformational isomers, making reference to literature data [5], and disappears some time or an other as shown in fig. 9c. From such Raman spectra one might suppose that some changes in the conformation of butoxyl groups of pol-Ti(OBu)₄ are within the range of possibility.

4.2. Electronic structure of rotational isomers (trans-to-gauche)

The calculated total and partial density of states (DOS) of B₃-1-1, B₃-2-1, B₄-1-1 ([Ti(OBu)(OBu')(OH)₄]²⁻) clusters are compared in fig. 11. O'(6), B'(α), B'(β), B'(γ), B'(δ) mean oxygen, α -, β -, γ -methylene and δ -methyl groups of OBu', and O(7), B(α), B(β), B(γ), B(δ) indicate oxygen, α -, β -, γ -methylene and δ -methyl groups of OBu, respectively. The DOS of the clusters B₅-2-2, B₅-1-2 ([Ti(OBu)(OBu')(OH)₄]²⁻) are compared in fig. 12. We confirmed that the DOS of clusters do not change significantly when the locations of OBu and OBu' are converted. Fig. 13 shows various DOS of the clusters B₂ ([Ti(OBu)₂(OH)₄]²⁻), B₃-3, B₄-2, B₅-3 ([Ti(OBu')₂(OH)₄]²⁻). These curves of DOS are obtained by the overlap of Gaussians with the width of 0.5 eV centered on each discrete level. The origin of energy corresponds to the mean of the highest occupied and the lowest unoccupied level. Various peak energies of the DOS are listed in table 1a.

From figs. 11, 12, and 13, it is found that partial DOS of Bu' are made of occupied bands located in the wide energy region below E_F and those of Bu are made of unoccupied bands situated above E_F . These are different from the partial DOS of alkyl groups of the clusters which were calculated in the previous work [2]. Fig. 14 shows the DOS of cluster B₃-2-1 extending in the energy region -18 to 10 eV to see these aspects. The partial DOS of O'(6) shifts about 0.5 eV more to the higher energy side than that of O(7) and the



Fig. 9. Observed Raman spectra in the CH stretching region for pol-Ti (OBu)₄ during the process of polymerization.



Fig. 10. CH stretching vibrational modes and frequencies (cm^{-1}) in parentheses of $n-C_4H_9OH$, calculated with the 4-31G basis set, and (a) $n-C_4H_9OH$ molecule.



Fig. 11. Partial and total DOS of B₃-1-1, B₃-2-1 and B₄-1-1 clusters: (-----) B₃-1-1; (---) $B_3-2-1; (\cdots) B_4-1-1.$



Fig. 12. Partial and total DOS of B₅-1-2 and B₅-2-2 clusters: (-----) B₅-1-2; (-----) B₅-2-2.



Fig. 13. Partial and total DOS of B_2 , B_3 -3, B_4 -2 and B_5 -3 clusters: (-----) B_2 ; (-----) B_3 -3; (-----) B_4 -2; (-----) B_5 -3.

Table 1								
Peak energy	(in eV)	of the	DOS fo	r various	clusters	and	monomer-	Ti(OBu) ₄

Cluster or molecule	A+F	B+F	C	D	D'+(F')	E+F'	Т
B ₂	1.6	3.2	-1.4(sh)	- 3.0	_	-6.4(E)	-
B ₃ -1-1	1.7	3.4	- 2.6	- 3.4	-	-6.3	-
B ₃ -2-1	1.4	3.3	- 3	0.0(C + D)	-5.4	-6.9	-1.3
B ₃ -3	1.0(A)	3.3(B)	- 3.0	-4.3(sh)	-5.5	7.0	-1.0
B ₄ -1-1	1.6	3.3	- 3	0.2(C + D)	-4.8(sh)	-6.3	- 1.4(sh)
B ₄ -2	1.2(A)	3.1(B)	- 2.7	-3.5(sh)	-	-6.1	-1.2(sh)
B ₅ -1-2	1.6	3.3	- 2	2.9(C + D)	-	-6.4	-
B ₅ -2-2	1.5	3.1	- 2.5(sh)	-3.5	- 4.9	(-6.3)	-1.1(sh)
B ₅ -3	1.2(A)	3.8	- 2.5	- 3.2	-4.9	(-6.1)	- 1.1(sh)
$A_2^{(a)}$	0.9	2.5	- 2.5	-4.2	_	6.6(E)	-0.8(L)
A _s	1.2(A)	3.4(B)	-2.0(sh)	-3.15	-4.3(sh)	-6.0	-1.0(sh,
2		. ,	. ,				L + T)
$\mathbf{B}_1^{(a)}$	1.7	3.4	-2.7(sh)	- 3.4	-	-6.3(E)	
T_1	2.5(A)	5.1(B)	-2.2	-5.2(sh, D+F')	-	-6.2	_
Mon- Ti(OBu) ₄	(1.8(A) 3.1(A')	5.8(B)	-2.0	-4.1(sh, D+F')	- {	(-5.6 (-6.5(sh)	-

^{a)} Previous calculation [2].

partial DOS of Bu' shifts about 3.5 more to the higher energy side than that of Bu. It is interesting that the energy bands of Bu' are located at significantly higher positions than the corresponding ones of Bu. The band C + D of the ligand O(2) or O(3) splits into the new states T and D', when the hydrogen atom of Bu' approaches closely and forms a strong covalent bond with it. When a hydrogen of Bu' comes near one of the O ions of the ligand, the upper part of the partial DOS of Bu' creates a characteristic peak (T) near $E_{\rm F}$. In fig. 11, the band T which is mainly an admixture of the O(3)2p and δ -C2p orbitals, appears near $E_{\rm F}$ when the O(3)-H(32) distance changes from 2.474 a.u. (B₃-1-1) to 1.860 a.u. (B₃-2-1), and the band T which is mainly composed of the O(3), O(4), O(5) 2p and β -C 2p orbitals, appears close to $E_{\rm F}$ when the O(3)-H(21) distance changes from 3.269 a.u. (B₃-1-1) to 1.875 a.u. (B₄-1-1). At the same time, a new band D' appears between bands E and D in the partial DOS of the TiO₄ unit for the clusters B_3 -2-1, B_4 -1-1 with the T state. The band D' is made up mainly of the ligand oxygen orbitals, which take part in a charge transfer and admix covalently with the approached methyl or methylene group of Bu'. The band F' of the partial DOS of Bu' appearing in the relevant energy region below $E_{\rm F}$, is the upper part of the occupied valence band of the butoxyl group, the energy of which is considerably raised as compared with that of OBu. The states in the band F' in the same energy region as the band D' are admixed considerably with the ligand oxygen, O(2)or O(3). On the other hand, the empty region of the DOS $(E > E_F = 0)$, (A + F) and (B + F), which are admixed with the lower peaks (F) of the partial DOS of Bu above E_F , for the [Ti(OBu)(OBu')(OH)₄]²⁻ clusters, is



Fig. 14. Partial and total DOS of B_3 -2-1 extending in the energy region -18 to 10 eV.

scarcely changed from those of the B_1 , B_2 clusters. The peak (A + F) appears at a slightly lower energy (1.4 eV) in the total DOS of the cluster B_3 -2-1 with the remarkable T state on δ -Bu' than those of the clusters B_3 -1-1, B_5 -1-2 (1.6-1.7 eV) without the T state, and the clusters B_4 -1-1, B_5 -2-2 (1.5-1.6 eV) with the shoulder of the T state on β -Bu'. On the other hand, the peak energy of (B + F) is scarcely changed. The change of the DOS of the clusters B_3 -2-1 and B_4 -1-1 with the T state, when the structure is converted by interchanging the position of OBu and OBu', is larger than the corresponding change of the cluster B_3 -1-1 without the T state. This effect is due to the fact that the potential for the O(2) and O(3) orbitals of OBu and OBu' is not the same. This effect is also related to the fact that the L state of the clusters A_1 , A_2 is almost localized on the O(3) atom as calculated previously [2].

As shown in fig. 12, the band T is created near E_F when the O(2)-H(21) distance changes from 4.435 a.u. (B₅-1-2) to 1.875 a.u. (B₅-2-2). In the cluster B₅-2-2 with the T state, the partial DOS of α -, β -, γ -methylene of Bu' contribute to the total DOS in the relevant energy region below E_F , and those of δ -methyl and γ -methylene of Bu contribute to the total DOS in the relevant energy region above E_F . On the other hand, in the cluster B₅-1-2 without the T state, the partial DOS of Bu' shifts by about 1 eV to the lower energy side and scarcely contributes to the total DOS in the relevant energy region below E_F , whereas the orbitals of γ -, δ -Bu' are admixed with the B band in the empty region of the DOS. The partial DOS of the O(2) and O(3) atoms for the cluster B₅-1-2 without the T state are similar to each other, and are close to that of O(3) (B₅-2-2) which does not show the D' band.

From fig. 13, a remarkable difference between the total and partial DOS of the $[Ti(OBu)_2(OH)_4]^{2-}$ (B₂) and the $[Ti(OBu')_2(OH)_4]^{2-}$ (B₃-3, B₄-2, B₅-3) is found, although the symmetry of the clusters is the same (C_i). The effect on electronic structures which is induced by the trans-to-gauche conformational change of butoxyl groups, such as the F', T, D' bands, is doubled by the changed of both butoxyl groups in the B2 cluster, as compared with the above-mentioned $[Ti(OBu)(OBu')(OH)_4]^{2-}$ clusters. The T band which is mainly an admixture of the O(2)2p and δ -C (B₃-3) or β -C (B₄-2, B₅-3) 2p orbitals, appears near $E_{\rm F}$ when the O(2)-H(17) distance is equal to 1.860 a.u. (B_3-3) , or when the O(2)-H(12) distance is equal to 1.875 a.u. (B_4-2, B_5-3) , as well as the corresponding [Ti(OBu)(OBu')(OH)₄]²⁻ clusters. This suggests that the effects can be induced by the special character of butoxyl groups, and is an interesting finding obtained by the present calculations. The partial DOS of Bu' contributes little to the total DOS in the energy region above $E_{\rm F}$ and is not admixed with the Ti 3d orbitals (A and B) for the clusters B_3 -3, B_4 -2. Thus the A and B bands of these clusters are strongly localized on the Ti site as compared with other clusters. For the B_5 -3 cluster, the partial DOS of δ -Bu' contributes little to the total DOS in the relevant energy region below $E_{\rm F}$, and those of γ -, δ -Bu' shift by about 2 eV to the lower energy side and are



Fig. 15. Comparison of DOS of A_2 and A_5 clusters: $(---)A_2$; $(---)A_5$.

admixed with the B band as shown in fig. 13. The A band for the clusters $[Ti(OBu')_2(OH)_4]^{2-}$ is located at a lower energy position than those for the clusters $[Ti(OBu)_2(OH)_4]^{2-}$, $[Ti(OBu)(OBu')(OH)_4]^{2-}$ as shown in table 1.

It is worthwhile to compare the electronic structure of the [Ti(OBu')(OMe) $(OH)_4]^{2-}$ (A₅) cluster with that of the $[Ti(OBu)(OMe)(OH)_4]^{2-}$ (A₂) cluster reported in the previous paper [2] in order to prepare a catalyst with higher activity, although a cluster such as A₅ has not been found in the preparation process. From fig. 15, it is noted that a special localized level L is changed to a state with the character of the T state, by the strong interaction between O(3)and H(24), the distance of which is chosen as 1.860 a.u. in the calculation. The energy gap of the total DOS of the A_5 cluster is broader than that of the A_2 cluster, and the $C \rightarrow A$ transition is very weak and the $D \rightarrow A$ transition energy for the A₅ cluster (4.35 eV) is larger than the C \rightarrow A transition energy for the A_2 cluster (3.4 eV) as seen from table 1 and fig. 15. Such changes might introduce a negative effect on photocatalytic activity of the catalyst. For the cluster A₅, the bands F' from Bu' are admixed with the lower part E of the occupied bands of the remaining TiO₆, and the partial DOS of Bu' contributes little to the total DOS in the empty region and is not admixed with the Ti 3d orbitals (A and B), as compared with that of the A_2 cluster.

4.3. Special state for the clusters $[Ti(OBu)(OBu')(OH)_4]^{2-}$, $[Ti(OBu')_2(OH)_4]^{2-}$, $[Ti(OBu')(OMe)(OH)_4]^{2-}$

As mentioned in section 4.2, a special level T (71a level, 37a, level and 59a level) emerges close to $E_{\rm F}$ for the clusters $[{\rm Ti}({\rm OBu})({\rm OBu}')({\rm OH})_4]^{2-}$ (B₃-2-1, B_4 -1-1, B_5 -2-2), $[Ti(OBu')_2(OH)_4]^{2-}$ (B_3 -3, B_4 -2, B_5 -3) and $[Ti(OBu')(OMe)]^{2-}$ $(OH)_4]^{2-}$ (A₅). This level of the clusters $[Ti(OBu)(OBu')(OH)_4]^2$, $[Ti(OBu')_2(OH)_4]^{2-}$ might play a crucial role in the photocatalytic process over pol-Ti(OBu)₄/SiG instead of the localized level L of the clusters A_1 and A_2 in solid [pol-Ti(OBu)₄ + CH₃OH]. The energy and the orbital components of the special level 71a and the 70a just below it are shown in table 2 for the cluster $[Ti(OBu)(OBu')(OH)_4]^{2-}$. Those for the clusters $[Ti(OBu')_2(OH)_4]^{2-}$ and $[Ti(OBu')(OMe)(OH)_4]^{2-}$ are given in tables 3 and 4, respectively. From table 2 and 3, it is found that the T level is not localized on the O(2) or O(3)atom as compared with the L level for the clusters A_1 and A_2 , but made mainly on the admixture between the O(2) or O(3)2p, and the δ - or β -C2p, orbitals. This indicates the charge transfer from the O(2) or O(3) atom to the δ - or β -carbon in the direction of z-axis. The level just below T is also mainly made of the admixture between O(3) or O(2)2p, and δ - or β -C2p,. This special level emerges close to $E_{\rm F}$ independent of the degree of cluster symmetry as shown in table 3. In cluster B_2 ([Ti(OBu)₂(OH)₄]²⁻, whose partial DOS of Bu contributes little to the total DOS in the relevant energy region below $E_{\rm F}$, the admixture of the Bu orbitals in the HOMO (37a, level) is found to be -1.2%, and it is -2.3% in the $36a_{\mu}$ level just below the HOMO. As a hydrogen of Bu' approaches the O(2) or O(3) ion, a considerable amount of negative charge is transferred from Ti to O(2) or O(3), and that from O(2) or O(3) to the OBu' is found to be as shown in table 5, and a remarkable admixture between the O(2) or O(3) orbitals and the Bu' orbitals is formed. The changes occur also in the A₅ ($[Ti(OBu')(OMe)(OH)_4]^{2-}$) cluster as shown in table 4. As compared with the L level of the A₂ cluster, in which about 80% of the L level state is localized on the O(3) atom, the orbital component of the T level on O(3) is reduced to 39.2% and transfered to the δ -carbon (43.0%) for cluster A₅. On the other hand, the difference in the 58a level between A_2 and A_5 is found to be small as shown in table 4.

The conditions of appearence of the T state is not clear, but the close approach of a hydrogen atom of the alkoxyl group to the ligand oxygen is a necessary condition. A moderate size of the alkoxyl group would be also important for the formation of the T state.

4.4. Electronic structure of a tetrahedral cluster and monomer- $Ti(OBu)_4$

The pol-Ti(OBu)₄ is polymerized from monomer-Ti(OBu)₄ which is a tetrahedral molecule around Ti(IV). In the process of polymerization, the

	71a			70a		
	B ₃ -2-1	B ₄ -1-1	B ₅ -2-2	B ₃ -2-1	B ₄ -1-1	B ₅ -2-2
Energy (eV)	-1.04	-1.23	-1.18	-1.48	-1.74	-1.188
Ti	-0.017	-0.014	-0.020	0.018	0.010	0.055
O(2) 2s			0.001	0.002	0.003	
$2p_z$			0.299	0.084	0.064	
$2p_{\nu}$			-0.003	0.107	0.088	
$2p_x$			-0.061	0.084	0.076	
Total	0.033	0.094	0.358	0.277	0.231	0.017
O(3) 2s	0.007	0.002			-0.003	0.004
$2p_z$	0.236	0.210			0.108	0.357
$2p_{v}$	0.001	0.001			0.033	0.034
$2p_x$	0.043	0.049			- 0.002	0.007
Total	0.287	0.262	0.079	0.012	0.136	0.402
O(4)	0.088	0.144	0.131	0.147	0.134	0.108
O(5)	0.061	0.262	0.032	0.290	0.042	0.045
O'(6)	-0.003	0.013	0.044	0.075	0.185	0.163
O (7)	0.021	0.047	0.030	0.017	0.005	0.137
Bu'(α)	-0.005	-0.003	0.002	0.001	0.024	- 0.002
$Bu(\alpha)$	-0.003	-0.006	-0.005	-0.004	0.004	0.008
$Bu'(\beta)$	0.022			0.006		
$C'(\beta)$ 2s		0.017	0.028		0.014	0.008
$2p_z$		0.150	0.292		0.214	0.021
$2p_v$		_	0.001		0.002	_
$2p_x$		0.001	0.001		0.007	0.011
$H'(\beta)$		0.010	0.005		0.011	-0.001
Total		0.178	0.327		0.248	0.039
$Bu(\beta)$	0.001	- 0.001	-0.004	-0.002	-0.002	_
Bu'(γ)	-0.009	0.016	0.014	0.001	0.004	0.006
Bu(γ)	-	_	~	-	-	-
$Bu'(\delta)$		0.008	0.002		-0.011	_
$C'(\delta)$ 2s	0.028			0.005		
$2p_z$	0.456			0.159		
$2p_y$	-0.004			-0.007		
$2p_x$	-			-0.004		
Η'(δ)	-			0.017		
Total	0.515			0.170		
Bu(δ)	-	_	_	-		_

Orbital components of the 71a and 70a levels

tetrahedral coordinated chains might partially be included. The cluster T_1 represents the $[Ti(OBu)_2(OH)_2]$ unit which is obtained by removal of such -Ti-O-Ti-O- chains beyond the nearest neighboring Ti ions and substituting a hydrogen atom for the removed part of the network, as shown in fig. 16. It is assumed that all interatomic distances in T_1 and mon-Ti(OBu)₄, whose electronic structure was calculated for the sake of comparison, are the same as

Table 2

	37a _u			34ag		
	B ₃ -3	B ₄ -2	B ₅ -3	B ₃ -3	B ₄ -2	B ₅ -3
Energy (eV)	-0.82	-0.93	- 1.00	-1.18	- 1.46	- 1.59
Ti	-0.013	-0.012	-0.015	-0.003	-0.001	0.009
O(2) 2s	0.006	0.003	0.003	0.007	-	-0.002
2p,	0.315	0.380	0.428	0.202	0.246	0.255
$2p_{y}$	0.001	0.017	-0.009	-0.001	0.009	0.006
$2p_x$	0.045	0.051	0.049	0.040	0.060	0.065
Total	0.367	0.451	0.471	0.248	0.315	0.324
O(3)	0.110	0.109	0.102	0.007	0.016	0.013
O'(Bu)	0.011	0.028	0.049	0.004	0.083	0.086
$Bu'(\alpha)$	-0.006	-0.008	-0.004	-0.003	0.035	0.029
$Bu'(\beta)$	0.028			0.013		
$C'(\beta)$ 2s		0.033	0.034		0.036	0.039
2p _z		0.336	0.325		0.468	0.475
$2p_{\nu}$		-0.002	-0.001		-0.002	0.002
$2p_x$		0.001	-0.002		-0.004	0.001
$\hat{\mathbf{H}'}(\boldsymbol{\beta})$		0.040	-0.004		0.047	0.020
Total		0.408	0.352		0.545	0.535
$Bu'(\gamma)$	-0.010	-0.007	0.020	-0.001	0.008	0.018
$Bu'(\delta)$		0.025	-0.001		0.003	0.006
$C'(\delta)$ 2s	0.026			0.039		
$2\mathbf{p}_z$	0.455			0.636		
$2p_{\nu}$	-0.004			-		
$2p_x$	-0.003			-0.006		
Η'(δ)	0.022			0.060		
Total	0.496			0.729		

Table 3 Orbital components of the $37a_u$ and $34a_g$ levels

those used in the previous calculation [2]. It is worthwhile to compare the electronic structure of the cluster T_1 and mon-Ti(OBu)₄ with that of the cluster B_1 reported in the previous paper [2]. The calculated total and partial DOS of the clusters B_1 , T_1 and mon-Ti(OBu)₄ are shown in fig. 17. Also, the peak energy of the total DOS and the net charge of the Ti atom and each ligand in the clusters and molecule are listed in tables 1 and 5, respectively. For cluster T_1 , a special level does not appear near E_F . This result suggests that the experimental facts mentioned in section 4.1 cannot be explained by a change in the coordination number from six to four. From fig. 17, it is found that the partial DOS of the butyl group contributes to the total DOS in the relevant energy region below E_F in T_1 , mon-Ti(OBu)₄, whereas that of B_1 does little. Band C is located at an energy position for T_1 , mon-Ti(OBu)₄, 0.5-0.7 eV higher than that for B_1 . The partial DOS of the O(2) ion of the T_1 cluster is scarcely changed from that of the B_1 cluster as shown in fig. 17, whereas the charge of the O(2) atom (O(2)-H ligand) is changed from -1.02 (-0.79) to

			504	
	$A_2^{a)}$	A ₅	$\overline{\mathbf{A}_{2}^{a)}}$	A ₅
Energy (eV)	-0.80	-1.06	-2.20	-1.82
Ti	0.074	-0.004	0.049	0.039
O(2)	-0.001	0.002		
O(2) 2s			0.002	0.001
2p,			0.259	0.213
$2p_v$			0.025	0.018
$2p_x$			0.248	0.250
Total			0.534	0.482
O(3)			0.045	0.017
O(3) 2s	0.008	0.004		
2p,	0.426	0.302		
$2p_{y}$	0.057	0.003		
2p _x	0.309	0.083		
Total	0.800	0.392		
O(4)	-0.007	0.092	0.123	0.020
O(5)	0.014	0.056	0.129	0.199
OMe	0.002	0.017	-0.014	-0.010
O(Bu) or	0.098		0.128	
O(Bu')		-0.004		0.210
$Bu(\alpha)$ or	0.015		0.002	
$Bu'(\alpha)$		-0.005		0.004
$Bu(\beta)$ or	0.001		0.007	
$Bu'(\beta)$		0.027		0.013
Bu(γ) or	-		_	
$Bu'(\gamma)$		-0.003		
$Bu(\delta)$ or	-		-	
$Bu'(\delta)$				
$C'(\delta)$ 2s		0.025		-0.001
$2p_z$		0.383		0.009
$2p_{y}$		-0.005		0.008
$2p_x$		- 0.001		0.007
Η'(δ)		0.028		0.008
Total		0.430		0.031

Orbital	components	of	the	59a	and	58a	levels
Orbital	components	O1	unc	59a	anu	50a	10,0013

^{a)} Previous calculation [2].

-0.95 (-0.57). The contribution to the total DOS of the butyl group for the T₁ cluster and mon-Ti(OBu)₄ is very small in the energy region above 0-5 eV, whereas that for the B₁ cluster is considerable. From the charge state of the Ti ion and the width of the band gap, the change from the covalent to the ionic character can be qualitatively seen with the increase of the coordination number of Ti from four to six. It is, therefore, concluded that the bond character changes from covalent (mon-Ti(OBu)₄) to ionic (pol-Ti(OBu)₄ or TiO₂) in the process of polymerization. The increment of ionicity in the bond

Table 4

e		0		()	•
Ti or ligand	B ₃ -1-1	B ₃ -2-1	B ₄ -1-1	B ₅ -1-2	B ₅ -2-2
Ti(1)	2.83	2.86	2.86	2.81	2.85
OBu	-0.83	-0.84	-0.82	-0.82	-0.82
OBu'	-0.96	-1.07	- 1.04	- 0.91	-1.01
O(2)-H	-0.76	-0.76	- 0.76	-0.75	-0.64
O(3)-H	-0.70	-0.63	-0.68	-0.79	-0.78
O(4)-H	-0.80	- 0.77	-0.79	-0.81	-0.81
O(5)-H	-0.79	-0.79	-0.77	-0.73	-0.79
Ti or ligand	B ₂	B ₃ -3	B ₄ -2	B ₅ -3	B ₁ ^{a)}
Ti(1)	2.78	2.89	2.90	2.90	2.83
OBu	-0.82	_	-	-	-0.82
OBu'	_	- 1.09	- 1.06	-1.02	-
O(2)-H	-0.77	- 0.61	-0.63	-0.64	- 0.79
O(3)-H	-0.80	-0.75	-0.76	-0.79	-0.81
Ti or ligand	A ₂ ^{a)}	A ₅	T ₁	mon-Ti(OBu) ₄	
Ti(1)	2.72	2.80			
OBu	-0.80	-			
OBu'	-	-1.04			
OMe	-0.78	-0.79			
O(2)-H	- 0.80	-0.79			
O(3)-H	-0.81	0.69			
O(4)–H	-0.81	-0.75			
O(5)-H	-0.72	-0.73			
Ti(1)			2.28		
OBu			- 0.56		
O(2)-H			- 0.57		
Ti(1)				2.17	
OBu				-0.54	

Charge of	Ti atom	and each	ligand in	various	clusters	and	monomer-Ti(O	Bu)
Charge of	11 atom	and each	ingand in	various	clusters	and	monomer-rico	DUIA

^{a)} Previous calculation [2].

Table 5



Elicity allu ol u	utar componer	in on me ni	אזוור אוזור		p manny or		III HIC CINSICIS	יום אווס 1, 1, 1, 100 חווס		זוברחוב
(1) B ₁ ^{a)}			-							
Level	35ag	36a _g	37ag	40ag	4lag	55a _g	53a _u	54a u	55a "	
Energy (eV) Ti	1.26	1.52	1.75	3.50	3.86	12.70	12.98	13.87	14.80	
(3s), 4s	0.001	0.001	- 0.001	0.005	I	1.083	I	I	ł	
(3p,), 4p,	I	I	I	I	I	I	0.002	0.341	0.636	
(3p.,), 4p.,	I	I	I	I	I	I	0.002	0.623	0.293	
(3p.), 4p.	I	1	I	I	I	I	0.981	0.003	I	
3d	0.853	0.010	1	0.002	0.004	i	I	ł	I	
3d	I	0.034	0.787	0.004	I	I	t	I	I	
3d	0.010	0.772	0.038	0.003	1	I	I	I	I	
3d.2	0.002	0.003	I	0.157	0.483	0.006	I	I	I	
$3d_{2}^{2}$	0.00	0.005	0.002	0.598	0.155	I	I	I	I	
Total	0.875	0.825	0.826	0.769	0.642	1.089	0.985	0.967	0.929	
0(2)	J	0.062	0.057	0.129	0.001	-0.052	0.050	-0.033	-0.021	
0(3)	0.045	0.092	0.001	0.027	0.079	-0.059	-0.041	0.026	-0.008	
O(Bu)	0.032	0.012	0.105	0.027	0.083	-0.016	-0.013	-0.017	0.040	
Bu	0.020	I	0.004	0.020	0.177	0.035	0.021	0.039	0.059	
(2) T ₁										
Level	26a ₁	7a2	12b ₁	20b ₂	27a ₁	$28a_1$	13b ₁	31a ₁	[28b ₂]	[37a ₁]
Energy (eV) Ti	1.68	1.88	2.32	2.62	2.76	5.12	7.94	8.21	11.94	12.56
(3s), 4s	-0.002)		I	0.012	0.555	1	0.022	ł	0.294
(3p,), 4p,	0.012	I	I	I	0.039	0.010	I	0.420	I	I

molecule Ti/OBm ş ٦ F α ÷ of the Ti orbitals in the . 2 -.: doidw f the and arbital or Table 6

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(3p _y), 4p _y	ł	ļ	ţ	0.091	I	ł	1		0.284	1
$(3p_y), 4p_x$	ł	1	0.015	1		I	0.775	***	1	J
$3d_{yz}$	ł	ł	I	0.702	1		I	***	0.022	ł
3d _{xz}	I	1	0.767	I	1	ł	0.009	1	ł	1
$3d_{xy}$	ł	0.768	I	I		-	ł	1	ł	t
3d _z ż	0.768			I	I	ł	I	0.001	I	1
$3d_{x^{2}-y^{2}}$	0.005	I	184.ch	I	0.733	0.010	1	0.006	l	0.004
Total	0.783	0.768	0.782	0.793	0.784	0.575	0.784	0.449	0.306	0.298
0(2)	0.162	0.098	0.077	0.055	0.085	0.012	-0.013	-0.011	-0.010	0.201
O(Bu)	0.032	0.135	0.090	0.110	0.091	0.007	-0.019	0.010	0.095	0.006
Bu	0.023	- 0.002	0.004	0.045	0.003	0.287	0.178	0.488	0.609	0.151
(3) monomer-Ti	(OBu)4									
Level	$20a_1$	6b ₁	19b ₂	24e	21a ₁	[21b ₂]	[27a ₁]	[35e]	37e	29b ₂
Energy (eV) Ti	1.58	2.08	2.98	3.21	5.76	16.7	11.95	12.84	13.91	14.58
(3s), 4s	1	ł	I	ł	0.318	ţ	0.308	I	I	1
$(3p_z), 4p_z$	ı	ł	0.097	ł	I	0.209	I	I	I	0.253
(3p _y), 4p _y (3p _x), 4p _x	I	**	ſ	0.077		ł	ł	0.210	0.279	1
3d ₂₂ 3d ₂₂	1	***		0.694	ŧ	ł	I	0.016	0.004	1
3dxv	1	0.757	i	1		I	1	1	ł	1
$3d_{z^2}$	0.892		I	ł		I	1	1	I	1
$3d_{x^2-y^2}$	I	I	0.680	ł	ł	0.037	I	I	ł	0.004
Total	0.892	0.757	0.777	0.771	0.318	0.246	0.308	0.226	0.283	0.257
O(Bu)	0.067	0.236	0.211	0.182	-0.007	0.035	0.074	0.063	ı	0.140
Bu	0.039	0.006	0.011	0.048	0.689	0.718	0.616	0.709	0.716	0.6U2
a) Previous calc	ulation [2].									



Fig. 17. Comparison of DOS of B_1 , T_1 clusters and monomer-Ti(OBu)₄ molecule: (-----) B_1 ; (------) T_1 ; (······) mon-Ti(OBu)₄.

character with the coordination number also affects the Ti 3d (4s, 4p) states in the empty region of the DOS of these clusters and molecule. Namely, the admixture of those Ti 3d states with the ligand orbitals decreases remarkably with an increase of the coordination number. The comparison is summarized in table 6.

5. Conclusion

The change in the electronic structure of pol-Ti(OBu)₄ due to the conversion from trans to gauche of butoxyl groups is fully investigated by DV-X α cluster calculations. In the [Ti(OBu)₂(OH)₄]²⁻ cluster, a characteristic state appears near the Fermi level by the effect of gauche-conformation of β -carbon for OBu, whereas rotational isomers of gauche-form for γ -, δ -carbons cannot produce such a state. This fact provides important information to interpret the experimental results obtained by the photolysis of water over pol-Ti(OBu)₄/ SiG and Raman scattering. For the clusters [Ti(OBu)(OBu')(OH)₄]²⁻ and [Ti(OBu')₂(OH)₄]²⁻, whose Bu' is transformed to gauche for β -carbon, the partial DOS of Bu' shifts by a few eV to the higher energy side than that of OBu. When a hydrogen of Bu' comes near one of the O ions of the ligand, the upper part of the partial DOS of OBu' creates the peak T near $E_{\rm F}$. This level might be considered to play a crucial role in the photocatalytic process as well as the L level of the $[Ti(OBu)(OMe)(OH)_4]^{2-}$ cluster. Such a state is unstable, and possibly makes use of a new catalyst by addition of an effective substance for stabilization which is different from the effect of methanol. Such conversions from trans to gauche of the butoxyl group in the $[pol-Ti(OBu)_4 +$ $CH_3OH]$ complex might introduce a negative effect on its photocatalytic activity, as speculated from the DOS by the DV-X α calculation for the $[Ti(OBu')(OMe)(OH)_4]^{2-}$ cluster.

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