

Theoretical study of ethylene polymerization on Ziegler–Natta catalysts and on metallocene catalysts

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Abstract

Ethylene insertion on O_h - $d^1CH_3Ti_n$ chloride clusters/ C_2H_4 (model systems of Ziegler–Natta catalysts) and T_d - d^0 , $d^1CH_3TiCp_2/C_2H_4$ (model systems of metallocene catalysts) were studied by using paired interacting orbitals (PIO) analysis and LFO calculation. Electron delocalization from catalytic site to ethylene and that from ethylene to catalytic site played a crucial role in ethylene insertion. The former depends on the nucleophilicity of the active site and the latter on the electrophilicity of the active site. They were quantitatively estimated by LFO calculation. In the case of O_h systems, the electrophilicity of the catalyst decreased because of the Cl anion located *trans* to the ethylene in the reaction plane. In the case of T_d systems, since the electrophilicity was not weakened because of the absence of the *trans* ligand to the ethylene, the nucleophilicity and electrophilicity were well balanced. The O_h - d^1Ti_4 cluster could be a suitable model of the active site on the $TiCl_3$ crystalline surface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Highly active Ziegler–Natta catalysts have modernized the manufacturing process of polyolefin. Since the discovery of highly active metallocene catalysts by Kaminsky et al., much interest has been directed to homogeneous catalysts because of their possibilities of producing versatile polymers: syndiotactic polypropylene, syndiotactic polystyrene, ethylene/ α -olefin copolymer with very sharp molecular weight distribution, etc. The needs of catalysts which enable to control molecular weight and its dis-

tribution, copolymerization ratio, regio- and stereoselectivities, and so on, are increasing more to produce polymers with desirable chemical and physical properties. It may be especially useful to know the difference between the polymerization mechanism on heterogeneous catalysts and that on homogeneous catalysts in order to develop such sophisticated catalysts. Theoretical study of polymerization mechanism is indispensable. As the recent progress in ab initio MO and ab initio MD computational calculations by using not only HF methods but also DF methods, many theoretical studies on polymerization mechanism have been reported [1–14].

From a practical point of view, ab initio calculations are not easy to apply to the large

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catalytic systems used in industry. In addition, MOs spread over the whole molecular system and, therefore, it is not easy to understand the catalytic interactions between the active site and the olefin molecule. The requirement of a not time-consuming method for analysing the calculated results and predicting the catalytic activities will increase as the catalytic systems become larger in size. Fujimoto et al. [15–18] proposed a method of determining unequivocally the orbitals which should play dominant roles in chemical interactions between two systems. Interactions were represented compactly in terms of a few pairs of localized orbitals. In each orbital pair, one orbital belongs to one fragment species, that is a catalyst, and the other orbitals to the other fragment species, that is a reactant. They called those orbitals “paired interacting orbitals” (PIO). Although this analysis was proposed originally for *ab initio* calculations, we reported that this approach was also useful in analysing the results of extended Hückel calculations [19–22]. Fujimoto et al. [23,24] and Omoto et al. [25] also proposed the way of estimating the electrophilicity and nucleophilicity of active sites based on electron delocalization. By using this method, we predicted the reactivities of ethylene insertion into the Ti-methyl bond in d^0 -methyltitanium complexes [26].

Most of the theoretical studies have been done assuming the model of homogeneous catalysts in which an active site has a tetrahedral (T_d) structure. In the case of heterogeneous catalysts, an active site has an octahedral (O_h) structure. In this paper, we study ethylene insertion on O_h - $d^1CH_3Ti_n$ chloride cluster/ C_2H_4 systems, as models of Ziegler–Natta catalysts, and on T_d - d^0 - $d^1CH_3TiCp_2$ / C_2H_4 systems, as models of metallocene catalysts, by using PIO analysis and LFO calculation.

2. Methods

2.1. Models

Many kinetic, morphological and crystallographic studies of Ziegler–Natta catalysts have revealed that the precursor of an active site is located on the edge of the basal face of violet $TiCl_3$ crystalline surfaces [27–36]. Fig. 1 shows the structure of a $CH_3Ti_{16}Cl_{47}$ cluster which has been removed from the edge of the basal face of the violet $TiCl_3$ crystalline. We employed four numbers of O_h - $d^1[CH_3Ti_nCl_{3n-1}]$: ($n = 4, 6, 8$) neutral clusters, as the active site model of heterogeneous catalysts, and T_d - d^0 - $d^1[CH_3TiCp_2]^m$: ($m = 1, 0$), as the active site model of homogeneous catalysts. They are shown in Fig. 2.

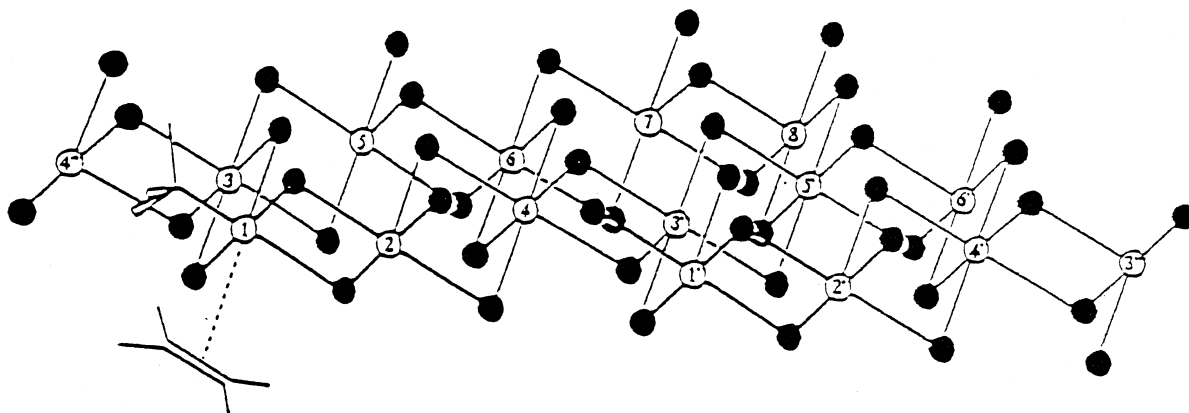


Fig. 1. A schematic illustration of a $CH_3Ti_{16}Cl_{47}$ cluster cut-off from the edge of the basal face of $TiCl_3$ crystalline.

2.2. PIO analysis

We have examined an ethylene coordinated state based on the Cossee insertion mechanism. The geometry optimization technique was not adopted for determining the structures of the ethylene coordinated state of the models. The details of the models are given in Appendix A. We then divided an ethylene coordinated state of model complex (combined system C) into a methyltitanium chloride portion (fragment A) and an ethylene molecule (fragment B). The geometries of [A] and [B] were the same as those in the original complex ([A–B][C]).

The MOs of [A], [B] and [C] were calculated by the extended Hückel method. The extended Hückel parameters are given in Appendix A. PIOs were obtained by applying the procedure that was proposed by Fujimoto et al. [15–18]. It is summarized as follows: (1) we expand the MOs of a complex in terms of the MOs of two fragment species, to determine the expansion coefficients $c_{i,f}$, $c_{m+j,f}$ and $d_{k,f}$, $d_{n+l,f}$ in Eq. (1)

$$\begin{aligned} \Phi_f = & \sum_{l=1}^m c_{i,f} \phi_i + \sum_{j=1}^{M-m} c_{m+j,f} \phi_{m+j} \\ & + \sum_{k=1}^n d_{k,f} \psi_k + \sum_{l=1}^{N-n} d_{n+l,f} \psi_{n+l}, \\ f = & 1, 2, \dots, m+n, \end{aligned} \quad (1)$$

where Φ is a MO of the complex [C], ϕ and ψ are the MOs of the fragment [A] and fragment [B], respectively, m and n indicate the number of the occupied MOs of A and B, respectively, and M and N represent the number of the MOs of A and B, respectively; (2) we construct an interaction matrix \mathbf{P} which represents the interaction between the MOs of the fragment [A] and the MOs of the fragment [B]

$$\mathbf{P} = \begin{pmatrix} P_{i,k} & P_{i,n+l} \\ P_{m+j,k} & P_{m+j,n+l} \end{pmatrix} \quad (2)$$

in which

$$\begin{aligned} P_{i,k} &= n_{t,u} \sum_{f=1}^{m+n} c_{i,f} d_{k,f} \\ i &= l \sim m, k = l \sim n \\ P_{i,n+l} &= n_{t,u} \sum_{f=1}^{m+n} c_{i,f} d_{n+l,f} \\ i &= 1 \sim m, l = 1 \sim N-n \\ P_{m+j,k} &= n_{t,u} \sum_{f=1}^{m+n} c_{m+j,f} d_{k,f} \\ j &= 1 \sim M-m, k = 1 \sim n \\ P_{m+j,n+l} &= n_{t,u} \sum_{f=1}^{m+n} c_{m+j,f} d_{n+l,f} \\ j &= 1 \sim M-m, l = 1 \sim N-n; \end{aligned}$$

(3) we get transformation matrix \mathbf{U}^A (for A) and \mathbf{U}^B (for B) by

$$\tilde{\mathbf{P}}\mathbf{P}\mathbf{U}^A = \mathbf{U}^A \mathbf{\Gamma} \quad (3)$$

$$\mathbf{U}_{s,v}^B = (\gamma_v)^{-1/2} \sum_r^N p_{r,s} \mathbf{U}_{r,v}^A \quad v = 1, 2, \dots, N \quad (4)$$

and, finally, (4) we obtain the PIOs by Eqs. (5) and (6)

$$\phi'_v = \sum_r^N \mathbf{U}_{r,v}^A \phi_r \quad (\text{for A}) \quad (5)$$

$$\psi'_v = \sum_s^N \mathbf{U}_{s,v}^B \psi_s \quad (\text{for B}) \quad (6)$$

The $N \times M$ ($N \leq M$) orbital interactions in the complex C can thus be reduced to the interactions of N PIOs, N indicating the smaller of the numbers of MOs of the two fragments, A and B.

2.3. LFO calculation

LFO energies were calculated according to the procedure proposed by Fujimoto et al.

[23,24] and Omoto et al. [25]. The reference orbital, which is determined by PIO analysis, denoted here by δ_r can be expanded in terms of the occupied MOs ϕ_i and the unoccupied MOs ϕ_j of a methyltitanium complex (A)

$$\delta_r = \sum_i^{\text{occ}} d_{i,r} \phi_i + \sum_j^{\text{unocc}} d_{j,r} \phi_j \quad (7)$$

Then, the occupied and unoccupied orbital that are the closest to δ_r are respectively defined by

$$\phi_{\text{occ}}(\delta_r) = \left(\sum_i^{\text{occ}} d_{i,r} \phi_i \right) / \left(\sum_i^{\text{occ}} d_{i,r}^2 \right)^{1/2} \quad (8)$$

$$\phi_{\text{unocc}}(\delta_r) = \left(\sum_j^{\text{unocc}} d_{j,r} \phi_j \right) / \left(\sum_j^{\text{unocc}} d_{j,r}^2 \right)^{1/2} \quad (9)$$

These orbitals are given by a linear combination of the occupied and unoccupied canonical MOs, respectively, and, therefore, the electron-donating and -accepting strength is evaluated by

$$\lambda_{\text{occ}}(\delta_r) = \left(\sum_i^{\text{occ}} d_{i,r}^2 \varepsilon_i \right) / \left(\sum_i^{\text{occ}} d_{i,r}^2 \right) \quad (10)$$

$$\lambda_{\text{unocc}}(\delta_r) = \left(\sum_j^{\text{unocc}} d_{j,r}^2 \varepsilon_j \right) / \left(\sum_j^{\text{unocc}} d_{j,r}^2 \right) \quad (11)$$

where ε_i and ε_j are the orbital energies of the component MOs ϕ_i and ϕ_j . With the same procedure as described above, we can obtain the electron-donating and -accepting strength of the ethylene molecule (B).

Then, a reactivity index (RI) is defined by Eq. (12).

$$\text{RI} = 1/(\lambda_{\text{A unocc}} - \lambda_{\text{B occ}}) + 1/(\lambda_{\text{B unocc}} - \lambda_{\text{A occ}}) \quad (12)$$

The first term on the right-hand side estimates the magnitude of electron delocalization from the ethylene molecule (B) to the methyltitanium complex (A) and the second term estimates that from A to B.

PIO and LFO calculations were carried out on *LUMMOX* system [37].

3. Results and discussion

3.1. PIO analysis

Eigenvalues of PIOs in the models, the AO components of PIO-1 and PIO-2 are summarized in Tables 1 and 2, respectively. Contour maps of PIO-1 and PIO-2 of the models are shown in Fig. 3.

We obtained 12 PIOs, PIO-1 to PIO-12. The eigenvalues tell us that PIO-1 and PIO-2 have much larger contribution to the interaction relative to 10 other orbital pairs. This is reasonable, because two bonds are formed in the insertion process. We examine PIO-1 and PIO-2 precisely.

3.2. O_h - d^1 methyltitanium chloride cluster / ethylene systems

Table 2 tells us that the main component of the ethylene part of PIO-1 is the π^* orbital in

Table 1
Eigenvalues of PIOs of the ethylene coordinated state of the model systems

Model system	PIO-1	PIO-2	PIO-3	PIO-4	PIO-5	PIO-6	...	PIO-12
O_h - $d^1(1)/C_2H_4$	0.469	0.159	0.067	0.050	0.037	0.017	...	0.000
O_h - $d^1(2)/C_2H_4$	0.523	0.155	0.066	0.049	0.039	0.017	...	0.000
O_h - $d^1(3)/C_2H_4$	0.599	0.155	0.066	0.051	0.039	0.017	...	0.000
O_h - $d^1(4)/C_2H_4$	0.635	0.157	0.066	0.051	0.041	0.017	...	0.000
T_d - $d^0(5)/C_2H_4$	0.194	0.130	0.051	0.031	0.018	0.013	...	0.000
T_d - $d^1(5)/C_2H_4$; α spin	0.172	0.046	0.013	0.011	0.006	0.004	...	0.000
T_d - $d^1(5)/C_2H_4$; β spin	0.049	0.033	0.013	0.008	0.005	0.003	...	0.000

Table 2

LCAO representation of PIO-1 and PIO-2 of the ethylene coordinated state of the model systems^a

PIO-1	
O _h -d ¹ (1)/C ₂ H ₄ ; catalyst part	$\phi'_1 = -0.21^5 \text{Tid}_{xy} + 0.58^5 \text{Tid}_{xz} + 0.24^{10} \text{Tid}_{xy} - 0.40^{10} \text{Tid}_{xz} - 0.41^{14} \text{Tid}_{yz} - 0.28^{17} \text{Tid}_{xz} + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.81 C_{\alpha} p_x - 0.80 C_{\beta} p_x + \dots$
O _h -d ¹ (2)/C ₂ H ₄ ; catalyst part	$\phi'_1 = 0.61^5 \text{Tid}_{xz} + 0.24^{10} \text{Tid}_{xy} - 0.48^{10} \text{Tid}_{xz} + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.81 C_{\alpha} p_x - 0.80 C_{\beta} p_x + \dots$
O _h -d ¹ (3)/C ₂ H ₄ ; catalyst part	$\phi'_1 = -0.21^5 \text{Tid}_{xy} + 0.66^5 \text{Tid}_{xz} + 0.24^{10} \text{Tid}_{xy} - 0.41^{10} \text{Tid}_{xz} - 0.24^{21} \text{Tid}_{xz} - 0.20^{28} \text{Tid}_{xy} + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.81 C_{\alpha} p_x - 0.81 C_{\beta} p_x + \dots$
O _h -d ¹ (4)/C ₂ H ₄ ; catalyst part	$\phi'_1 = 0.71^5 \text{Tid}_{xz} + 0.28^{10} \text{Tid}_{xy} - 0.35^{10} \text{Tid}_{xz} - 0.24^{14} \text{Tid}_{yz} + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.82 C_{\alpha} p_x - 0.81 C_{\beta} p_x + \dots$
T _d -d ⁰ (5)/C ₂ H ₄ ; catalyst part	$\phi'_1 = -0.74^5 \text{Tid}_{x^2-y^2} + 0.38^5 \text{Tid}_{z^2} + 0.22^5 \text{Tid}_{xz} + 0.21^7 \text{Cp}_x + 0.21^{16} \text{Cp}_y - 0.29^{18} \text{Cp}_y + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.78 C_{\alpha} p_x + 0.44 C_{\beta} p_x + \dots$
T _d -d ¹ (5)/C ₂ H ₄ ; α spin, catalyst part	$\phi'_1 = -0.22^1 \text{Cp}_x - 0.21^5 \text{Tid}_{z^2} + 0.88^5 \text{Tid}_{xz} + 0.23^6 \text{Cp}_y + \dots$
C ₂ H ₄ part	$\psi'_1 = 0.80 C_{\alpha} p_x - 0.82 C_{\beta} p_x + \dots$
β spin, almost the same values as those of the T _d -d ⁰ (5) model system	
PIO-2	
O _h -d ¹ (1)/C ₂ H ₄ ; catalyst part	$\phi'_2 = -0.47^5 \text{Tid}_{x^2-y^2} + 0.35^5 \text{Tid}_{z^2} + 0.29^6 \text{Cl}_s + 0.54^6 \text{Clp}_x + 0.23^8 \text{Clp}_x + 0.34^9 \text{Clp}_x + \dots$
C ₂ H ₄ part	$\psi'_2 = -0.20 C_{\alpha} s + 0.50 C_{\alpha} p_x + 0.52 C_{\beta} p_x - 0.20^{10} \text{Hs} + \dots$
O _h -d ¹ (2)/C ₂ H ₄ ; catalyst part	$\phi'_2 = -0.45^5 \text{Tid}_{x^2-y^2} + 0.34^5 \text{Tid}_{z^2} + 0.31^6 \text{Cl}_s + 0.53^6 \text{Clp}_x + 0.22^8 \text{Clp}_x + 0.36^9 \text{Clp}_x + \dots$
C ₂ H ₄ part	$\psi'_2 = -0.21 C_{\alpha} s + 0.48 C_{\alpha} p_x + 0.51 C_{\beta} p_x - 0.21^{10} \text{Hs} + \dots$
O _h -d ¹ (3)/C ₂ H ₄ ; catalyst part	$\phi'_2 = -0.45^5 \text{Tid}_{x^2-y^2} + 0.34^5 \text{Tid}_{z^2} + 0.31^6 \text{Cl}_s + 0.54^6 \text{Clp}_x + 0.23^8 \text{Clp}_x + 0.35^9 \text{Clp}_x + \dots$
C ₂ H ₄ part	$\psi'_2 = -0.21 C_{\alpha} s + 0.49 C_{\alpha} p_x + 0.50 C_{\beta} p_x - 0.20^{10} \text{Hs} + \dots$
O _h -d ¹ (4)/C ₂ H ₄ ; catalyst part	$\phi'_2 = -0.44^5 \text{Tid}_{x^2-y^2} + 0.34^5 \text{Tid}_{z^2} + 0.31^6 \text{Cl}_s + 0.53^6 \text{Clp}_x + 0.23^8 \text{Clp}_x + 0.35^9 \text{Clp}_x + \dots$
C ₂ H ₄ part	$\psi'_2 = -0.21 C_{\alpha} s + 0.49 C_{\alpha} p_x + 0.50 C_{\beta} p_x + 0.20^{10} \text{Hs} + \dots$
T _d -d ⁰ (5)/C ₂ H ₄ ; catalyst part	$\phi'_2 = 0.56^1 \text{Cp}_x - 0.48^1 \text{Cp}_z - 0.22^2 \text{Hs} + 0.27^5 \text{Tid}_{x^2-y^2} + \dots$
C ₂ H ₄ part	$\psi'_2 = 0.49 C_{\alpha} p_x - 0.78 C_{\beta} p_x - 0.27^{11} \text{Hs} - 0.27^{12} \text{Hs} + \dots$
T _d -d ¹ (5)/C ₂ H ₄ ; α spin, catalyst part	$\phi'_2 = -0.74^5 \text{Tid}_{x^2-y^2} + 0.44^5 \text{Tid}_{z^2} + 0.25^7 \text{Cp}_y + 0.20^9 \text{Cp}_y + 0.24^{11} \text{Cp}_y - 0.26^{18} \text{Cp}_y + \dots$
C ₂ H ₄ part	$\psi'_2 = 0.63 C_{\alpha} p_x + 0.62 C_{\beta} p_x + \dots$
β spin, almost the same values as those of T _d -d ⁰ (5) model system	

^aA suffix number at the left shoulder of the atomic formula indicates the number of the atomic formula in the models shown in Fig. 2.

all the O_h-d¹ model systems. This signifies that PIO-1 represents electron delocalization from the occupied orbitals of the catalyst part which are mainly composed of the Ti d(t_{2g}) orbitals (see Table 2), to the ethylene π^* orbital: that is back-donation. On the other, the main components of the ethylene part of PIO-2 are the π orbital and some few other occupied orbitals, and the main components of the catalyst part of PIO-2 are the mixtures of some unoccupied orbitals and some occupied orbitals in all the O_h-d¹ model systems. This indicates that PIO-2 represents electron delocalization from the ethylene π orbital to the unoccupied orbitals of the catalyst part which are composed of Ti d(e_g) orbitals: that is donation, but a repulsive interaction intervenes between the occupied C 2s and

H1s orbitals of ethylene and the occupied Cl 3p orbitals of the catalyst.

These results are compactly shown with the contour maps of PIO-1 and PIO-2 of the model systems. One example is shown in Fig. 3(a).

3.3. T_d-d⁰[CH₃TiCp₂]⁺¹/C₂H₄ system

The main component of the ethylene part of PIO-1 of the T_d-d⁰(5)/C₂H₄ system is the π orbital and the main components of the catalyst part of PIO-1 are the unoccupied orbitals which are mainly composed of the Ti d(e_g) orbitals. In contrast, the main components of the ethylene part of PIO-2 of this system are the π^* orbital and some few other occupied orbitals and the main components of the catalyst part of PIO-2 are the occupied orbitals which mainly com-

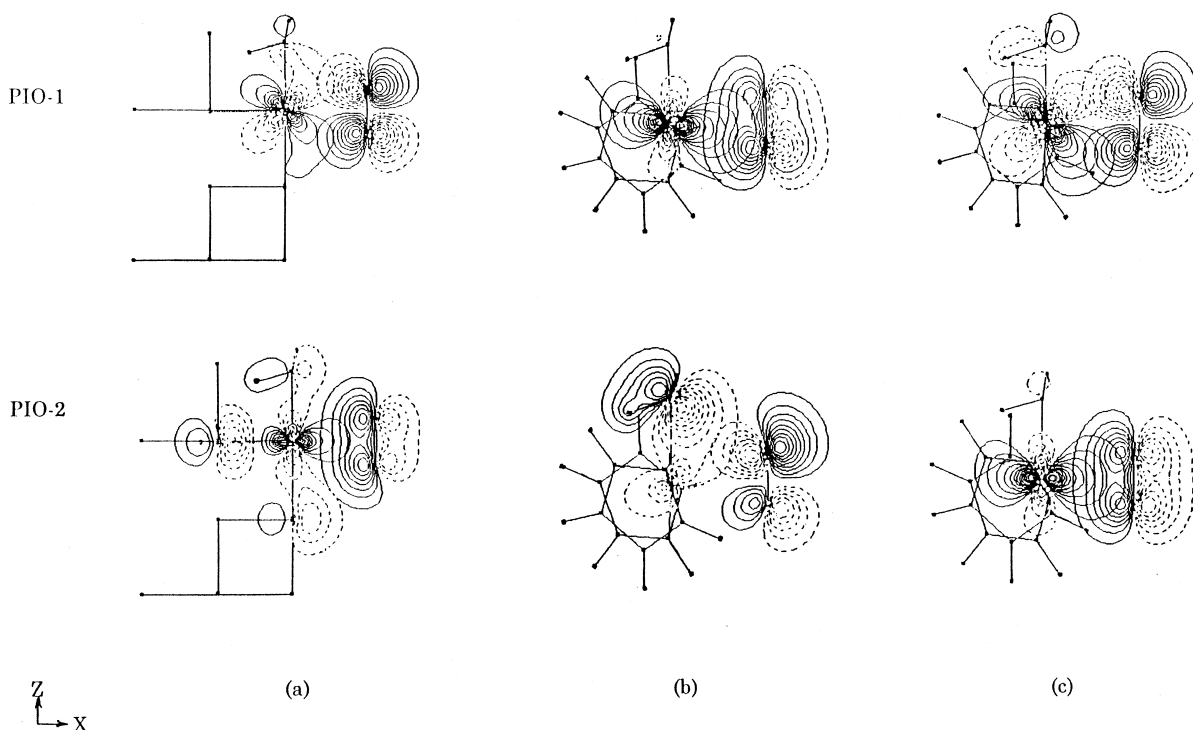


Fig. 3. Contour maps of PIO-1 and PIO-2 of model systems; (a) $O_h-d^1(1)/C_2H_4$, (b) $T_d-d^0(5)/C_2H_4$, (c) $T_d-d^1(5)/C_2H_4$ α spin.

posed of the methyl Cp orbitals and $Ti d(e_g)$ orbitals. In the case of $T_d-d^0(5)/C_2H_4$ system, main interaction is electron delocalization from the ethylene to the catalyst: that is donation, and subsidiary one is electron delocalization from the catalyst to the ethylene: that is back-donation.

Contour maps of PIO-1 and PIO-2 of $T_d-d^0(5)/C_2H_4$ system are shown in Fig. 3(b).

3.4. $T_d-d^1[CH_3TiCp_2]/C_2H_4$ system

3.4.1. α spin system

The main component of the ethylene part of PIO-1 of the $T_d-d^1(5)/C_2H_4$ system is the π^* orbital and the main components of the catalyst part are the occupied orbitals which are composed of the mixture of the Cp orbitals of the methyl group, the $Ti d$ orbitals and the Cp orbitals of the Cp group. The PIO-1 of this model

system represents electron delocalization from the catalyst to the ethylene molecule: this is also back-donation. The main component of the ethylene part of PIO-2 of this model system is π^* orbital and the main components of the catalyst part are the unoccupied $Ti d(e_g)$ orbitals. The PIO-2 indicates electron delocalization from the ethylene molecule to the catalyst: this is donation. Contour maps of PIO-1 and PIO-2 of $T_d-d^1(5)/C_2H_4$ system; (α spin), are shown in Fig. 3(c).

3.4.2. β spin system

The PIOs of the β spin system of $T_d-d^1(5)/C_2H_4$ system are almost the same PIOs as those of $T_d-d^0(5)/C_2H_4$ system.

From the discussions described above, we can conclude that electron delocalization from the catalyst to the ethylene molecule and that from the ethylene molecule to the catalyst play crucial roles in ethylene insertion. The former

Table 3

LFO energies, nucleo- and electrophilicity of the methyltitaniums and the RI of ethylene insertion of methyltitaniums/C₂H₄ systems

	$\lambda_{A_{occ}}$ (eV)	$\lambda_{A_{unocc}}$ (eV)	$\lambda_{B_{occ}}$ (eV)	$\lambda_{B_{unocc}}$ (eV)	Nucleophilicity [1/($\lambda_{B_{unocc}} - \lambda_{A_{occ}}$)]	Electrophilicity [1/($\lambda_{A_{unocc}} - \lambda_{B_{occ}}$)]	RI
O _h -d ¹ (1)/C ₂ H ₄	-10.43	-1.07	-17.54	-8.29	0.472	0.061	1.07
O _h -d ¹ (2)/C ₂ H ₄	-10.41	0.07	-18.03	-8.30	0.474	0.055	1.06
O _h -d ¹ (3)/C ₂ H ₄	-10.69	0.46	-18.02	-8.30	0.418	0.054	0.94
O _h -d ¹ (4)/C ₂ H ₄	-10.34	0.36	-18.02	-8.30	0.490	0.054	1.09
T _d -d ⁰ (5)/C ₂ H ₄	-13.32	-8.47	-13.20	-6.65	0.150	0.211	0.72
T _d -d ¹ (5)/C ₂ H ₄ ; α spin	-10.44	-8.23	-13.20	-8.25	0.457	0.201	0.66
T _d -d ¹ (5)/C ₂ H ₄ ; β spin	-13.32	-8.47	-13.20	-6.65	0.150	0.211	0.36
							1.02

depends on the nucleophilicity (electron donability) of the catalytic site and the latter depends on the electrophilicity (electron acceptability) of the catalytic site. The next thing to do is to estimate the strength of the nucleo- and electrophilicity of the catalyst quantitatively by using the LFO scheme.

3.5. RI of the model systems

According to the results of the PIO analysis on the model systems described above, we determined a reference orbital δ_r . We show reference orbitals of the O_h-d¹(1)/C₂H₄ system for an example. Four reference orbitals are determined as follows: for the occupied orbital space of the catalyst;

$$\begin{aligned}
 (\delta_r)_{A_{occ}} = & -0.16^1 C p_z - 0.21^5 Ti d_{xy} \\
 & + 0.58^5 Ti d_{xz} + 0.14^5 Ti d_{yz} \\
 & - 0.11^9 Cl p_z + 0.24^{10} Ti d_{xy} \\
 & - 0.40^{10} Ti d_{xz} - 0.15^{11} Cl p_x \\
 & + 0.11^{11} Cl p_z - 0.12^{13} Cl p_z \\
 & - 0.12^{14} Ti d_{xy} - 0.13^{14} Ti d_{xz} \\
 & - 0.41^{14} Ti d_{yz} + 0.15^{15} Cl p_y \\
 & - 0.28^{17} Ti d_{xz} + 0.15^{17} Ti d_{yz},
 \end{aligned}$$

¹ for the unoccupied orbital space;

$$\begin{aligned}
 (\delta_r)_{A_{unocc}} = & 0.18^1 C p_x - 0.11^5 Ti s + 0.12^5 Ti p_x \\
 & - 0.47^5 Ti d_{z^2} + 0.29^6 Cl s \\
 & + 0.54^6 Cl p_x - 0.16^6 Cl p_y \\
 & + 0.11^7 Cl p_x + 0.16^7 Cl p_y \\
 & + 0.23^8 Cl p_x + 0.11^9 Cl s \\
 & + 0.34^9 Cl p_x + 0.13^{10} Ti p_y \\
 & + 0.11^{10} Ti p_z + 0.16^{14} Ti s \\
 & - 0.14^{14} Ti p_y - 0.16^{14} Ti d_{x^2-y^2} \\
 & - 0.14^{14} Ti d_{xy},
 \end{aligned}$$

for the occupied orbital space of the ethylene;

$$\begin{aligned}
 (\delta_r)_{B_{occ}} = & -0.20 C_\alpha s + 0.50 C_\alpha p_x \\
 & - 0.15 C_\beta s + 0.52 C_\beta p_x \\
 & - 0.17^9 H s - 0.20^{10} H s \\
 & - 0.14^{11} H s - 0.13^{12} H s,
 \end{aligned}$$

for the unoccupied orbital space; $(\delta_r)_{B_{unocc}} = 0.81 C_\alpha p_x - 0.80 C_\beta p_x + 0.10^9 H s - 0.11^{12} H s$.

LFO energies, nucleo- and electrophilicity of the methyltitaniums and the RI for the ethylene insertion are summarized in Table 3. The differences of these values are not large in the O_h-d¹(1)–(4)/C₂H₄ systems. It can be sufficient to

¹ A suffix number at the left shoulder of the atomic formula indicates the number of the atomic formula in the models shown in Fig. 2.

Table 4
Bond lengths (Å) and bond angles (°) of models

Bond length (Å)	Bond angle (°)		
Ti– ¹ C ^a	2.030	¹ C–Ti–Cl	90.0
Ti– ^c Cp ^b		Cl–Ti–Cl	90.0
Ti–Cl	2.220	¹ C–Ti–C _α	105.64
Ti–C _α , C _β	2.510	¹ C–Ti– ^c Cp	105.64
		^c Cp–Ti– ^c Cp	123.60
C _α –C _β	1.350	Ti–C _α –C _β	74.36
C–C	1.540	Ti– ¹ C– ² H	74.70
C– ² H	1.190	* (1) ^c –C _α –C _β	173.40
C–H	1.080	* (2) ^c –C _α –C _β	173.40
		H–C–H	109.50
		H–C–C (in Cp)	108.00
		H–C _α , C _β –H	120.00

^aA suffix number at the left shoulder of the atomic formula indicates the number of the atomic formula in the models shown in Fig. 2.

^bCp means a center of Cp ring.

* (1) or * (2) means a middle point of the two hydrogen atoms of the methylene group of the ethylene molecule.

employ O_h-d¹methyltitanium chloride cluster(1) as a model of the active site of the TiCl₃ catalyst. It is also observed in the case of O_h-d¹methyltitanium complexes that the nucleophilicity is markedly large in comparison with the electrophilicity. The decrease of the electrophilicity is caused by the Cl anion located *trans* to the coordinated ethylene molecule. This is a characteristic feature of the O_h structure of the model systems. In the case of T_d systems (metallocene type catalysts), since the electrophilicity of the catalyst is not weakened because of the absence of the Cl anion located *trans* to the ethylene molecule the nucleophilicity and the electrophilicity of the catalyst are well balanced. RI of the T_d-d¹ system is large in comparison with that of the T_d-d⁰ system owing to the contribution of the nucleophilicity of the spin part of the T_d-d¹ system. The RI of the T_d-d¹ system and those of the O_h-d¹ systems are almost the same, however further investigation is needed as for the comparison between the real catalytic activities of them because the balance of the nucleophilicity and the electrophilicity of both systems is rather different.

4. Conclusion

The difference between the structure of the O_h and T_d model systems is that in the former system there are two ligands (two Cl anions) in the ethylene insertion plane, which is composed of the Ti atom, the carbon atom of the methyl group and two carbon atoms of the ethylene, whereas in the latter, none of the ligands is located in the plane. Since a ligand located *trans* to the ethylene in the insertion plane decreases the electrophilicity of the catalyst, the driving force of the ethylene insertion mainly depends on the Ti3d electron delocalization to the ethylene in the O_h model systems. On the other hand, disappearing such a limitation, mutual electron delocalizations are well balanced in the T_d model systems. By using LFO calculations based on PIO analysis we can estimate the electrophilicity and the nucleophilicity of the catalyst and can predict the RI of the ethylene insertion.

Finally, we mention stereospecificity of the catalyst. The origin of the stereospecificity of the T_d model systems comes from *c*₂ symmetry structure of the models. On the other, the O_h model systems belong to *c*₁ symmetry structure. In addition, both of a position for the ethylene coordination and a route of the ethylene to the position are restricted to only one in the O_h systems. The O_h systems are favorable to give isotactic polymers.

Table 5
Extended Hückel parameters

Orbital	H _{ii} (eV)	ζ 1	ζ 2	C1	C2
H 1s	-13.60	1.30			
C 2s	-21.40	1.625			
C 2p	-11.40	1.625			
Cl 3s	-30.00	2.033			
Cl 3p	-15.00	2.033			
Ti 4s	-8.97	1.075			
Ti 4p	-5.44	0.675			
Ti 3d	-10.81	4.533	1.40	0.4206	0.7389

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Appendix A

Geometrical parameters of models are given in Table 4. Coulomb integrals and orbital exponents are listed in Table 5.

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