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Ab Initio Molecular Orbital Study of the Electron Emission Mechanism of TiCl_3 as a Reductant for an Electroless Deposition Process

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The oxidation mechanism of TiCl_3 as a reductant for an electroless deposition process was studied by ab initio molecular orbital method. The reaction process of TiCl_3 proceeds with the substitution of Cl^- to OH^- . Net charge and spin density of the reactant, product, and intermediates were evaluated. It was suggested that the electron emission of TiCl_3 , which is originated by the oxidation of Ti(III) to Ti(IV) , took place when Cl is replaced by OH^- to form Ti(OH)_4 . The catalytic activity of the metal surface, which is one of the most important factors for the electroless deposition process, was studied using a Pd_4 cluster as a model surface. It was suggested that the Pd_4 cluster enhanced the reaction of TiCl_3 to emit the electron. The effect of solvation is also taken into account in terms of the dielectric field constant. It was indicated that the heat of oxidation reaction shifted to an exothermic reaction with decreasing dielectric constant, indicating that the reaction preferentially proceeds in the vicinity of solid/liquid interface. However, it was indicated that the reaction could proceed in the bulk solution, suggesting that appropriate stabilization such as formation of complex is required for the application of the TiCl_3 to the electroless deposition process.

Key Words : Electroless Deposition Process, Molecular Orbital Study, TiCl_3 , Effect of Solvation

1 Introduction

Electroless deposition processes are widely used in the various fields of micro and nano fabrication, featuring its capability to form precise deposits on to wide, non-flat surfaces.¹⁾ In the electroless deposition process, the electron is supplied by the oxidation reaction of the reductant. Since the deposited metal surface should act as the catalyst for this oxidization reaction, combinations of the reductant and the metal species, which could be deposited, are limited.

In our previous studies, the oxidation mechanisms of various reductants were studied at the elementary reaction level using ab initio molecular orbital (MO) method.^{2–4)} The major advantage of this approach is its ability for quantitative evaluation of the energy and electronic structure of the reaction intermediates, which cannot be detected by the conventional analysis methods. Through this approach, we have investigated the reaction mechanism of representative reductants such as dimethylamine borane (DMAB)²⁾ and hypophosphite ion³⁾ in

detail. We also carried out preliminary study for the TiCl_3 reductant,¹⁾ which is known to be applied for “non-traditional” species for the electroless deposition such as $\text{In}^{5)}$ and $\text{Sb}^{6)}$. Based upon this result, in this study, we investigated the reaction mechanism of TiCl_3 reductant in detail.

2 Computational Method

In the preliminary study, we have proposed the electron emission reaction of TiCl_3 as Scheme 1.⁴⁾

The OH^- in the solution coordinates to TiCl_3 and the substitution reaction of Cl^- by OH^- proceeds to form Ti(OH)_4 . It should be noted that the electron emission of TiCl_3 takes place by the oxidation of Ti(III) to Ti(IV) ,⁴⁾ while that of hypophosphite ion and DMAB, which are typical reductants for the electroless deposition, proceeds by the substitution of H by OH^- .

Based upon this reaction pathway, we compare in terms of geometry, net charge, and spin density of intermediates to analyze the mechanism of electron emission.

Scheme 1 Reaction pathway of TiCl_3 via five-coordinate intermediates (2, 4, and 6).

The geometry of each intermediate was optimized at the Hartree-Fock (HF) level. The electron correlation was taken into account for the single-point energy calculations by the Møller-Plesset 2nd perturbation (MP 2) method.

In order to investigate the catalytic activity of the metal surface for the oxidation reaction of the reductant, Pd (111) surface, expressed by a Pd₃ cluster, was used as a model surface. Following the results of our previous study on the electron transfer property and energy depend on the size of cluster for the reductant such as hypophosphite ion,³⁾ the adsorbate was put at the hollow site of the Pd₃ cluster. The solvation effect was taken into account by the self-consistent reaction field method with an isodensity surface polarized continuum model (SCR-IPCM),⁷⁾ which utilized the dielectric constant value. In the IPCM calculations, the dielectric constant is changed from 1.0 (in non-polar solvent) to 78.3 (in pure water⁸⁾).

The calculations were performed using the Gaussian 98 rev a.9.⁹⁾ The Gaussian basis sets used in the present calculations were Huzinaga's all-electron (14s10p5d)/[5s4p2d] type¹⁰⁾ for titanium, the AUG-cc-pVDZ¹¹⁾ for oxygen and chlorine, and the cc-pVDZ¹²⁾ for hydrogen. For palladium, Kr core was replaced by an effective core potential by Hay and Wadt¹³⁾ and a valence electron was represented by a (5s5p4d)/[3s3p2d] basis set.

3 Results and Discussion

3.1 Isolated state

Table 1 shows the HF level bond lengths of the reaction intermediates. The calculated value for the bond length of Ti-OH in Ti(OH)₄ is 1.829 Å, which agrees well to the experimental value of 1.80 Å,¹¹⁾ indicating the validity of the calculated model. The table indicates that the bond length of Ti(III) are slightly longer than those of Ti(IV). As for the Ti-Cl bond, their lengths estimated by sum of the covalent radius and ionic bond radius are 2.31 Å and 2.61 Å, respectively.^{15, 16)} The calculated bond lengths for the intermediate species of Ti(III) are longer than that of the covalent bond, suggesting that the Ti-Cl bond possesses the ionic bond like characters. On the

other hand, the bond lengths estimated by sum of the covalent radius and ionic bond radius for Ti-OH⁻ are 1.98 Å and 2.20 Å, respectively,^{15, 16)} and the calculated bond lengths for the intermediate species of Ti(III) and Ti(IV) are shorter than that estimated from the covalent bond radius. It is generally known that the covalent bond with the effect of ionic bond resonance possesses shorter length than the simple covalent bond.¹⁷⁾ Thus, it is expected that the Ti-OH⁻ bond is stabilized by this effect.

In our preliminary study, it was indicated that the reaction of TiCl₃ spontaneously proceeds and that the electron emission took place at the step (7) reaction.⁴⁾ In order to examine this point in more detail, we compare net charges and spin densities of the intermediates. The net charge and the distributions of spin densities of the intermediates before and after the electron emission are shown in Table 2, which were calculated at the MP 2 level. It is indicated that the charge of Cl and OH changes to positive when TiCl₃(OH) turns from trivalent to tetravalent, whereas no significant changes are observed for the charge of Ti. Similar tendency is observed for the trivalent and tetravalent Ti(OH)₄ species at which the electron transfer takes place. This indicates that the charge is mainly transferred from the ligand (Cl, OH) parts. However, the spin density of these intermediates suggested that Ti becomes unstable since there are whole spin densities. These results indicate that this reaction system is strongly influenced by the ligands. It is also suggested that change in bond strength between Ti-Cl and Ti-OH⁻, *i.e.*, the covalent bond character of Ti-OH initiates the electron emission.

3.2 On the Pd cluster

In the previous section, the reaction of TiCl₃ in its 'iso-

Table 2 Net charge and local spin density of TiX₄ (X = Cl and/or OH). Ti(III) and Ti(IV) express TiX₄⁻ and TiX₄, respectively.

		(1)	(3)	(5)	(7)
		TiCl ₃ (OH)	TiCl ₂ (OH) ₂	TiCl(OH) ₃	Ti(OH) ₄
		X ₁₋₃ : Cl	X ₁₋₂ : Cl	X ₁ : Cl	
		X ₄ : OH	X ₃₋₄ : OH	X ₂₋₄ : OH	X ₁₋₄ : OH
net charge	Ti	+1.731	+2.001	+2.024	+2.154
	X ₁	-0.685	-0.751	-0.756	-0.788
	Ti(III)	X ₂	-0.685	-0.751	-0.754
		X ₃	-0.678	-0.750	-0.754
		X ₄	-0.682	-0.750	-0.760
		Ti	+1.907	+2.029	+2.125
	Ti(IV)	X ₁	-0.472	-0.505	-0.537
		X ₂	-0.472	-0.505	-0.530
		X ₃	-0.472	-0.510	-0.530
		X ₄	-0.490	-0.510	-0.530
	spin density	Ti	+1.008	+0.958	+1.015
		X ₁	0.000	+0.016	-0.005
		Ti(III)	X ₂	0.000	+0.016
			X ₃	-0.003	+0.005
			X ₄	-0.006	+0.005

Table 1 Bond lengths of TiX₄ (X = Cl and/or OH). Ti(III) and Ti(IV) express TiX₄⁻ and TiX₄, respectively.

		(1)	(3)	(5)	(7)
		TiCl ₃ (OH)	TiCl ₂ (OH) ₂	TiCl(OH) ₃	Ti(OH) ₄
		X ₁₋₃ : Cl	X ₁₋₂ : Cl	X ₁ : Cl	
		X ₄ : OH	X ₃₋₄ : OH	X ₂₋₄ : OH	X ₁₋₄ : OH
		/Å	/Å	/Å	/Å
Ti(III)	Ti-X ₁	2.395	2.439	2.460	1.951
	Ti-X ₂	2.395	2.439	1.936	1.951
	Ti-X ₃	2.372	1.880	1.936	1.951
	Ti-X ₄	1.848	1.880	1.936	1.951
Ti(IV)	Ti-X ₁	2.205	2.232	2.254	1.829
	Ti-X ₂	2.205	2.232	1.781	1.829
	Ti-X ₃	2.205	1.761	1.781	1.829
	Ti-X ₄	1.723	1.761	1.781	1.829

Table 3 Change in net charge and spin density of the reaction pathway via five-coordinate intermediates (2, 4, and 6).

		(1)	(2)	(3)	(4)	(5)	(6)	(7)
		$\text{TiCl}_3(\text{OH})^-$	$\text{TiCl}_3(\text{OH})_2^{2-}$	$\text{TiCl}_2(\text{OH})_2^-$	$\text{TiCl}_2(\text{OH})_3^{2-}$	$\text{TiCl}(\text{OH})_3^-$	$\text{TiCl}(\text{OH})_4^{2-}$	$\text{Ti}(\text{OH})_4^-$
reductant	net charge	-0.668	-1.050	-0.841	-1.087	-0.231	-1.720	-0.089
	spin density	+0.999	+0.033	+1.000	+0.055	+0.190	+1.001	+0.017
Pd cluster	net charge	-0.332	-0.950	-0.159	-0.913	-0.769	-0.280	-0.911
	spin density	+0.001	+0.967	0.000	+0.945	+0.810	-0.001	+0.983

Fig. 1 Solvation effects on the substitution reaction of TiCl_3 .

lated' state was evaluated as fundamental examination. Based upon these results, in this section, the reaction of TiCl_3 on the Pd surface is investigated to evaluate the effect of its catalytic activity, which plays a key role for the overall reactions.

In our previous study,⁴⁾ it was indicated that all of the intermediate species were stabilized at the surface of Pd cluster. In order to investigate this in detail, the mechanism is examined in terms of net charge and spin density.

Table 3 shows the change in net charge and spin density of intermediates via five-coordinate intermediates pathway. First, in the case of the four-coordinate intermediates, (1) and (3), charge and spin remain at the reductant part, whereas they begin to shift to the Pd metal cluster part in the case of (5), and are finally transferred to the metal cluster part for the intermediates (7). This result indicates that the electron emission takes place to form $\text{Ti}(\text{OH})_4^-$. On the other hand, charge and spin are transferred to the metal cluster part for the five-coordinate intermediates (2) and (4). Such an electron transfer from dianion state intermediates to the metal part leads further stabilization compared with the case of the four-coordinate intermediates. However, charge and spin remain at the reductant part in the case of (6), since they are transferred to the Pd cluster part on (5). Thus, it is expected that the reductant is much reactive and driving the next reaction step, *i.e.* the electron emission. Divalent changes in charge at the reductant part which

are accompanied by the reaction from (6) to (7), are due to emission of Cl^- anion plus electron transfer to the metal cluster part. Change in charge is +0.631 at the Pd cluster part. Thus, the oxidation of Ti from trivalent to tetravalent state took place to accept electron to the Pd cluster from reductant species, whereas it occurred to form $\text{Ti}(\text{OH})_4$ on isolated state. These results indicate that the Pd surface enhances the reaction of TiCl_3 and electron emission.

3. 3 Solvation effects

Next, we examine the solvation effect using the SCRF-IPCM method, focusing upon the reaction heat (Q) defined by

which is calculated to be +436.1 kJ/mol in isolated state. The value of Q decreases exponentially as the dielectric constant (ϵ) becomes higher; namely, from +465.6 kJ/mol at $\epsilon = 1.0$ to 269.1 kJ/mol at $\epsilon = 78.3$.

Fig. 1 shows the change of Q by taking the solvation effect into account. In this figure, we show two levels corresponding to the dielectric constants of the inner and outer Helmholtz layers, which are estimated by the Bockris-Devanathan-Muller model¹⁸⁾ to be 6.0 and 32.0, respectively.

In Fig. 1, the results for hypophosphite ion³⁾ and DMAB¹⁹⁾ are also plotted. The results for these reduc-

tants show that only the reaction in the inner layer is exothermic. Therefore, their oxidation reaction is expected to proceed preferentially at the solid/liquid interface. Such a tendency is also expected from the calculated value of the heat of electron emission reaction for TiCl_3 (+559.3 kJ/mol), indicating the exothermic state. On the other hand, the heat of TiCl_3 is still exothermic where the dielectric constant is near the pure water, indicating that TiCl_3 is reactive even in pure water. This corresponds to the case with practical bath system in which TiCl_3 must be stabilized using complex compound such as EDTA.⁵⁻⁶⁾

4 Summary

In the present work, we have investigated the electron emission mechanism of the TiCl_3 reductant for the electroless deposition by ab initio MO method.

The reaction of TiCl_3 proceeds with substitution reactions of Cl^- by OH^- . As the reaction proceeds, the energy of the intermediates was stabilized due to the difference in the stability between Ti-Cl and Ti-OH⁻ bonds and it is expected that the electron emission of TiCl_3 took place at the reaction of $\text{TiCl}(\text{OH})_3$ and OH^- to produce $\text{Ti}(\text{OH})_4$, by changing the valence of Ti from trivalent to tetravalent, while that of hypophosphite ion and DMAB, which are typical reductants, proceeds by the substitution of H by OH^- . Furthermore, it was also expected that all of the intermediate species were stabilized on the surface of the metal such as Pd, which enhances the electron emission reaction of TiCl_3 by accepting the emitted electron from the reductant species. From the analysis on the effect of solvation, it was indicated that the reaction was influenced significantly, and could proceed even in pure water corresponding to the case with practical system.

As a result, by means of the MO method, the electron emission mechanism of TiCl_3 was clarified in addition to typical reductant, and the practical characteristics, that is, metal surface enhances the reaction and TiCl_3 is a reactive reductant was demonstrated and elucidated. In future, it is expected that this method could analyze for reaction mechanism of various reductants and, moreover, achieve total modeling of the electroless deposition process including metal deposition and catalytic activity in combination with experimental approaches.

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