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Structure and Lewis acid sites in alumoxane compounds

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Abstract

With a view to clarifying the characteristics in alumoxanes as an effective Lewis acid cocatalyst in homogeneous olefin polymerization, ab initio quantum chemical calculations were carried out for model fragment structures of the compound. The relative strength of Lewis acidity was compared for different aluminum sites and the energetics in the ligand exchange process with group IV metallocene complex were discussed.

1. Introduction

Recently the chemistry of alumoxane compounds, of generic formula $(RAlO)_n$, has been the center of a great deal of interest in relation to homogeneous olefin polymerization catalysis. Initiated by Shinn et al., [1] alumoxane compounds, especially methylalumoxane (MAO), have been utilized as the most effective cocatalyst with group IV metallocene catalysts in the olefin polymerization process. Through studies by XPS, NMR spectroscopy, and other characterization methods, [2] it is now understood that the alumoxane compounds work as a Lewis acid to extract anionic ligands, such as chloride (Cl^-) or methyl (CH_3^-) anion from metallocene, e.g., Cp_2ZrCl_2 or $Cp_2Zr(CH_3)_2$, and stabilize the resulting cationic species by forming an ion pair to it:

$$Cp_2ZrL_2 + MAO \rightarrow [Cp_2ZrL]^+ [MAO - L]^-,$$

$$L = Cl, CH_3 \qquad (1)$$

However, the structure of active MAO species and the Lewis acidic site in there still remain ambiguous. [3] It is generally observed that aluminum tends to be four- to six-coordinated and the hydrolysis of aluminum alkyls results in oligomers in which most of the aluminum centers are four-coordinated.

In this work, we carried out ab initio quantum chemical calculations in order to characterize the local nature of alumoxane compounds. We studied the magnitude of Lewis acidity in various multi-center aluminum sites. We also present the energetics in a ligand abstraction step from the metallocene complex by these sites. Then the coordinating nature of the resulting alumoxane anion against the cationic metallocene species is discussed based on the obtained energetics.

2. Results and discussion

2.1. Fragment structures of alumoxane compounds

Molecular mechanics and semi-empirical QC approaches were used to study the possible oligomer structures of alumoxane compounds. Pre-

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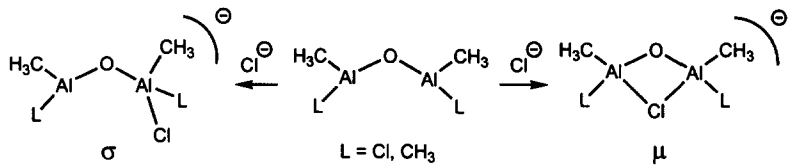


(2)

liminary results suggested that aluminum centers tend to have the coordination number of four, but it is not always the case for all of the aluminum centers involved in the molecule of stoichiometry $(AlRO)_n$. In order to avoid the arbitrariness in the structure, only two- and three-center aluminum sites are considered as candidates with $R = CH_3$ in the following study.

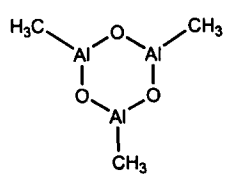
2.2. *Lewis acidity of aluminum sites*

We applied density functional theory (DFT) calculations to selected fragment structures of alumoxane and studied the strength of the Lewis acidity of these sites. The strength of Lewis acidity was evaluated by the binding energies of chloride ion (Cl^-) to the site.

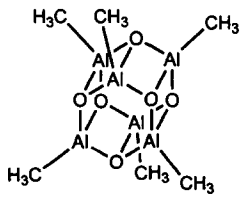
We selected model sites consisting of two aluminum centers, in which chloride is bound either by forming a σ bond with an aluminum atom (σ) or by forming a bridged bond with two aluminum atoms (μ), (see Eq. (2)).

Bond distances between aluminum and chlorine atoms were determined in the range of 2.236–2.253 Å (σ) and 2.408–2.429 Å (μ) by DFT calculations.

We also considered six-membered ring structures consisting of three aluminum centers as Cl^- binding sites. At these sites, chloride is bound to above the centroid position of the aluminum centers. The DFT calculations determined the distances to 2.071 Å (MAO_3) and 1.956 Å (MAO_6).



MAO_3



MAO_6

Table 1 gives the relative strength of the two- and three-center aluminum sites toward Cl^- binding. It also includes the trimethylaluminum case for reference. We found that the oxo-bridged two-center aluminum sites, in which each aluminum is three-coordinated, are generally favorable for Cl^- binding through the bridged bond formation (μ in Table 1) against Cl^-. This is in contrast with one-center Cl^- binding (σ in Table 1), in which the binding energies are ca. 7–8 kcal/mol smaller than the bridged bonding. In the MAO_3 case, each aluminum site also has the coordination number of three and Cl^- is bound to above the centroid position of the MAO_3 ring. Consequently the coordination at each aluminum is very different from the tetrahedral bonding and thus the binding energy is smaller than the μ bonding case even though three aluminum centers are involved in the bonding. In Table 1, MAO_6 shows slightly stronger binding energies than MAO_3 due to the additivity of the Lewis acidic aluminum atoms. In actual alumoxane compounds, the possibility that

Table 1
Binding energies of chloride ion at various aluminum sites[a]

Aluminum site	Binding energy (kcal/mol)	
	σ[b]	μ[c]
$(CH3)_2Al–O–Al(CH_3)_2$	49.0	56.8
$(CH_3)(OH)Al–O–Al(CH_3)(OH)$	52.6	60.0
MAO_3	49.8	
MAO_6	52.4	
$Al(CH_3)_3$	47.7[d]	

[a]Binding energies were computed by the DFT method for optimized molecular geometries.
[b]Cl^- is bound to an aluminum atom.
[c]Cl^- is bound to two aluminum centers.
[d]Trimethylaluminum exists as a dimer. The binding energy reduces to 42.6 kcal/mol including half of the dissociation energy (5.12 kcal/mol) of the dimer.

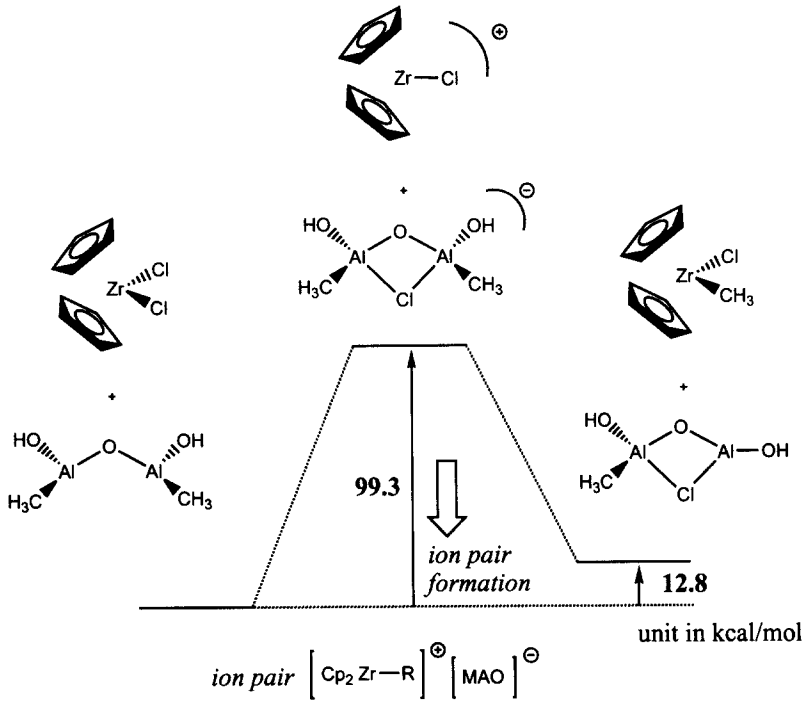
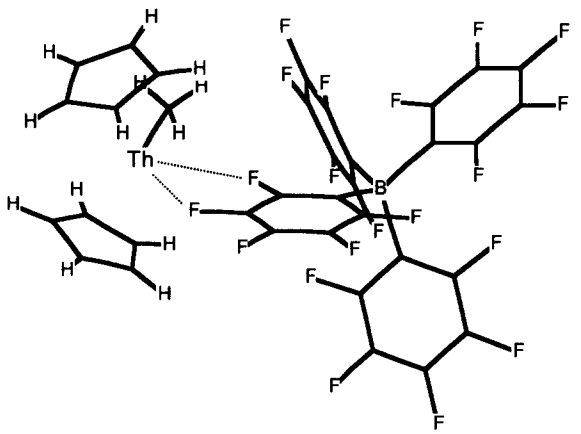


Fig. 1. Energy profile in the ligand exchange process of zirconocene and MAO model compound. The energy of each state is given by the sum of the total energies of each molecule at the state. Energies were computed by the DFT method for optimized molecular geometries.



$Cp_2Th(CH_3)^+ + B(C_6F_5)_4^- \longrightarrow Cp_2Th(CH_3)^+ B(C_6F_5)_4^-$

ΔE (coulomb) = -63.6 kcal/mol

Fig. 2. A model structure, $Cp_2Th(CH_3)^+ B(C_6F_5)_4^-$, used to evaluate the ion pair formation energy. The structure was taken from a crystal structure (ref. [5]) and Th ligands were simplified from Cp* to Cp in order to reduce the computational size. The distances between Th and the two nearest fluorine atoms are 2.675 and 2.756 (Å), respectively. See text for details of the energy evaluation.

Table 2
Partial atomic charges in $Cp_2ThCH_3^+$ and $B(C_6F_5)_4^-$. Atomic charges were computed by fitting the HF electrostatic potential of the molecule with two body Coulomb potential terms. Here the average atomic charges in the same group of atoms are given for clarity. In the electrostatic energy evaluation, the actual charge value for each atom was used

	Partial charge[a]
$Cp_2ThCH_3^+$	
Th	1.74
C (Cp)	−0.13 (0.08)
C (methyl)	−0.72
H (Cp)	0.09 (0.04)
H (methyl)	0.11 (0.03)
$B(C_6F_5)_4^-$	
B	1.87
F	−0.25 (0.01)
C_1	−0.79 (0.04)
C_2	0.35 (0.05)
C_3	0.24 (0.02)
C_4	0.17 (0.02)

[a]Average partial charge value in the same group of atoms. Standard deviations are given in parentheses.

these aluminum sites are formed might be rare, but, once formed, they will work to extract Cl^- and CH_3^- ligands from the metallocene catalyst according to their relative strengths of Lewis acidity.

2.3. *Energy profile in the ligand exchange process*

The role of MAO is supposed to generate the active cationic species of catalyst for olefin polymerization and stabilize the system by ion pair formation (Eq. (1)). Then the study in terms of the total energy change in the formation of the ion pair will provide a clue about the characteristics of MAO anion and other effective anion species. [4] To this end, we studied the ligand abstraction and ligand exchange processes by DFT calculations and obtained the energy profile shown in Fig. 1. The profile shows that the process is 99.3 kcal/mol uphill without formation of an ion pair, while the net energy change is 12.8 kcal/mol uphill at the final state. An estimation of the ion pair formation energy is very difficult as we do not know anything about the structure of the active anionic species in MAO. Still our results suggest that the MAO anionic species should have a coordinating energy of approximately 100 kcal/mol to the cationic zirconocene complex in order to satisfy thermoneutrality at the ligand abstraction step.

Our preliminary results on the ion pair formation energy are given in Fig. 2. Here we evaluated the energy based on an X-ray crystallographic structure of group IV metallocene and a coordination anion, $ThCp_2CH_3^+$ and $B(C_6F_5)_4^-$, respectively. [5] We carried out ab initio HF level calculations on both species and obtained atomic charge distributions in Table 2. Then the electrostatic interaction energy was evaluated when these ionic species were combined to give the structure in Fig. 2. Although this is a crude estimate of the coordinating energy of the counterion to cationic catalyst species, we note that the energy is far less than the coordinating energy of Cl^- and CH_3^- anions which are strongly bound to the metal center. Calculations in Fig. 1 gave the binding energy of Cl^- and CH_3^- to the Zr center to be 159.4 and 207.2 (kcal/mol), respectively. (Note that such a large binding energy corresponds to the heteric scission energy of a ligand.) The binding energy of Cl^- to Th in the model shown in Fig. 2 was estimated to be 162 kcal/mol by electrostatic energy evaluation.

With a coordinating energy of 63.6 kcal/mol, the energy profile in Fig. 1 is still uphill, about 40 kcal/mol toward the ion pair formation. Such a difference may be explained by the stronger coordinating ability of MAO to the cation complex as the negative charge is more localized in oxygen and abstracted metallocene ligands in MAO that will be predominantly bound to the metal center. In order to fully understand the coordinating nature of MAO to the cationic metallocene species, we are at present studying possible MAO oligomers in the catalytic system by theoretical approaches.

3. Details of calculations

The DFT calculations were carried out by using DGauss ab initio DFT codes. [6] Valence double zeta (VDZ) plus polarization quality basis set (DZVP/A1) were used and non-local corrections are included by the Becke–Perdew formalism in the calculations. Electrostatic potentials are computed by restricted Hartree–Fock (RHF) level of theory with VDZ basis set (D95V) and the effective core potential for thorium. [7] The calculations were carried out by using the Gaussian-92 program. [8] For atomic charge fitting, default VDW radii in the program are used except $R = 1.5$ Å for Th.

4. Conclusion

We studied two- and three-center aluminum sites as candidate Lewis acidic sites in alumoxane compounds. Of these, oxo-bridged dialuminum centers exhibit strong Lewis acidity toward the

chloride ion binding. When the binding energy is compared with the ligand abstraction energy from the zirconocene complex, the system destabilizes approximately 100 kcal/mol. This amount of energy should be compensated for by cation–anion pair formation and thus corresponds to the coordinating ability of anionic species in effective alumoxane compounds.

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