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Substituent effect of Cp₂TiCl₂ catalyst for ethylene polymerization: A DFT study

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ABSTRACT

The substituents on cyclopentadienyl (Cp) can regulate the electronic effect and hindrance of the active center in the metallocene catalyst. This modification can greatly change the catalytic activity of the catalyst and affect some features of the polymer. In order to study the effect of alkyl substituents on Cp in the performance of a typical metallocene catalyst Cp_2TiCl_2 for ethylene polymerization, two types of catalyst active centers were designed, including non-bridge $[Cp_2(R)TiCH_3]^+$ and bridge $[NCP_2(R)TiCH_3]^+$ (R = H, Me, iPr). The effects of alkyl substituent steric hindrance were explored by density functional theory on the complex of catalyst active center with ethylene and the formation of transition state. The results showed that the increase of substituent steric hindrance was unfavorable to complex between ethylene monomer with catalyst active center. Moreover, the bigger alkyl substituent, the greater the activation energy of ethylene insertion into catalyst active center and the more difficult is ethylene polymerization. Therefore, the performance of metallocene catalysts could be regulated by the substituent on Cp. **Polyolefins J (2023) 10: 35-43**

Keywords: Titanocene; ethylene polymerization; mechanism; hindrance effect; density functional theory.

INTRODUCTION

Since the discovery of Ziegler-Natta catalyst in 1953, researchers pay attention to develop the high-performance catalysts for olefin polymerization. In 1959, Breslow and Natta[1] respectively studied the homogeneous polymerization of ethylene with metallocene as catalyst, which is composed of Cp_2TiCl_2 and Et_2AlCl . The active center Ti^{4+} in Cp_2TiCl_2 is easily over reduced

by Et_2AlCl and loses polymerization activity, so the catalyst polymerization activity of Cp_2TiCl_2/Et_2AlCl system is low. Sinn[2] and Kaminsky[3] accidentally found that adding a small amount of water to $Cp_2ZrMe_2/AlMe_3/ethylene$ system can make the original inactive system have high polymerization activity in 1980s[4]. This important discovery made a breakthrough in



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the development and application of metallocene catalysts. Kaminsky observed that AlMe, was partially hydrolyzed to methylaluminoxane (MAO) [5]. MAO can activate Cp₂ZrMe₂ and greatly improve the ethylene polymerization activity [6]. Metallocene catalyst has extremely high activity, narrow molecular weight distribution and adjustable structure of polyolefin compared to traditional Ziegler-Natta heterogeneous catalyst system [7-10]. The polymer has narrow molecular weight distribution and uniform composition distribution, and three-dimensional controlled polymerization could be effectively carried out by the metallocene catalysts [11,12]. The molecular structure of the catalyst is controlled by ligand modification, which regulates the performance of the catalyst [13,14]. The substituents on Cp can regulate the electronic effect and hindrance of the active center of the catalyst. Metallocene complexes with different structures can be designed and synthesized through the regulation of substituents[15-17]. This modification can greatly change the catalytic activity of the catalyst and affect some features of the polymer, such as molecular weight [18,19] and comonomer content [20,21]. Metallocene catalysts with some symmetry factors can also realize the stereoselective control of olefin polymerization [22,23], such as isotactic polypropylene [24,25], syndiotactic polypropylene [26] and random polypropylene [27,28]. By controlling the polymerization conditions and modifying the molecular structure of the catalyst [29-31], polyolefins with specific stereoregularity can be prepared, so polyolefin products suitable for various market needs can be easily obtained[32-35]. Cp,TiCl, is a classical metallocene catalyst for olefin polymerization. In this paper, we study the effect of steric hindrance of alkyl substituents on Cp on the performance of a typical metallocene catalyst Cp₂TiCl₂ for ethylene polymerization by density functional theory (DFT). The mechanism of the effect of steric hindrance is revealed, which guided the design of new metallocene catalysts.

CALCULATION DETAILS

The active centers of the catalysts were non-bridge

metallocene $[Cp_2(R)TiCH_2]^+$ (Figure 1a) and bridge metallocene $[NCp_2(R)TiCH_2]^+$ (Figure 1b) (R = H, Me, iPr). All DFT calculations were completed with Dmol3 software. Geometry optimization had been performed via Becke-Lee-Yang-Parr (BLYP) function within the generalized gradient approximation (GGA) [36]. The dispersion function was Tkatchenko-Scheffer (TS) in all calculations considering the van der Waals force. The localized double numerical basis sets with polarization functions (DNP) basis sets were used to expand the Kohn-Sham orbitals. The geometry optimization adopts full geometry optimization without any restriction of molecular symmetry. The convergence criteria of energy, force and displacement were 1×10⁻⁵ Ha, 0.001 Ha/Å, and 0.005 Å. In the process of geometry optimization, all reactants, intermediates and products have real frequencies. The transition state path and transition state structure adopt the complete Linear Synchronous Transit/Quadratic Synchronous Transit (LST/QST) method [37]. Each transition state was confirmed to have only one imaginary frequency, and the vibration direction can correctly connect the reactant and product.

RESULTS AND DISCUSSION

The selection of basis set

Substituent steric hindrance effect of Cp_2TiCl_2 catalyst for ethylene polymerization was studied in Dmol3 using GGA-BLYP. B3LYP/6-31G (d, p) basis set in Gaussian 09 was used in order to verify the accuracy of results. $[Cp_2(Me)TiCH_3]^+$ was used as active center, the model was optimized structure, and reacted with ethylene by Gaussian 09. The corresponding results



Figure 1. Metallocene catalyst (a) and bridge metallocene catalyst (b) active center.

Active center	Cp ₁ -Ti-Cp ₂ (°)	d(Cp ₁ -Ti) (Å)	d(Cp ₂ -Ti) (Å)	d(Ti-CH ₃) (Å)	Q _{Ti} (e)	Complex energy (kJ/ mol)	E _{act} (kJ/mol)
GGA-BLYP	134.584	2.119	2.12	2.18	0.653	-246.3	85.1
B3LYP/6-31G (d, p)	134.533	2.201	2.13	2.19	0.655	-243.2	84.6

Table 1. Structural and reaction parameters of $[Cp_2(Me)TiCH_3]^+$.

are list in Table 1, which show that the result of GGA-BLYP was consistent with that of B3LYP/6-31G (d, p). Hence, GGA-BLYP was adopted to improve the computational efficiency in different substituent models.

Active center structure

The catalysts studied in this chapter are Cp_2TiCl_2 and methylene bridge NCP_2TiCl_2 . The catalyst reacts with MAO to active centers:

$$Cp_{2}TiCl_{2} + (Al-O)_{n} \longrightarrow [Cp_{2}Ti-CH_{3}]^{*} + (Al-O)_{n}^{*}$$



Figure 2. Geometric parameters and Mulliken charge of the optimized structure of catalyst active center.

The structures of the active centers $[Cp_2(R)TiCH_2]^+$ and $[NCp_2(R)TiCH_3]^+$ (R=H, Me, iPr) and the Mulliken charge of the active species Ti⁴⁺ cations are regulated by the substituents on the cyclopentadienyl (Cp) group. The Cp group moves and rotates with different substituents in $[Cp_2(R)TiCH_2]^+$, whereas the bridge structure fixes the Cp group and limits its activity range in the bridge $[NCp_2(R)TiCH_2]^+$ active center. Figure 2 shows the optimized structure of active centers. When the volume of the substituent was increased in the non-bridge $[Cp_2(R)TiCH_2]^+$ active center, the angle Cp₁-Ti-Cp₂, the distance between the metallocene ring and the Ti⁴⁺ cation of the active center, and the Mulliken charge on the Ti⁴⁺ cation of the active center also was increased because of the repulsion between the alkyl substituent on the Cp group and the methyl in the active center. Thus, the complex ability between the Cp group and the active center of the catalyst was weakened. In the bridge $[NCp_2(R)TiCH_2]^+$ active center, the angel Cp₁-Ti-Cp, was smaller than that of non-bridge $[Cp_2(R)TiCH_3]^+$ due to the limitation of methylene bridging. In the [NCp₂(R)TiCH₂]⁺/ethylene complex system, Cp₁-Ti-Cp₂ decreased slightly with increasing of the volume of substituent on Cp group due to the repulsion between alkyl substituent on Cp group and methyl group of catalyst active center. The distance between the Cp and the Ti⁴⁺ cation in the catalyst active center only was lengthen slightly, however the complex ability between the Cp group and the catalyst active center decreases because the Mulliken charge of the Ti⁴⁺ cation in the catalyst active center was increased.

Complexation of ethylene with active center of catalyst

The first step is the catalyst active center complex with ethylene in the polymerization process. The π electron on the C=C bond of ethylene transfers to the d orbital of the catalyst active center Ti⁴⁺ cation to form the ethylene/catalyst active center complexation. The bond length of the C=C bond was elongated, which



was between the C-C single bond and the C=C bond. The structure of the active center and the Mulliken charge was also changed. Figure 3 and Table 2 showed the optimized structure and structural parameters of the catalyst active center with ethylene complexation. The catalyst active center adsorbed ethylene, the bond length between Cp and Ti4+ cation and the bond length of Ti-CH₃ were all elongated because ethylene weakened the bond of Ti⁴⁺-Cp and Ti⁴⁺-CH₃. Mulliken charge of Ti⁴⁺ cation in the complex was decreased, which π electrons on the C=C transferred to the d orbital of Ti⁴⁺ cation. The angel Cp₁-Ti-Cp₂ was decreased from about 140° to about 134° in the non-bridge catalyst system. The angle of Cp1-Ti-Cp, was only decreased from 123° to 121° in the bridge catalyst system because of the fixed structure. The angle Cp₁-Ti-Cp₂ was decreased with complexing ethylene, ethylene could close easily to the catalyst active and formed a stable complex because the steric hindrance was reduced.

The steric hindrance of alkyl substituents on Cp has a great influence on the structure of ethylene/catalyst active center complex. The optimized structural geometric parameters of the complex indicated that the steric hindrance was the smallest, the distance between ethylene and the catalyst active center Ti⁴⁺ cation was the closest and the complex was the closest. The distance between carbon atom on ethylene and Ti⁴⁺ cation was 2.981 Å when there was no substituent on the Cp group in the $[Cp_2(R)TiCH_3]^+$ active center. When substituents on Cp were Me- and iPr-, the Mulliken charge of the catalyst active center increased, which was more conducive to complex with ethylene because of the large steric hindrance of substituents. The distance between carbon atom on ethylene and Ti⁴⁺ cation increased to 3.036 Å and 3.030 Å, and the complex was relatively decentralization. The C=C bond length in ethylene was 1.349 Å when ethylene complexed with [Cp₂TiCH₂]⁺, whereas the C=C bond length in the complex system was 1.348 Å when Cp had substituents. It indicated that the steric hindrance of substituents had an impact on the stability of the complex system. The smaller the steric hindrance, the substituents are the more conducive to ethylene complexation. The structural changes of the complex in the bridging system were also studied. The rotation and movement of the bridging system were limited because methylene connected two Cp groups and fixed its structure. The angel Cp₁-Ti-Cp₂ was small, and the angel between two Cps was large, which was conducive to ethylene approaching the active center Ti⁴⁺ cation. The optimized structural parameters of the active center complex system in the bridge system indicated that the substituent had no significant effect on the volume of the substituent.

In order to study the stability of the complex system, the complex energies were calculated. Table 3 shows the complex energy of non-bridge $[Cp_2(R)TiCH_2]^+$ and bridge $[NCp_2(R)TiCH_3]^+$ with ethylene. The results indicated that the ethylene complex process was an exothermic reaction, and the heat released decreased with increasing the volume of substituents. The steric hindrance effect of substituents was particularly significant in the non-bridge $[Cp_2(R)TiCH_2]^+$ system. The complex energy was -25.06 kJ/mol when there was no substituent on Cp, whereas their complex energies were -24.63 kJ/mol and -18.28 kJ/mol when Cp had methyl and isopropyl groups. The steric hindrance has little effect on its complex energy in the bridge $[NCp_2(R)TiCH_2]^+$ system. When the substituents were H-, CH₃- and iPr- in the bridge $[NCp_2(R)TiCH_3]^+$, the complex energies were -26.64 kJ/mol, -25.341 kJ/ mol and -24.03 kJ/mol, respectively. Compared with the non-bridge structure, the complex energy of bridge active center was larger and the complex was more stable. Farther, the larger the volume of alkyl group

Table 2. Structural parameters of the active center and Mulliken charge of	of Ti in catalyst active	center/ethylene complex.
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Active center	Cp ₁ -Ti-Cp ₂ (°)	d(Cp ₁ -Ti) (Å)	d(Cp ₂ -Ti) (Å)	d(Ti-CH ₃) (Å)	Q _{Ti} (e)
[Cp₂TiCH₃]⁺	134.584	2.119	2.12	2.18	0.653
[Cp₂(Me)TiCH₃]⁺	134.093	2.133	2.125	2.171	0.668
[Cp₂(iPr)TiCH₃]⁺	133.911	2.15	2.127	2.17	0.674
[NCp ₂ TiCH ₃] ⁺	120.913	2.11	2.109	2.159	0.661
[NCp₂(Me)TiCH₃]⁺	121.214	2.118	2.108	2.157	0.671
[NCp₂(iPr)TiCH₃]⁺	121.592	2.136	2.113	2.158	0.672



Figure 3. Optimized structure of catalyst active center and ethylene complex.

on Cp, the smaller the complex energy and the more unstable the complex system.

Formation process of transition state in ethylene polymerization

According to Cossee-Arlman mechanism, ethylene polymerization includes three steps: (1) Ethylene is close to the active center to form a complex; (2) The complex reacts to form a four-ring transition state; (3) Ethylene is inserted into the Ti-CH₃ active center to form the product. The structures during the formation of reaction transition state and energies were studied. Figure 4 and Table 4 show the optimized structure and the geometric parameters of the transition state. The elongation of C=C bond in ethylene was close to the C-C bond in the formation process of transition state,

 Table 3. Complex energy between catalyst active center and ethylene (kJ/mol).

R	Н	CH3	iPr
[Cp₂(R)TiCH₃]⁺	- 25.06	- 24.63	-18.28
[NCp₂(R)TiCH₃]⁺	- 26.64	- 25.31	- 24.03

ethylene was further close to the active center of the catalyst, the distance from the active center Ti⁴⁺ cation was close to the chemical bond length, the bonding between the active center Ti⁴⁺ cation and ethylene was enhanced, and the bonding between Cp and methyl was weakened, then the catalyst active center formed a four rings transition state with ethylene. The Mulliken charge of Ti⁴⁺ cations decreased due to the flow of π electrons on ethylene to the d orbital of Ti4+ cation in the active center. The angel Cp₁-Ti-Cp₂ decreased from about 134° of the active center to about 130 ° in the transition state. In the bridge structure, the angle Cp₁-Ti-Cp₂ changed significantly because of the fixed structure, and the R- in the transition state of [NCp₂(R)TiCH₃]⁺ system was H-, CH₃- and iPr-, and the angle Cp₁-Ti-Cp₂ was 96.4°, 115.7° and 91.9°, respectively. The results indicated that the angle Cp₁-Ti-Cp₂ decreased during the formation of transition state, which was conducive to reducing the steric hindrance, making ethylene as close to the active center as possible and forming chemical bonds. In this $[NCp_{2} (CH_{3}) TiCH_{3}]^{+}$ active center, the angle Cp₁-Ti-Cp, was the smallest because the Ti-CH₃ bond was extended to 4.123 Å during the insertion of ethylene into the catalyst active center. The Ti-CH₃ bond was almost completely broken, and ethylene was directly inserted into the Ti-CH₂ bond.

The steric hindrance of alkyl substituent on Cp group had a great influence on the structure of transition state. The steric effect of substituents was particularly significant in the non-bridge $[Cp_2(R)TiCH_3]^+$ catalytic system. The optimized structure of the transition state showed that the alkyl substituent on the Cp could hinder the insertion of ethylene during the insertion of ethylene into the Ti-CH₂ bond of the catalyst active center, and the structure of the catalyst active center was changed in order to reduce the hindrance. The changes of catalyst active center structure included the decreased angel Cp1-Ti-Cp2, and the increased the distance of Ti⁴⁺-Cp and Ti⁴⁺-CH₃. The structure of transition state was slightly different with substituent because methylene bridging fixes the structure of the catalyst active center in the bridge $[NCp_2(R)TiCH_2]^+$ catalytic system. The distance between the ethylene and the catalyst active center was longer than that of the non-bridge catalyst active center in its transition



Active center	Cp ₁ -Ti-Cp ₂ (°)	d(Cp ₁ -Ti) (Å)	d(Cp ₂ -Ti) (Å)	d(Ti-CH ₃) (Å)	QTi(e)
[Cp₂TiCH₃]⁺	130.104	2.322	2.337	3.952	0.605
[Cp₂(Me)TiCH₃]⁺	129.037	2.262	2.287	3.723	0.605
[Cp₂(iPr)TiCH₃]⁺	130.04	2.687	2.37	3.985	0.651
[NCp₂TiCH₃] ⁺	96.409	2.616	2.723	2.858	0.69
[NCp₂(Me)TiCH₃]⁺	115.669	2.34	2.215	4.123	0.491
[NCp_(iPr)TiCH_] ⁺	91.857	2.448	2.392	3.627	0.517

Table 4. Structural parameters of catalyst active center and Mulliken charge of Ti in transition state of ethylene polymerization.

state with ethylene because the bridging restricts the free rotation and movement of Cp. The proximity of ethylene to the active center of the catalyst was hindered. Here, the steric hindrance effect of Cp substituents was relatively significant. When the substituents R- were H- and iPr-, respectively, their Cp₁-Ti-Cp₂ were basically the same, and the distance between ethylene and the active center increased with increasing the steric hindrance. However, when



R- is Me-, the steric hindrance between ethylene and the active center was weakened due to the elongate bond of Ti-CH_3 . Therefore, Cp_1 -Ti-Cp₂ was changed a little, and the distance between ethylene and the active center of the catalyst was the smallest.

Moreover, the reaction heats and activation energies of ethylene insertion into the active center of the catalyst were calculated, which are listed in Table 5. The results indicated that the spatial effect of substituents had a great influence on the catalyst ethylene polymerization process. The activation energy of ethylene polymerization process increased with increasing substituent volume, which indicated that the substituent volume was not conducive to the insertion of ethylene into the active center of the catalyst. The steric effect of substituents was more obvious in the non-bridge $[Cp_2(R)TiCH_2]^+$ catalytic system. The reaction exothermic decreased significantly and the activation energy increased significantly with the increasing substituent volume. The reaction heat increased slightly with increasing the steric hindrance of the substituent in the bridge $[NCp_2(R)TiCH_2]^+$ catalytic system. However, the activation energy increased obviously, which indicated that the steric hindrance of the substituent was unfavorable for ethylene to insert into the Ti-CH₂ bond of the active center. The obtained results are consistent with titanium tris(amino)phosphinimide complexes reported in literature[38].

Table 5. Reaction heat and activation energy in transition state of ethylene polymerization.

Active center	ΔE(kJ/mol)	E _{act} (kJ/mol)	
[Cp₂TiCH₃]⁺	- 61.8	71.2	
[Cp₂(Me)TiCH₃]⁺	- 35.3	85.1	
[Cp₂(iPr)TiCH₃]⁺	- 26.1	98.3	
[NCp₂TiCH₃]⁺	- 32.0	78.2	
[NCp₂(Me)TiCH₃]⁺	- 32.2	81.5	
[NCp ₂ (iPr)TiCH ₃] ⁺	- 35.8	94.8	

CONCLUSION

The effect of steric hindrance of alkyl substituents on Cp during ethylene polymerization by typical metallocene catalyst Cp₂TiCl₂ was studied by DFT. Two types of catalyst active centers with non-bridge $[Cp_2(R)TiCH_2]^+$ and bridge $[NCp_2(R)TiCH_2]^+$ (R = H, Me, iPr) structures were used. The mechanisms of ethylene polymerization were studied in catalyst active center with different alkyl substituents. The results indicated that the substituent steric hindrance was unfavorable to complex ethylene with catalyst active center and ethylene polymerization. The bigger alkyl substituent, the greater the activation energy of ethylene insertion into catalyst active center and the more difficult is ethylene polymerization. Therefore, properties of metallocene catalysts could be regulated by the substituent on Cp.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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