Tight-Binding Quantum Chemical Molecular Dynamics Study of the Propylene Polymerization by Ziegler-Natta catalyst

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In this work we investigated the polymerization process of propylene on a realistic heterogeneous Ziegler-Natta catalyst by our tight-binding quantum chemical molecular dynamics method. The catalyst of Ti (IV) active site supported on $MgCl_2$(110) surface is adopted in this work. The results from our calculations showed that the π-complex was formed on the 4-fold catalytic center in a barrierless way at the initial state of the insertions reaction. A transition state with high energy between the π -complex and the final product has been found by our simulation. The detailed description of the geometrical structure for this transition state has been given. The structure and energy have been obtained in the initiation and propagation steps, which are consistent with the previous experimental findings. Furthermore the simulation of complete process of the catalysis supplied detailed information of the reaction pathway. It is obviously that our tight-binding quantum chemical molecular dynamics method program can provide reliable results in the application of tracking reaction process of polymerization reactions. Our new simulator was found to be a good theoretical tool to deal with catalytic reaction, especially for the heterogeneous catalysis on a supported surface, which has large number of atoms and thus are difficult for the other methods.

Key words: Propylene, Ziegler-Natta, Polymerization, Transition state, Accelerated quantum chemical molecular dynamics method.

1. Introduction

The polypropylene is one of important polymeric materials in the world. Actually, the production of polypropylene has been growing and getting up to more than 30×10^6 tons per year. It is predicted that the need of polypropylene will rise continuously in a higher rate in the future. Therefore, finding the methods to produce polypropylene with high quality and lower cost has been important research field and a large of efforts has been done on it. Ziegler-Natta (ZN) catalyst is the most important industrial heterogeneous catalyst in the production of polyolefins, especially polypropylene [1]. The catalytic reactions based on it have gained an overwhelming importance in several industrial applications where the production of polymers with a high degree of enantioselectivity is required [2-5]. Its discovery can be dated back to the early 1950s [6,7]. Since then, several generations of such catalysts have been put in place which exhibit orders of magnitude, higher activity, and efficiency [8]. The third generation of Ziegler-Natta catalysts is a kind of supported catalyst that has been developed since 1975 in order to increase

the amount of active Ti by using inorganic chlorides, such as $MgCl_2$ as supporters [9]. The high activity of these catalysts make the use of low catalyst concentrations to be possible. Thus, the catalyst residues can remain in the polymer. Although the performances of these catalyst are very good, but it is still not enough to completely control the character of polymer chain obtained, such as microtacticity, molecular weight distribution and so on. Therefore, a well understanding on the reaction process and mechanism of the catalytic system will be important to improve the properties of polymer.

Attempts to understand the nature and basic steps of ZN catalyst in the catalytic process, has been done by means of several calculation methods due to the difficulties of experimental studies [10]. However the problem has been met during calculation because of the complexity of the reaction system. A comprehensive study of the properties in the active centers and the role of the supporting surfaces are needed.

In this study, we have investigated the

Ziegler-Natta heterogeneous catalysis system by an ab initio quantum chemistry of density functional theory and tight-binding quantum chemical molecular dynamics method. The complete process of the first propylene inserted to Ti-alkene reaction was performed by our tight-binding QCMD simulation method. The important intermediate geometries during this insertion reaction are described.

2. Computational method

The tight-binding quantum chemical molecular dynamics (QCMD) calculations were carried out using the 'Colors' code developed in our laboratory [11-15]. This program, which is based on the tight-binding theory is over 5,000 times faster than the first principles molecular dynamics approach. The equations, which have to be solved, are shown in the Eqs. (2.1) and (2.2):

$$HC = SC \ \varepsilon \qquad (2.1)$$
$$C^TSC = I \qquad (2.2)$$

Where H is the Hamiltonian matrix, S is the overlap integral matrix, C is the eigenvector, ε is the eigenvalue, and C^T is the transformation matrix of C. The total energy is expressed by Eqs. (2.3).

$$E = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + \sum_{k=1}^{OCC} \mathbb{O}_k + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^{N} \sum_{j>i}^{N} E_{repuls}(r_{ij})$$

(2.3)

Where m_i is the atomic weight, v_i is the atomic velocity, e is the elementary electric charge, R_{ij} is the internuclear distance, and Z_i is the atomic charge. In the equation (2.3), the first term refers to the kinetic energy, the second term is the summation of the eigenvalues for all occupied orbitals, and the third term represents the Coulombic interaction. The fourth term corresponds to the short-range exchange-repulsion energy, which can be calculated by equation (2.4):

$$E_{replus}(R_{ij}) = (b_i + b_j) \exp\left(\frac{a_i + a_j - R_{ij}}{b_i + b_j}\right)$$

(2.4)

The force in the system is calculated using the equation of 2.5.

$$F_i = \sum_{j \neq i}^{N} \sum_{k=1}^{OCC} C_k^T \frac{\partial H}{\partial r_{ij}} C_k + \sum_{j \neq i}^{N} \sum_{k=1}^{OCC} \varepsilon_k C_k^T \frac{\partial S}{\partial r_{ij}} C_k -$$

$$\sum_{j \neq i}^{N} \frac{Z_i Z_j e^2}{r_{ij}^2} + \sum_{j \neq i}^{N} \frac{\partial E_{repuls}(r_{ij})}{\partial r_{ij}}$$

(2.5)

In order to increase the accuracy the parameters for the hamiltonian in the tight-binding approxination were determined by our new parameterization procedure based on the first principles density functional theory (DFT) calculations. Temperature was controlled by means of scaling the atom velocities. The simulations were performed for 5000 steps with a time interval of 0.1 fs. The Verlet algorithm was used for the calculation of atomic motions. The temperature of 343 K was used in this simulation, which is same with the reaction temperature of experiment.

The geometrical structures of reactant in this work are determined by Amsterdam Density Functional (ADF1999) [16] program. In ADF, the calculation was done by the triple-zeta basis sets containing a polarization functional with Perdew-Wang (PW91XC) exchange and correlation potential functional at the generalized gradient approximation (GGA) level [17]. The inner electrons within the core shells (1s for C; 2p for Cl, 2p for Ti) were frozen. The relativistic terms have been calibrated by a combined scalar relativistic zero order regular approximation (ZOPA) [18]. The initial model was built by computer graphics molecular visualization program CERIUS2 [19].

3. Results and Discussion

The most important step of polymerization process is to activate the catalyst. Experimentally, the Ti centers are activated by introducing AlR_3 (R= methyl or ethyl) into the reaction chamber [20]. Then the alkylation of Ti are finished by substituting one of Cl atoms with methyl or ethyl groups. In fact, the polymerization can start only beside the vacant site due to the steric hindrance. The bond of metal-carbon will be formed in this process. Therefore in this work, we set up our initial model by replacing one of the exposed Cl atoms of Ti with a C_2H_5 group as the activated center, which acts as a chain terminator unit. The formal oxidation state of the catalyst was chosen to be Ti(IV), because it is quite clearly identified Ti(IV) as the dominant catalytic species in several experiments although other possibilities are not excluded.

The high reactivity of the Ti 4-fold center has been already discussed. For ethylene, this center was found to be one of the most important reaction centers. We shall show here that it also plays an important role for propylene and has strong stereoselective properties. However, before beginning the discussion of the
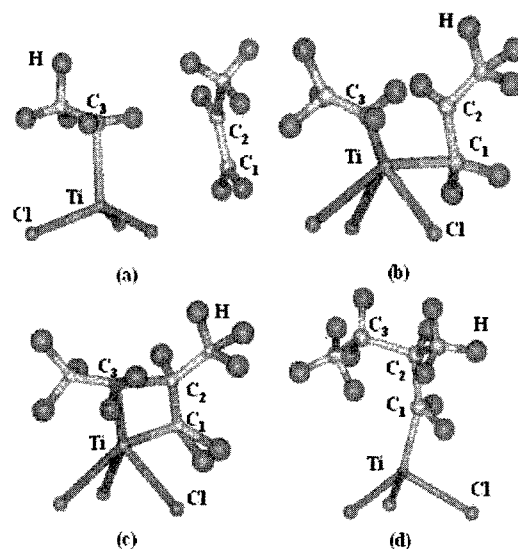

Fig.1. The insertion process of the first propylene molecule on the active site of Ziegler-Natta catalyst. (a) Optimized initial structure; (b) the structure of π-complex; (c) the transition state; (d) the final product.

propylene, it is useful to recall briefly the main findings on ethylene in view of the analogies and differences. In the case of ethylene, the first step in the polymerization process was the complexation of the monomer with the activated 4-fold site, leading to the so-called π -complex. This process was barrierless and led to an energy gain. From the π -complex, the reaction proceeds to a transition state. Hence the transition barriers relative to that of the π -complex can be measured. The olefin addition process followed this path, making the first insertion somewhat atypical and underscoring the need to simulate the process in all its complexity. Actually, the mechanism of olefin polymerization is repeating this kind of insertion reactions again and again.

We now proceed to study the first propylene insertion on the 4-fold activated site, where one of the Cl atoms has been replaced by the chain terminator (in this case, a C_2H_5 group) (Figure 1a). The major changes relative to the case of ethylene come from the extra steric interaction due to a large volume of C_2H_5, which hinders the approach of the propylene molecule to the catalytic center, that is, Ti(IV) atom.

The optimized structures of the reaction system are obtained by ADF and 'Colors' program (Figure 1a). The dynamical simulation starts from this initial structure to form the alkyl chain, by introducing propylene molecule in the vicinity of the active center as shown in Figure 1a. As soon as the propylene molecule is introduced in the vicinity of the active site a π -complex forms in a barrierless way. However it has been found that there is a non-negligible energy barrier between this π -complex and the product, represented by the polymer chain (Figure 1d). Therefore reaction does not occur spontaneously. Thus we employ a tight-binding quantum chemical molecular dynamics simulation in order to find the structure of this transition state. The dynamical simulation begins from a stable π -complex shown in Figure 1b. By our results of simulation the transition state of this insertion reaction are found to be a four-membered ring structure shown in Figure 1c. It is observed that this geometry is a large tilted geometry of the chain terminator ethyl group. This tilted structure reduces the steric hindrance, thus the olefin can approach the active center and brings one of the H atoms of the C_2H_5 group close to the Ti atom by a value of 1.832 Å. Remarkably this value is shorter than its initial value (2.14 Å). Meantime, the bonds between Ti atom and the substrate are weakened temporarily due to the steric interactions occurred in the insertion phase. After going the transition states, the final product are rapidly reached, which is represented by the structure in Figure 1d. The chain propagation, after the first insertion process, will goes in a pathway that is basically similar from the point of the formation and cleavage of bonds. However several differences have also been noticed. A second propylene molecule can approach the catalyst only from the left side. It can be understood clearly from the structure shown in Figure 1d, where the catalyst is unscreened. After the first and second insertion, the polymerization will be performed repeatedly.

The results of overlap bond population during the process of the first propylene insertion to Ti 4-fold

activated center reactions are shown in Figure 2. It is clear from this figure that the bonds between four atoms (Ti, C_1, C_2, C_3 shown in Figure 1) have undergone large changes. The values of overlap population of the bond between Ti and C_3 is decreased and after a time period it reaches nearly zero, which indicates that the bond of Ti-C_3 is weakened and then is broken. However, for the bonds of C_2-C_3 as well as Ti -C_1, the values change from zero to a relative high one, showing the formation of new bonds. The bond between C_1 and C_2 is weakened at first and then with the time going it is nearly constant. It represents a transform from the double bond (between C_1 and C_2) to a single bond during the first propylene inserting on the Ti activated site. Obviously our results of tight-binding quantum chemical molecule dynamics simulation by 'colors' program, have well described the transformation of the bonds during the first propylene insertion on Ti (IV) activated site. Based on the above results of the first propylene insertion reaction, the large periodic model (the first propylene insert 4-fold catalytic activated center reaction on the support of $MgCl_2$ surface) is set up in order to make our simulation closer to the real reaction conditions. Our 'colors' program also performs the calculation and the results are shown in Figure 3.

As it is known the $MgCl_2$ (100) surface and $MgCl_2$ (110) surface are thought as two kinds of best useful surfaces in Ziegler-Natta catalyst. However it is also proposed that the $MgCl_2$ (100) is a good active surface for coordinating epitactically of the chiral dinuclear Ti_2Cl_6 species [21]. Therefore in this study we choose the $MgCl_2$ (110) surface as the active surface. In the present calculation, the supercell has been adopted including 36 Mg atoms and 72 Cl atoms in a periodic unit. It can be seen clearly from Figure 3 that during the relaxation process, the layers are kept well and all layers are terminated at 4-fold Mg sites. That is, the relaxation does not give rise to any reconstruction. The angle of Cl-Mg-Cl is 156° on the surface while the Mg-Cl bond lengths fall into the range of 2.32 and 2.38 Å.

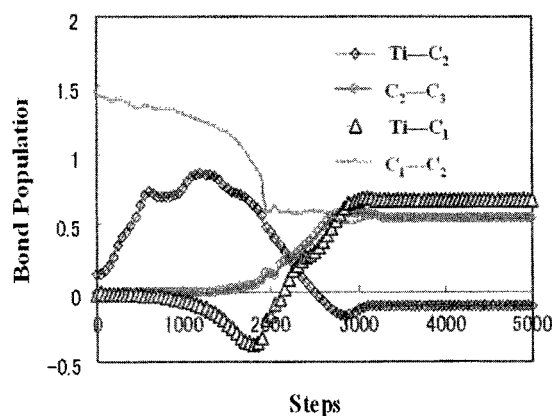Our results show that a π -complex can be formed in a barrierless way only when the molecule is oriented

Fig.2. The change of the bond overlap population during insertion reaction of the first propylene obtained by tight-binding quantum chemical molecule dynamics program.

at the position as shown in Figure 3b. There are not steric hindrances between the ethyl group in the incoming propylene and the growing polymer chains. Thus a stable complex is generated. Our results indicated that the complexation energy is reduced in the polymerization of propylene molecule in comparison with that of ethylene, which is about 21.1 kcal/mol in propylene and 24.0 kcal/mol in ethylene. This difference is originated from the fact that the Ti-alkene distance is larger in Ti-propylene than that in Ti-ethylene, resulting in a lower complexation energy [1]. The energy difference between the final product (Figure 3d) and the initial structure (Figure 3a) of this insertion reaction is 13.5 kcal/mol. The lower energy in the case of Figure 3d indicates a more stable structure of the growing polymer chain has been formed. This energy is very close to the activation barriers of the first propylene inserting to 5-fold activated site (12.6 kcal/mol) in the successive insertion reactions reported by other research [1]. From these observations, it is clear that the stereoselectivity is a consequence of the local geometry of the active site carrying the growing chain. These results support the propylene insertion reaction mechanism proposed by experimentalist (9.5-12.0 kcal/mol).

4. Conclusion

We performed an investigation of the properties and the mechanism of the first propylene insertion reaction catalyzed by Ziegler-Natta heterogeneous catalyst using tight-binding quantum chemical molecular dynamics method. The catalyst of Ti (IV) active site supported on $MgCl_2$ (110) surface was adopted. The results from our calculations showed that the π -complex was formed in a barrierless way at the initial state of the insertions reaction. Then it passed through a
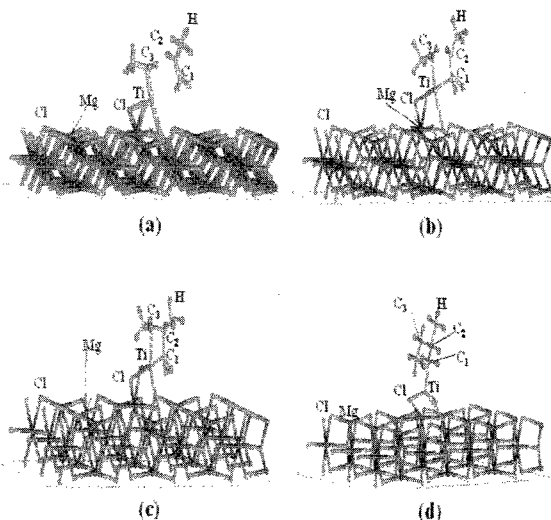

(a)   (b)

(c)   (d)

Fig.3. The insertion process of the first propylene molecule to Ti 4-fold activated site on the $MgCl_2$ (110) surface calculated by tight-binding quantum chemical molecule dynamics program. (a) the initial structure; (b) the π -complex (c) the transition state; and (d) the final product.

transition state to form the product of first polymerization. The detailed structure and energy has been obtained in the initiation and propagation steps, which are consistent with the experimental findings. Furthermore the mechanism proposed according to our calculation reasonably explained the reaction pathway depicted in some experiment [3]. Obviously our tight-binding quantum chemical molecule dynamics program is a good tool to deal with catalysis system with large number of atoms to mimic the practical conditions and it can provide good results in the application of tracking reaction process of polymerization reactions.

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