

1P21 Tight-binding Quantum Molecular Dynamics Study on Ethylene Polymerization Reaction Using CpSiH₂NHTiCl₂ - Constrained Geometry Catalyst

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【1. Introduction】

Olefin polymerization by transition metal (TM) complexes has been the main focus of attention of the field of polymer chemistry for over 50 years. The recent development in the metallocene technology is the novel single site constrained geometry catalyst (CGC) of the form of CpSiR₂NRMX₂ where M is group 3, 4 transition metal and X is Cl [1]. CGCs activated by methylaluminoxane (MAO) produce a new family of linear polyethylene, which possess very desirable properties. Electronic and atomic level investigation of ethylene polymerization process of CGC/MAO catalytic system was calculated using both density functional theory (DFT) and tight binding quantum chemical molecular dynamics (QCMD) program, Colors [2] developed by our laboratory.

【2. Method】

We have determined the Hirshfeld charge, S, P, D atomic population and bond population for each atom in the catalytic system using first principles DFT method and compared with Colors results. After accurate parameter fitting, these parameters were employed in dynamics calculation. The CpSiH₂NHTiCl₂ precatalyst, linear molecule of MAO and 50 molecules of ethylene were used as reactants.

【3. Results and discussion】

The molecular dynamics (MD) study of precatalyst and MAO revealed that MAO react with precatalyst within 85 fs and alkylate Ti active center by removing 1 chlorine atom, leading to form a polarized ion pair. (Fig. 1) Some theories suggest that polarized ion pair dissociate into active cation in presence of monomer, while the others debated that ion pair does not dissociate before monomer insertion. We found out that, upon the first monomer insertion to the ion pair, the coulomb energy and bond energy of Ti and Cl atom became smaller, indicating the dissociation of ionic pair. The activation barrier for first and second ethylene insertion into cationic model was calculated by Colors program as well as DFT. We found out that the energies calculated by Colors are in good agreement with DFT results, as shown in Table 1.

Table 1. DFT and Colors calculated energies of first and second monomer insertion into cationic model (energy in kcal/mol)

| | First ethylene insertion | | Second ethylene insertion | |
|---------------------------|--------------------------|--------|---------------------------|--------|
| | DFT | Colors | DFT | Colors |
| π Complexation Energy | -21.65 | -16.54 | -29.63 | -30.46 |
| Activation Energy | 6.66 | 9.20 | 5.65 | 5.23 |
| Reaction Energy | -23.83 | -28.63 | -29.03 | -26.39 |

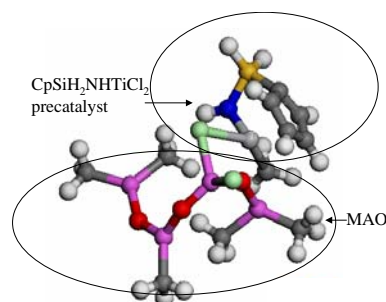


Fig. 1 formed ion pair after 85 fs in MD simulation

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