

289p Olefin Polymerization by Single-Site Ti and Zr Aryloxy Complexes

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Density function theory has been used to study the mechanism of olefin polymerization catalyzed by Ti and Zr organometallic complexes of the form $[\text{CpTi}(\text{OAr})\text{Me}^+]$ $[\text{MeB}(\text{C}_6\text{F}_5)_3^-]$ which contain one aryloxy and one cyclopentadienyl ligand. Detailed reaction mechanisms, transition states, and energies for each reaction step have been computed for several catalysts in order to explore relationships between catalyst structure and reactivity. The reaction steps studied were catalyst activation, olefin adsorption, chain initiation, chain propagation (via frontside and backside mechanisms), chain transfer to monomer (beta hydrogen transfer to monomer), chain termination (beta hydrogen transfer to metal), and catalyst deactivation (two mechanisms). The overall activation barriers for frontside and backside insertion were found to be similar. Catalyst activation was found to have a lower activation energy barrier than insertion, while chain transfer, chain termination, and catalyst deactivation had larger barriers. Chain transfer to monomer was found to be more favorable than chain termination. Density functional theory has also been used to show which orbitals are important for the transfer of electrons during olefin insertion.