

The Copolymerization of Ethylene and Propylene by a Heterogeneous Ziegler-Natta Catalyst Studied by Density Functional Theory Calculations.

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Abstract

Heterogeneous $\text{TiCl}_4/\text{MgCl}_2$ type catalysts and the many related catalysts are used to produce enormous quantities of copolymers of ethylene with other α -olefins. The properties of the resulting polymer depend not only upon the identity of the second olefin but also on the ratio of ethylene:olefin present in the material. In this work the various possible propagation reactions that could take place were considered using density functional theory calculations. The second olefin was chosen to be propylene as the simplest possible case and a model for the active site was taken from earlier work. π -complexation energies and insertion barriers were calculated for both monomers. A number of possible models for the growing polymer chain were chosen each constituting the product of one of the several possible insertion reactions. The π -complexation energy of propylene was found to be greater than that of ethylene with the same active site and, surprisingly, the propagation barriers were found to be lower for the propylene monomer than the ethylene monomer. However, the results do suggest that as more steric bulk is introduced around the active site then the preference for propylene over ethylene is reduced. This indicates that a more sterically hindered model of the active site may be more reasonable.