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Case study: Material science

Role of electron donors in propylene polymerization

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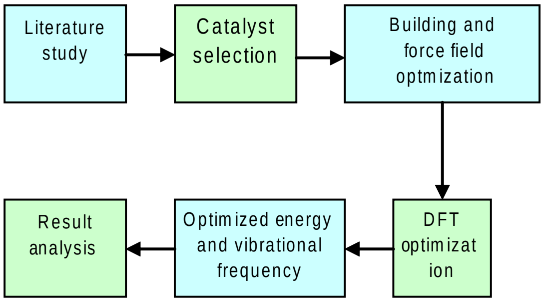
Customer type

A leading polymers and petrochemicals company

Software modules

VLife Engine
ProViz
Gaussian



Application

Reaction mechanistic studies

Techniques

Building and initial force field optimization

DFT optimization

Energy and frequency

Background:

Electron donors play vital role in Ziegler-Natta olefin polymerization. Due to addition of electron donors, stereo-selectivity as well as stereo-specificity is achieved during propylene polymerization which influences isotacticity of the polypropylene product.

The activity of catalyst is significantly reduced in presence of electron donors like ethyl benzoate and p-ethoxy ethyl benzoate.

Design challenge:

The customer was interested in the know-why of the above experimental facts. This study investigated the role of electron donors in propylene polymerization with Ziegler-Natta catalyst by using rigorous computational methods like Density Functional (DFT) methods.

Project work:

The reaction mechanism of propylene insertion in the catalyst in presence of electron donors was studied using DFT for molecular level understanding. Ziegler Natta model catalyst $[TiCl_2CH_3]^+$ was used and the density functional B3LYP/6-31G** method was used to study propylene insertion in the catalyst in presence of methyl benzoate(MBz) and p-methoxy methyl benzoate(p-OMe-MBz) as model monoester electron donors for their real ethyl analogs.

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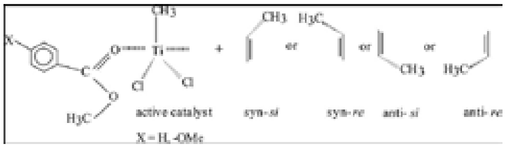

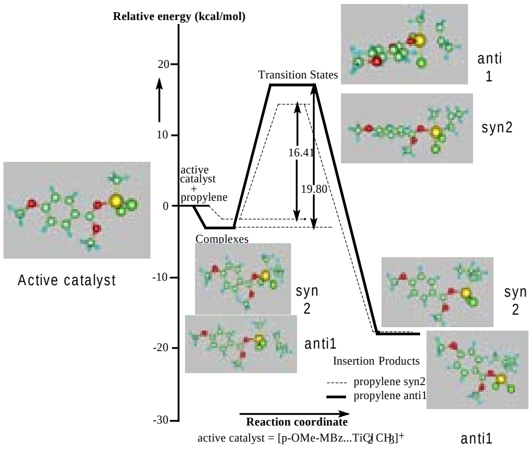

Representative reaction profile on $[p\text{-OMe-MBz..TiCl}_2\text{CH}_3]^+$ active catalyst

DFT optimized structures at the B3LYP/6-31G** level of propylene complexes of active catalyst, transition states and propylene inserted products and the corresponding relative energy profile of syn and anti propylene insertions for $[\text{MBz..TiCl}_2\text{CH}_3]^+$ and $[p\text{-OMe-MBz..TiCl}_2\text{CH}_3]^+$ active catalysts were computed. In the relative energy diagram, 1= si and 2= re in standard si, re notation for enantiospecificity and syn, anti refers to the regioselectivity of propylene insertion.

Result analysis:

The computed relative energetics reveal the following trends that have excellent match with experiments:

1. For both the electron donors, propylene inserts in Ti-CH3 bond in syn- (anti-Markovnikov) fashion rather than anti-fashion and has lower activation barriers (Eact).
2. Regioselectivity (anti-Markovnikov) of propylene insertion maintained in the presence of electron donors
3. Coordination of electron donors increases activation barriers of propylene insertion (by 4.5-5.0 kcal/mol), explaining the experimentally observed drop in catalytic activity of $[\text{TiCl}_2\text{Me}]^+$ on addition of electron donors.

Reference:

Density functional study on the role of electron donors in propylene polymerization using Ziegler-Natta catalyst, S. Mukhopadhyay, S. A. Kulkarni, S. Bhaduri, J. Orgmet. Chem. 690 (2005) 1356-1365.