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DFT investigation of the regiospecificity of a model catalyst site for propene polymerisation

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Abstract

Density functional theory calculations were used to study the mechanism of regioregular and regioirregular propene insertions to a model catalyst site ($TiMg_2Cl_6CH_3$). Further regioregular insertions to Ti–2-butyl and Ti–2-methylpropyl bonds were simulated to study the reactivity after the first insertions. It was found that after the first regioregular insertion there exists two minimum energy conformations for the chain: α-agostic and β-agostic. The formation of a π-complex between propene and the active site was only possible with the α-agostic conformation. After the regioirregular insertion there is no minimum energy conformation with α-agostic interaction and so further insertions are hindered. In contrast to propene, ethene is found to be able to coordinate also to β-agostic site and is therefore able to reactivate polymerisation after a regioirregular insertion.

Keywords: Heterogeneous Ziegler–Natta catalyst; Regiospecificity; Polypropylene

1. Introduction

Heterogeneous Ziegler–Natta (Z–N) catalysts are widely used in the industrial production of polyethylene and polypropylene (PP). Since the discovery of Z–N type catalysts in the early 1950s the development with respect to the catalyst activity and stereospecificity of the polymerisation has been remarkable. The current fourth generation catalysts in PP production are based on $MgCl_2$-supported $TiCl_4$ with internal and external donors added to increase the isotacticity of the polymer, which can be as high as 99% (mmmm-%). Compared to this development the mechanistic understanding of the reaction is lagging behind. For further development of the catalyst and for accurate control of the polymer materials and their properties it is important that the polymerisation mechanism is understood fully.

The general polymerisation scheme proposed by Cossee and Arlman [1–3] is already by now well accepted. It involves an under-coordinated titanium with one Ti–C bond as the active site. The incoming olefin first coordinates from the double bond to the Ti atom. The insertion proceeds through a four-member transition state involving the Ti–C bond and the olefin double bond carbons. An agostic interaction between Ti and one of the hydrogens of the growing polymer chain stabilizes the reaction [4]. By now many quantum chemical simulations of the first and also second olefin insertion have been performed which provide support for this model [5–12]. One of the aspects in propene polymerisation that has not been studied much theoretically is the 2,1-insertion of propene. Experimental results show that isotactic polypropylene contains only a small amount of regioerrors formed as a result of 2,1-insertion [13]. It has been hypothesized that after 2,1-insertion the active site is not able to polymerise propene anymore. Rather than being deactivated completely, the site becomes ‘dormant’ and it can be reactivated for example by chain transfer to hydrogen. This explains the reversible activation effect of hydrogen in propene polymerisation [14]. Experimental evidence for this mechanism has been found with end-group analysis [15] and stopped-flow method [16].

To understand the mechanism of these reactions, we have performed density functional theory (DFT) calculations on a model catalyst site. Two different sites have recently been

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used to study polymerisation on a heterogeneous Z–N system. Boero et al. [9] studied both the polymerisation of ethene and propene using Carr–Parrinello molecular dynamics simulations. They used a five-coordinated $TiCl_4$ coordinated on a (110) $MgCl_2$. This site is similar to the one first identified by Puhakka et al. [8] in their calculations. The site was found to be active for both ethene and propene polymerisation and also highly stereospecific in the latter case. In addition, 2,1-insertion of propene was studied with this site and it was found to be disfavoured. Cavallo et al. [12] have studied propagation and termination reactions in ethene polymerisation using non-local DFT. They chose a hypothetical model site ($TiMg_2Cl_6CH_3$), where the oxidation state of titanium (Ti(III)) corresponds to experimental findings [17].

Since we are interested in the 2,1-insertion of propene, we chose to use the same site as Cavallo et al., which is not expected to be stereospecific [15]. Using DFT calculations, the relative probability of 1,2- and 2,1-insertions was first determined. These insertions yield sites with 2-butyl and 2-methylpropyl groups, respectively. Reactivity towards further polymerisation was evaluated by simulating additional 1,2-insertions to these sites.

2. Computational methods

DFT calculations were carried out with the $DMol^3$ program versions 4.0 and 4.2 (Accelrys Inc.) [18]. The geometries were optimised using non-local DFT with Becke's exchange functional [19] and the Lee–Yang–Parr correlation functional [20] (BLYP). Due to the small size of the $TiMg_2Cl_6$ cluster the Cl–Ti–Cl angles were constrained to 90° and the rings were held planar in all geometry optimisations. These are the same constraints that Cavallo et al. [12] applied. Double numeric basis sets augmented with polarization functions (DNP) [18] were used in all calculations. Due to the expected agostic interactions polarisation functions were used also in hydrogens. Because of the paramagnetism of the system the unrestricted method was used. SCF convergence criterion was 10^{-7} Hartrees.

We were unable to use the transition state search algorithm of $DMol^3$ due to problems in the use of lagrangian constraints with the system. Instead, the transition state energies were obtained by extrapolation from 8 to 10 highest values using a quadratic equation. In all cases, the R^2 value of the fits was over 0.95. In Schemes 1–4, the transition state structure corresponds to the optimised structure with the value of the reaction coordinate closest to the interpolated value. Reaction energies were calculated using equation $\Delta E = \sum E_{\text{reactants}} - E_{\text{products}}$. Graphics visualisation was done using Cerius2 and Materials Studio programs (Accelrys Inc.) and calculations were performed on an SGI Origin 2000 system of CSC (Center for Scientific Computing Ltd., Espoo, Finland).

3. Results and discussion

First step in the olefin insertion reaction is the formation of a π-complex. Earlier study [6] has shown that the lowest energy structure for the π-complex corresponds to the one where the double bond is perpendicular to the Ti–C bond. In the case of propene, this leaves four possible conformations differing in the orientation of the propene methyl group (Fig. 1). Optimisation of all these structures yielded stable π-complexes. In all the structures, propene is coordinated asymmetrically due to the bulky methyl group. There is also a weak agostic interaction between one of the α-hydrogens and Ti, which can be seen from the stretched C_α–H_α bond (1.103 Å). Compared to ethene the distance from titanium (C_1–Ti) is also considerably longer (over 3.1 Å compared to 2.6 Å).

The relative energies of these complexes are all within 0.7 kcal/mol. For this study, we chose the structure (**4**) corresponding to the lowest energy as the starting geometry. Because we are not interested in stereospecificity, the other structures are not considered. For the structure (**4**) the energy gain (ΔE) of the π-complex is 1.7 kcal/mol. Basis set superposition error (BSSE) estimated as the difference between $\sum E_{\text{reactants}}$ and E_{products} with sufficient separation is 0.6 kcal/mol. For ethene, Cavallo et al. found ΔE to be 6.6 kcal/mol [12] and Boero et al. [9] obtained 3.6 kcal/mol for the Ti(IV) complex and propene.

3.1. First insertions

For the first insertion (1,2) the distance between C_1 of propene and C_α was chosen as the reaction coordinate.

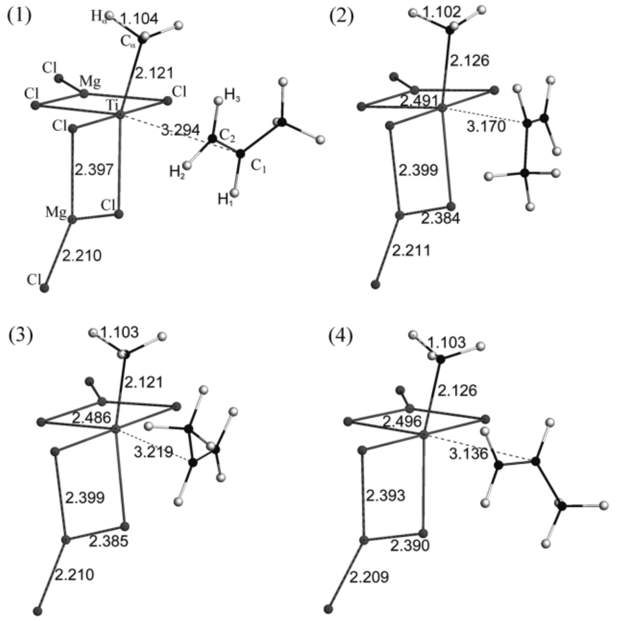
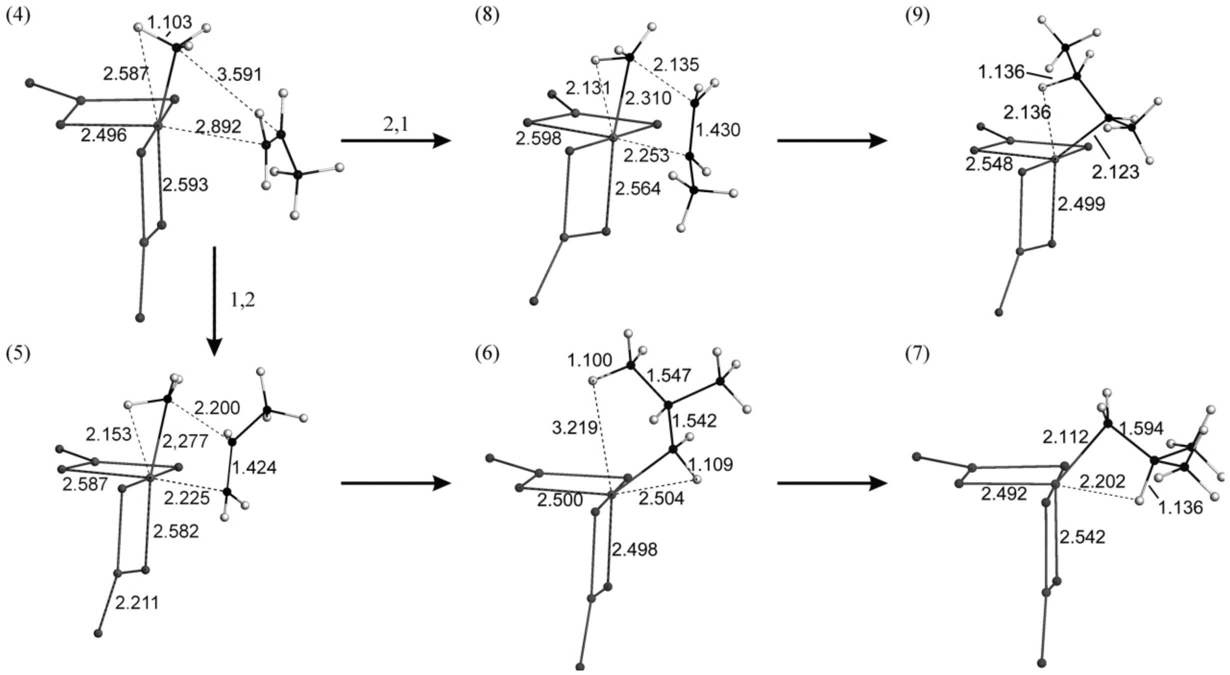


Fig. 1. The four π-complexes between propene and the model catalyst site. The energies of the structures **1**, **2** and **3** are 0.06, 0.18 and 0.69 kcal/mol higher than the energy of structure **4**.



Scheme 1.

When this distance is shortened the reaction proceeds through a four-member transition state. First propene turns so that the double bond is parallel with the Ti–C_α bond. At distance 2.20 Å the transition state (Scheme 1, structure **5**) is formed (14.4 kcal/mol). After the transition state the product (**6**) is formed with an energy gain of 9.9 kcal/mol. This conformation is stabilised by an α-agostic interaction (C_α–H_α = 1.109 Å). Rotation around the C_α–C_β bond by 60° brings the β-hydrogen close to the titanium. Optimisation of this structure yields the final product (**7**) of this insertion reaction with an energy gain of 11.7 kcal/mol. We also checked for the existence of a γ-agostic state, by starting an optimisation from a conformation in which the Ti–H_γ distance was minimised by rotation of the C_α–C_β bond. The result is, however, also α-agostic and although the geometry is slightly different from the first α-agostic structure, it probably belongs to the same wide minimum area. These results are in line with experimental estimates (9.5–12.0 kcal/mol) [21,22] and also quite close to the values obtained by Boero et al. with the stereospecific five-fold site in second insertion (activation energy 10.8 kcal/mol and final energy gain 16.7 kcal/mol) [9].

The corresponding 2,1-addition was simulated starting from the same π-complex (**4**). This time the distance between C_2 of propene and C_α was used as the reaction coordinate. The reaction proceeds very similarly to the 1,2-insertion. The activation energy is 2.8 kcal/mol higher and the transition state (**8**) is formed at a slightly shorter distance of 2.14 Å. The product (**9**) is, however, directly formed in the β-agostic conformation and the energy gain is 2.3 kcal/mol lower than in the 1,2-insertion.

In both of these insertions there is a strong agostic stabilisation during the reaction. Fig. 2 shows distance changes between the atoms involved in the reactions. The facilitating agostic interaction is clearly seen in the C_α–H_α distances (solid lines), which pass through a maximum before the transition state. Fig. 3 summarises the results. As expected, the 1,2-insertion is the preferred reaction. The difference between the activation energies of 1,2- and 2,1-insertions is 2.8 kcal/mol.

3.2. Second insertions

The relative probability of further 1,2-insertions to the two sites (**7**) and (**9**), determines whether the 2,1-insertion results in a dormant site for polymerisation. Because the β-agostic state corresponds to the minimum energy structure, it was used as the starting conformation for both second insertion simulations. To save CPU time the 2-butyl group was replaced with an isopropyl group (**14**). Also for these reactions, only the orientation of approaching propene corresponding to π-complex (**4**) is considered in this study.

The formation of the π-complexes for the second step did not proceed as simply as in the first case. Starting a geometry optimisation from a conformation with propene brought close (2.6 Å) to the titanium in the site containing isopropyl, did not yield a stable structure. During the optimisation the β-agostic bond (Ti–H_β) first opened to yield space for the propene, but when the optimisation was continued the Ti–H_β distance started to decrease again and the propene spontaneously migrated away. The same thing occurred with the site containing 2-methylpropyl and even if the Ti–C_1 distance was initially constrained. With the same model catalyst site Cavallo et al. reported a barrierless

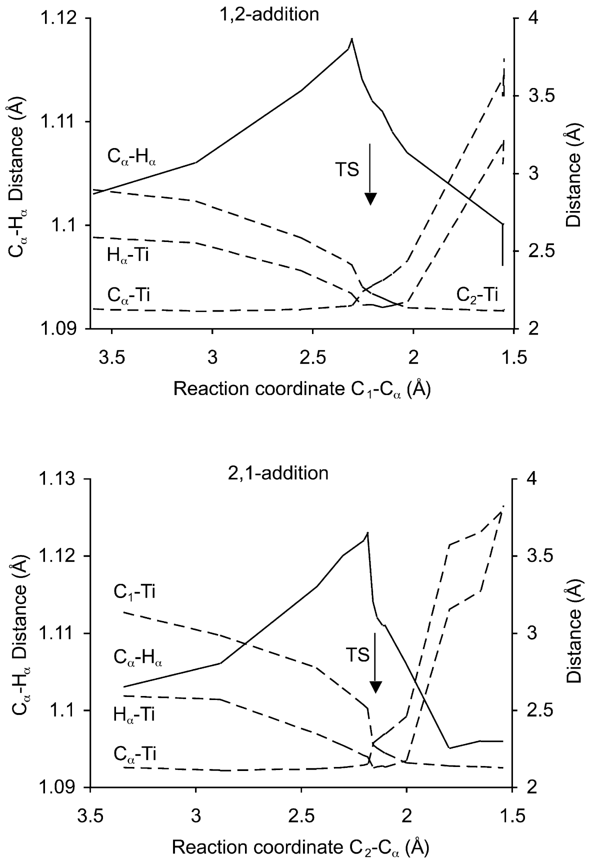


Fig. 2. Some relevant distance changes during the 1,2- and 2,1-insertion reactions. Transition states are marked with an arrow.

insertion of ethene to the β-agostic ethyl complex (structure **10** in Ref. [12]). To confirm this result we optimised the same β-agostic ethyl complex and indeed a stable structure was obtained. However, in our case the distance of ethene from the Ti was 0.3 Å higher than what Cavallo et al. obtained with the ADF package (Ti and Mg: uncontracted triple-ζ STO, Cl, C and H: double-ζ STO augmented with 3d and 2p polarization functions, respectively. Frozen core approximation was used for the $1s^2 2s^2 2p^6$ configuration on Ti, Mg and Cl and for the $1s^2$ configuration on C). As a result of the π-complex formation, the agostic Ti–H_β distance increased from 2.2 to 3.3 Å.

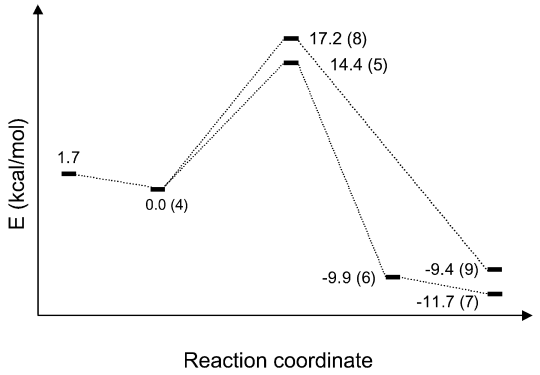
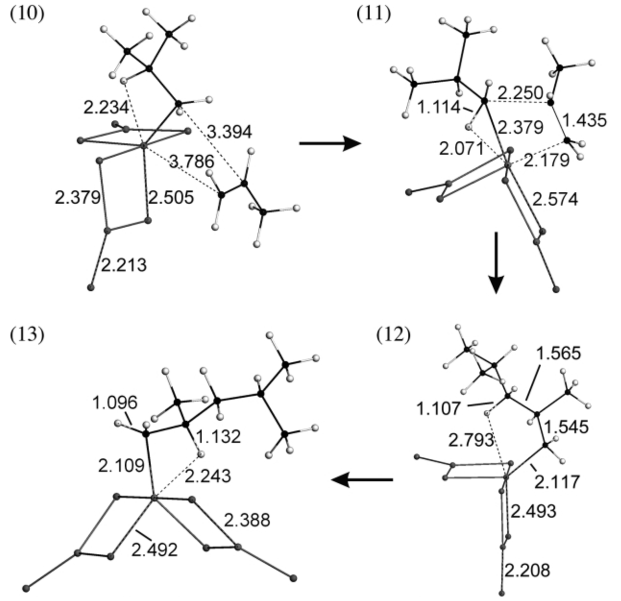
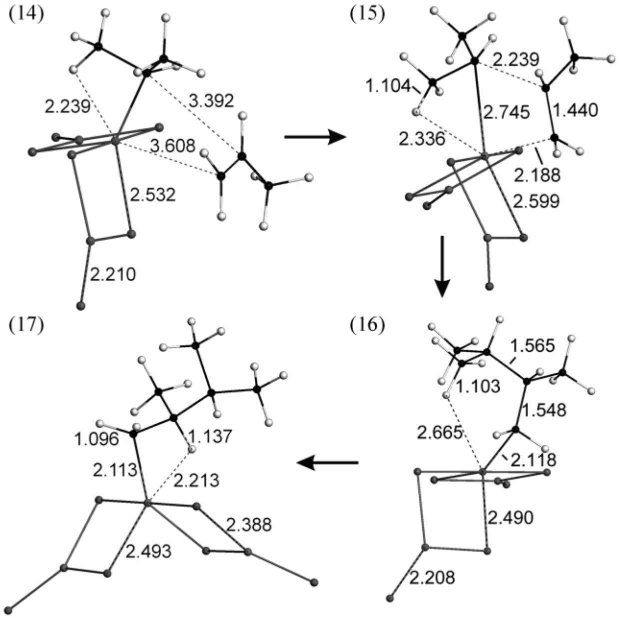


Fig. 3. Energy diagram of the first insertion reactions. Number of the structure in parenthesis (Scheme 1).



Scheme 2.

To determine the insertion barriers for propene we started the reactions with propene about 3.7 Å away from Ti. The basic mechanism of these reactions is similar to the first insertions: propene double bond aligns itself parallel with the Ti–C_α bond and the four-member transition state is formed at C_α–C_1 distance of 2.24–2.25 (Schemes 2 and 3). Because the starting structures are β-agostic, there are, however, also differences as shown in Fig. 4. The dashed lines show changes in the C–H bond lengths, which are involved in the agostic interactions. In case of the 2-methylpropyl site the β-agostic interaction starts to break at



Scheme 3.

$C_\alpha{-}C_1$ distance of about 2.6 Å, simultaneously with the formation of an α-agostic interaction, which stabilises the transition state (**11**). The formation of the α-agostic interaction is possible due to the rotation of the 2-methylpropyl chain around $Ti{-}C_\alpha$ bond as $C_\alpha{-}C_1$ distance is shortened.

In the case of the isopropyl site the β-agostic interaction vanishes already at $C_\alpha{-}C_1$ distance of 3.0 Å. In contrast to the insertion to the 2-methylpropyl site the chain does not rotate to prepare the way for the α-agostic interaction. The transition state (**15**) is formed at $C_\alpha{-}C_1$ distance of 2.24 Å with only weak β-agostic stabilisation. The activation energy for this reaction is 2.6 kcal/mol higher than for the insertion to the 2-methylpropyl site. The weaker stabilisation, which leads to the higher activation energy, is also visible in the more stretched $Ti{-}C_\alpha$ distance (2.75 Å compared to 2.28–2.38 Å in structures **5**, **8** and **11**).

The initial product (**12**) from the insertion to the 2-methylpropyl site is formed with an energy gain of 11.8 kcal/mol. The structure is similar to structure (**6**) with both weak α- and γ-agostic stabilisation. The lowest energy β-agostic product (**13**) is again formed by rotating the $C_\alpha{-}C_\beta$-bond of the chain by 60°. This rotation stabilises the product by additional 1.8 kcal/mol. In case of the insertion to the isopropyl site, the initial energy gain is 10.7 kcal/mol. This product (**16**) is stabilised by a very weak agostic interaction with the hydrogen of the fourth carbon of the chain. Formation of the β-agostic product (**17**) requires a much more drastic 180-degree rotation, but the final energy gain is over 15 kcal/mol (Fig. 5).

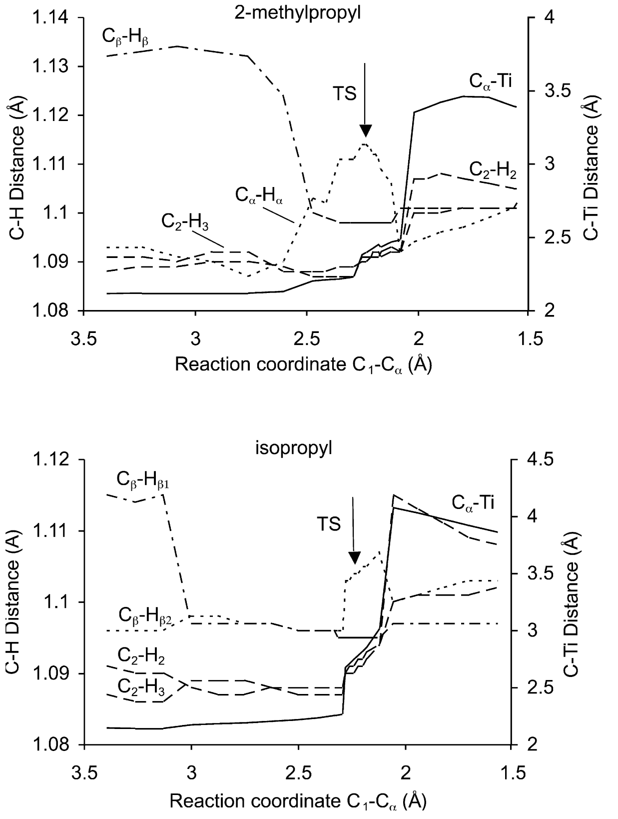


Fig. 4. Some relevant distance changes during the insertion to the sites containing 2-methylpropyl and isopropyl group. Transition states are marked with an arrow.

Although these results show that the addition after 1,2-insertion is preferred, the activation energies of the second insertions (20.6 and 23.2 kcal/mol) are surprisingly high compared to the first insertions or to the experimental estimates (9.5–12.0 kcal/mol) [21,22]. This in conjunction with the lack of stable π-complexes, could mean that the calculated paths are not the preferred reaction paths. With the five-fold site Boero et al. [9] found that the activation energy for the second insertion is comparable to the first insertion energy (10.5 kcal/mol). In their case also the second insertion was α-agostic assisted, because the rotation of the chain to β-agostic state was not barrierless.

To find out if 1,2-insertion is possible to an α-agostic isopropyl site we tried to form a π-complex between propene and an α-agostic isopropyl site. Starting from a suitable structure close to the minimum a stable structure was obtained. 1,2-Insertion from this structure (Scheme 4, **18**) proceeds normally with an activation energy of 13.5 kcal/mol (**19**), which is lower than the first insertion activation energies by 0.9–3.7 kcal/mol. The initial product is α-agostic (**20**) but the rotation of the chain yields the final product (**17**), already obtained in the insertion to the β-agostic site. The final energy gain from this reaction is 3.5–5.6 kcal/mol higher than in the first insertions.

Because the insertion to the isopropyl site from an α-agostic π-complex is of comparable energy to the first insertions, the rate-determining step for insertion must be the formation of the π-complex. This requires conversion of the β-agostic structure to an α-agostic. To find out the barrier for the conversion between the α-agostic and β-agostic structures, we calculated the energy diagram for the torsion of the dihedral angle $Cl{-}Ti{-}C_\alpha{-}C_\beta$ for both isopropyl and 2-methylpropane sites. Fig. 6 shows the results of the scan for the isopropyl group. Due to the symmetry of the system only 180° is shown. 60° rotation of the isopropyl group from the β-agostic minimum shows a

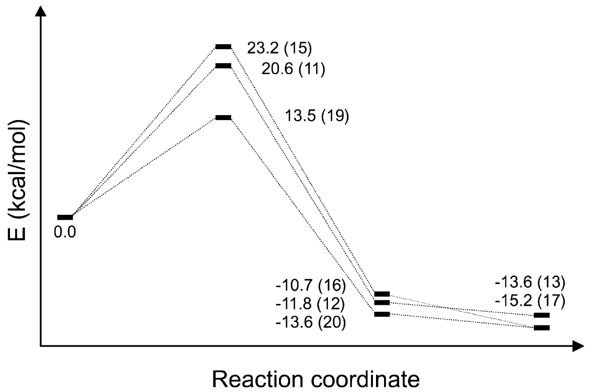
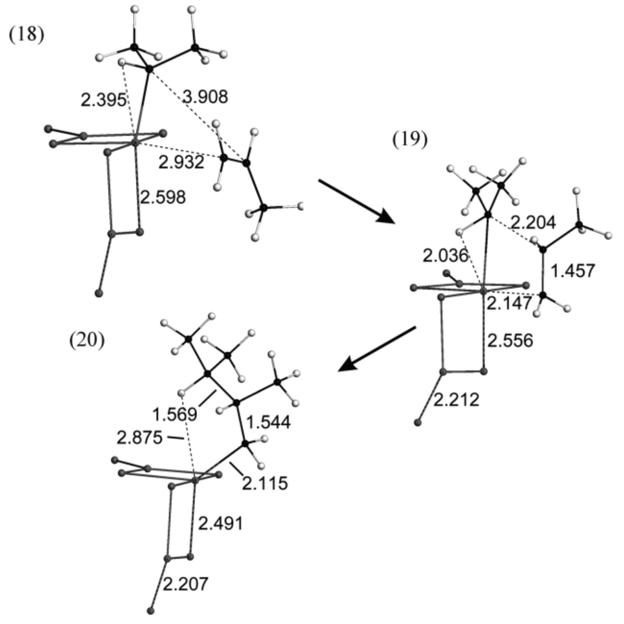


Fig. 5. Energy diagram of the second insertions. Number of the structure in parenthesis (Schemes 2–4).



Scheme 4.

small barrier of 1.1 kcal/mol for the formation of the second β-agostic minimum with the other methyl group. Further rotation by 60° brings the system to the α-agostic structure. There is, however, no minimum for this structure. Instead, the α-agostic state represents a maximum, which is 6.5 kcal/mol higher than the β-agostic conformations. Further rotation by 60° brings the system to a state, which is equivalent to the starting conformation. The absence of an α-agostic minimum seems strange. As shown by the small arrow (I in Fig. 6) there is a clear stretching of the α-hydrogen bond, which indicates an agostic interaction. On both sides of this maximum there is, however, the stretching of the $C_\beta-H_\beta$ bonds (II and III) associated with the two lower energy β-agostic states. The net effect is a maximum of the energy instead of a minimum. The result of this missing minimum was already seen in the 2,1-insertion reaction, in which the product formed directly in the β-agostic state.

For the 2-methylpropyl site a 90° scan (Fig. 7) shows two minima: one for the β-agostic starting conformation and one for the α-agostic state. The β-agostic state is lower by 1.9 kcal/mol, but the barrier for rotation is not very high (2.7 kcal/mol from IV to V in Fig. 7).

According to these results the 1,2-insertion to the site containing isopropyl chain is disfavoured by over 5 kcal/mol. The limiting step is the formation of the π-complex, which can only form with the α-agostic state. After a 1,2-insertion the chain is initially formed in the α-agostic state and even though it is not the global minimum the rotation barrier is not very high. After a 2,1-insertion the chain will rotate directly to the β-agostic state. Insertion to this site requires a concerted rotation of the chain and a monomer attack. This kind of a reaction is very unlikely, but it allows to hypothesize that increase of monomer concentration will increase regioerrors in atactic polymer chains.

The mechanism found in this study is markedly different from the one found for the *rac*-$Me_2C(3\text{-}t\text{-}Bu\text{-}1\text{-}Ind)_2ZrCl_2$/MAO homogeneous catalytic system [23]. In that system isopropyl blocked the active site in a conformation with double β-agostic interaction with the metal. This kind of interaction was not found for the present system.

4. Conclusions

A model catalyst site was used to study the regioirregular insertion reaction in propene polymerisation. The results show that the model ($TiMg_2Cl_6CH_3$) represents an active site for propene polymerisation. In the first insertion the 1,2 reaction is favoured by 2.8 kcal/mol over the 2,1-insertion. For the second insertion, the case is complicated by the

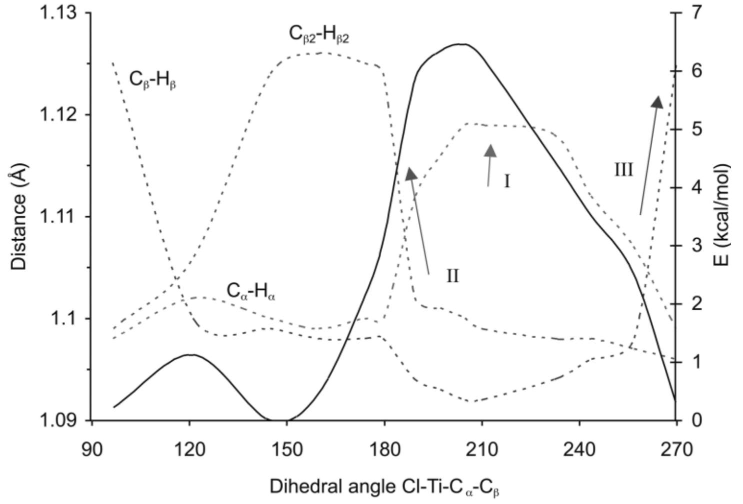


Fig. 6. Energy diagram for the rotation of the dihedral angle Cl–Ti–C_α–C_β (solid line) and relevant distance changes (dashed lines) in the site containing isopropyl group. Stretching of the bonds caused by α- and β-agostic interactions are marked with arrows (I and II, III, respectively).

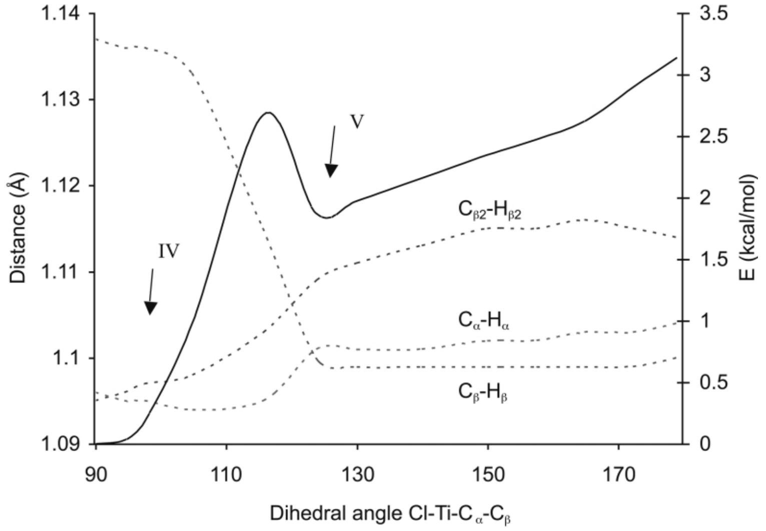


Fig. 7. Energy diagram for the rotation of the dihedral angle Cl–Ti–C_α–C_β (solid line) and relevant distance changes (dashed lines) in the site containing 2-methylpropyl group. α- and β-agostic minimum energy conformations are marked with arrows (V and IV, respectively).

possible rotation of the chain. Minimum energy conformation corresponds to the one with an agostic interaction between β-hydrogen of the chain and Ti. Propene insertion through this state is not favoured due to high activation energy and the absence of a stable π-complex. This explains why the polymerisation cannot proceed after 2,1-insertion. After 1,2-insertion the chain is formed in an α-agostic state, but for the isopropyl group there is no minimum energy conformation with an α-agostic interaction. A concerted rotation of the isopropyl group and an attack of propene can, however, still lead to a stable π-complex and to an insertion reaction.

An interesting observation is that ethene is able to form a stable π-complex with the β-agostic chain. This explains the experimental finding that ethene can reversibly enhance the rate of propene polymerisation and that hydrogen does not activate ethene polymerisation [24].

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