

Hartree–Fock and density functional theory analysis of propylene insertion in $\text{Al}(\text{CH}_3)_3/\text{TiCl}_3/\text{TiO}_2$ (red.) in the presence of a Lewis base

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Abstract

Titanium tetrachloride heterogenized on reduced TiO_2 was recently described as an active catalyst for ethylene polymerization. This catalytic system also permits propylene polymerization with lower activity, however, with low polydispersity, high molecular weight and with the good isotacticity of 78%. The isotacticity of this polymer can be increased by addition of a Lewis base. The behavior of the active site, in the presence of a Lewis base, was studied by ab initio Hartree–Fock and density functional theory. The atomic charge values obtained suggest that methyl benzoate used as a Lewis base makes the active site more susceptible to coordination with propylene. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the beginning of the 1950's, the synthesis of polyolefins was radically changed by Ziegler's discovery [1]. He found that ethylene can be polymerized under mild temperature and pressure conditions with the use of TiCl_4 in combination with triethyl aluminium as co-catalyst. Using the system developed by Ziegler, Natta's group found that propylene could also be polymerized yielding a mixture of crystalline and amorphous fractions [2]. Natta characterized TiCl_3 crystallites as the active sites, which were

found to improve either the amount of product or its isotacticity.

Much effort has been devoted towards improving both the activity of the catalyst and the isotacticity of the polypropylene produced. TiCl_4 supported on magnesium dichloride yields 40% isotactic polypropylene [3]. However, adding a Lewis base such as ethyl benzoate, methyl *p*-toluate, 2,2,6,6-tetramethylpyridine triethylamine [4], phenyltriethoxysilane [5] or *tert*-butyl methyl ether in combination with ethyl benzoate and dibutyl phthalate [6] can improve the isotacticity of polypropylene by up to 97% [7,8].

The significant improvements in the degree of isotacticity found with the use of Lewis bases warrants closer studies in order to model and

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understand how these compounds act on the active sites of Ziegler–Natta catalysts. Computational methods combined with experimental data were used to explain the interactions between the active site and the α -olefin. Giunchi et al. [9] and Novaro et al. [10] were the first to study the Cossee [11] mechanism. They used an ab initio all-electron restricted Hartree–Fock method to study a complete cycle of ethylene insertion in the active site of the Ziegler–Natta catalyst. The binding energies of a π -complex between propylene and the metallic center ($\text{CH}_3\text{TiCl}_2^+$) in a homogeneous system was found to be $-52.6 \text{ kcal mol}^{-1}$ with a transition state of $-35.8 \text{ kcal mol}^{-1}$ and an activation energy of $16.8 \text{ kcal mol}^{-1}$, as calculated using Hartree–Fock theory [12]. This value is in good agreement with the experimental activation energy ($11.6 \text{ kcal mol}^{-1}$) found in the literature for this polymerization [13].

Theoretical methods have also been used to study active sites of TiCl_4 and TiCl_3 heterogenized on the surface of MgCl_2 or SiO_2 in the presence or not of an internal electron donor [14]. The extended Hückel method was used to study the interaction between 2,2,6,6-tetramethylpiperidine and TiCl_4 on a MgCl_2 surface [15]. The interactions between alcohols, ketones, esters and the active site of a $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$ cluster was studied by means of the Hartree–Fock level calculations with the 3-21G basis set [16]. The insertion of ethylene and propylene in $\text{R-Ti}(\text{Cl}_2\text{AlH}_2)(2)(+)$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7$) was examined using ab initio self consistent field (SCF) methods and the many bodies perturbation theory [17]. Insertion of propylene into TiCl_4 on a MgCl_2 surface was also studied by means of density functional theory (DFT) [18–20].

The literature also describes the use of TiO_2 as support for Ti-based Ziegler–Natta catalysts [21,22]. However, the activity of TiCl_4 supported on TiO_2 for polymerization of ethylene is lower than $20 \text{ kg PE/mol cat h bar}$. It is possible to improve the activity of the catalytic system by the reduction of the Ti(IV), found on the anatase surface, to Ti(III) which can be

accomplished by ultraviolet irradiation or adding organometallic reagents. Using this improved catalyst, the activity for ethylene polymerization was found to increase from $20 \text{ kg PE/mol Ti h bar}$ [23] to $7600 \text{ kg PE/mol Ti h bar}$ [24]. The catalytic system is also active for propylene polymerization, giving $300 \text{ kg PP/mol Ti h bar}$ with the high isotacticity of 78% [25]. The high molecular weight ($410\,000 \text{ kg/mol}$) of the polyethylene produced with this catalyst and the relatively low polydispersity ($M_w/M_n = 2.2$) is comparable to those obtained with homogeneous metallocene catalysts. No theoretical study of this catalytic system is described in the literature.

In this work, we report the first simulation of the insertion of propylene in TiCl_3 heterogenized on reduced anatase. Ab initio calculations of Hartree–Fock and density functional level theory were used to calculate energies and obtain electronic information about the $\text{TiCl}_3\text{-TiO}_2$ (red.) system. The behavior of a Lewis base, such as methyl benzoate, on this new catalytic system was also studied. The experimental results of the propylene polymerization with $\text{Al}(\text{CH}_3)_3/\text{TiCl}_3$ on the surface of reduced anatase, obtained by Schuchardt et al. [25] were used as a guide for the theoretical investigations.

2. Computational methods

The geometries and energies of reactants, intermediates, transition states, and products were calculated using two different levels: restricted Hartree–Fock and density functional theory. The structures of all compounds were fully optimized at the Hartree–Fock level with the 3-21G basis set. Electronic correlation effects were included in the density functional calculations using the B3LYP functional and a 3-21G basis set. The calculations using the B3LYP functional were carried out on opti-

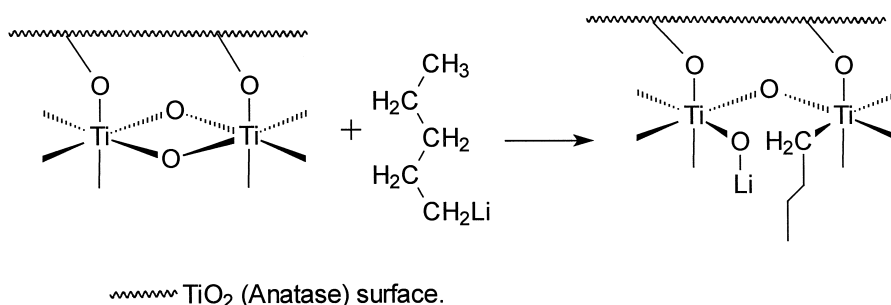


Fig. 1. Reduction of the anatase surface by butyl lithium.

mised geometries obtained at the HF level. Atomic charges were computed using Mulliken's populational analysis at both levels of the HF theory. All calculations were done using the GAUSSIAN 94 program [26].

3. Results and discussions

Experimental steps, carried out in our laboratory for the preparation of polypropylene, were used to model the basic structures of the reactants and other molecular species in this theoretical work.

The first experimental step is the reduction of titanium dioxide. In this reaction, butyl lithium is attached to the TiO₂ surface (anatase). The reaction is presented in Fig. 1. The addition of butyl lithium causes the reduction of Ti(IV) to Ti(III). This causes the appearance of defects at

the edges of the crystals where titanium tetrachloride will impregnate in a second step. This second reaction is represented in Fig. 2. The reduced TiO₂ surface reacts with TiCl₄ giving off lithium chloride.

The theoretical simulation of these two initial steps was carried out considering that the TiO₂ (anatase) surface could be approximately described by Ti structure **1** as shown in Fig. 3. Hydrogen atoms were used in order to saturate the valence electrons of Ti, thus providing an octahedral structure as observed in anatase. Although the hydrogen atoms are not the best species to represent the effect of the neighbourhood of titanium, they provide a feasible computational device necessary to lower computational costs. The reaction of Ti complex **1** with TiCl₄ is shown in Fig. 3. The calculated Hartree–Fock energy of this step was found to be $-51.5 \text{ kcal mol}^{-1}$, suggesting a reasonable release of energy by this reaction. The evolution

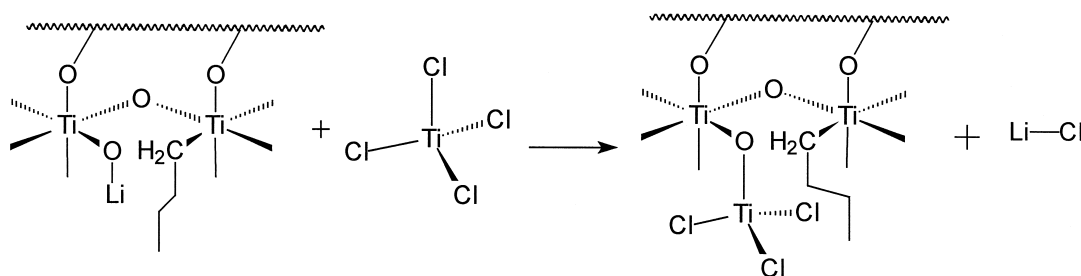


Fig. 2. Reaction of titanium tetrachloride with the reduced anatase surface.

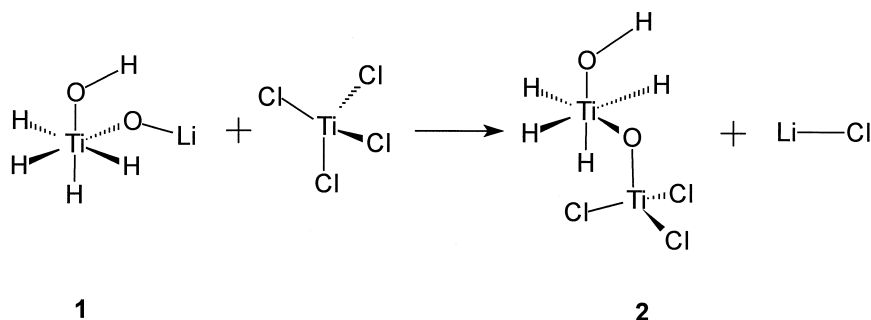


Fig. 3. Schematic representation of the reaction of anatase with titanium tetrachloride.

of this reaction by the DFT method provided a smaller release of energy, $-24.8 \text{ kcal mol}^{-1}$. However, even with a significant difference between the results, the product, **2**, is considerably more stable than the reactants.

The next step in the simulation of the catalyst preparation is the insertion of the co-catalyst, trimethylaluminium, which produces the active site (Fig. 4). The energy of the resulting structure **3**, is predicted to be lower than that of a TiCl_3 crystallite on a titanium dioxide surface by $-33.0 \text{ kcal mol}^{-1}$ using Hartree–Fock and $-20.2 \text{ kcal mol}^{-1}$ using the B3LYP functional. The proposed structure for the active site follows Cossee’s mechanism, where the co-catalyst participates in the formation of this site. The effective participation of the co-catalyst can be described by a shift of an alkyl group from the co-catalyst to the heterogenized Ti chloride (Fig. 4). The aluminium atom in this structure

has tetrahedral geometry while the active titanium is converted to a trigonal bipyramid. Some interesting electronic aspects can also be observed in the catalyst. The Ti atomic charge of the active site presents a significant change independent of calculations using the Hartree–Fock or the B3LYP level. The charge changed from 1.510 in **2** to 1.660 for **3** at the SCF level. At the DFT level, the change was from 1.090 to 1.190. This reduction of electron density at Ti suggests that the active site is more electrophilic, favouring coordination of the olefin as a π -complex.

The preparation of the catalyst is completed with the coordination of a Lewis base as internal donor. The schematic representation for this reaction is shown in Fig. 5. Once more, the SCF and DFT results indicate a stable final complex, **4**. The SCF energy for this reaction was found to be $-29.9 \text{ kcal mol}^{-1}$ while DFT gave a

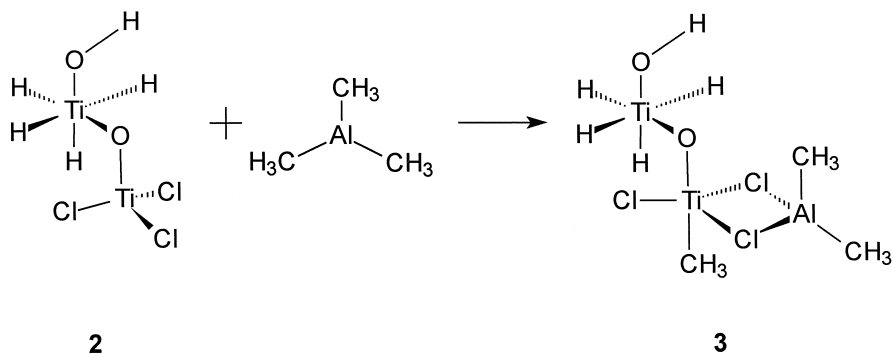


Fig. 4. Insertion of trimethylaluminium in heterogenized TiCl_3 .

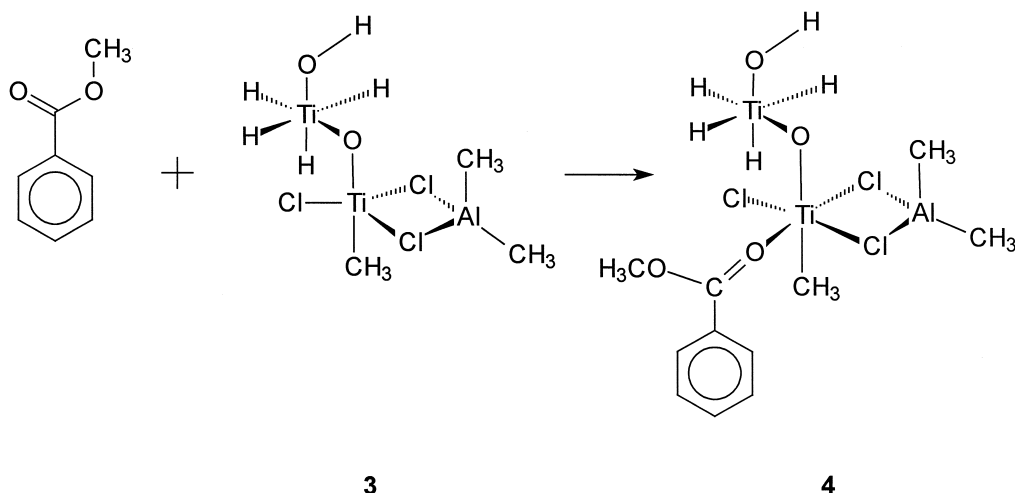
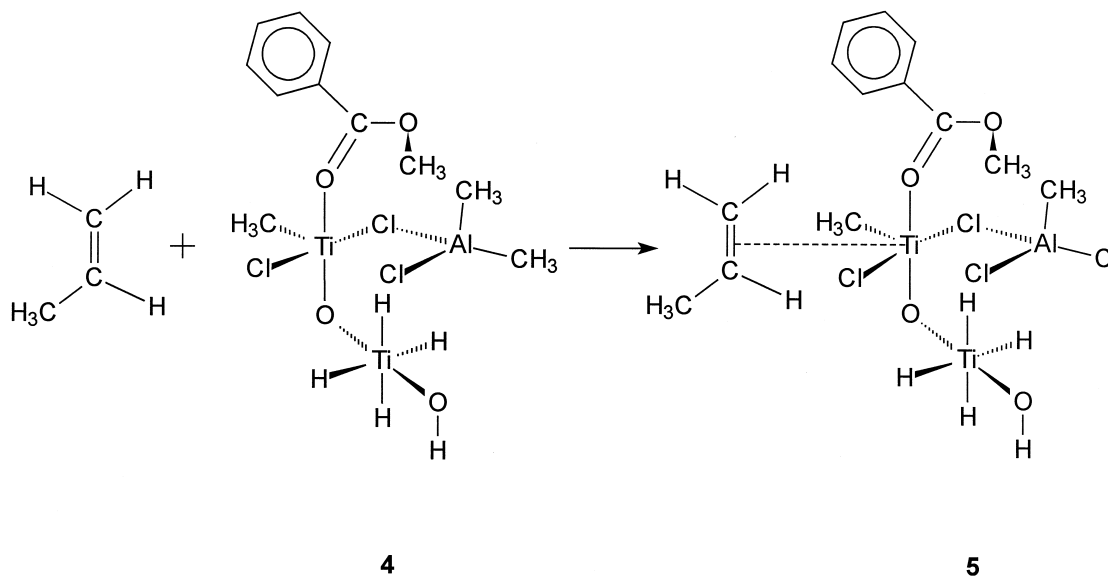


Fig. 5. Coordination of methyl benzoate to the active site.

change in energy of $-29.5 \text{ kcal mol}^{-1}$. A comparison between the results shows an excellent agreement between both methods. The atomic charge of titanium in **4** became more positive than in the previous species **3**. It is equal to 1.799 at the SCF level and 1.281 using the B3LYP functional, and the Lewis base coordinates to the transition metal through the oxy-

gen of the carbonyl group. The increase in the atomic charge is consistent with suggestions reported in the literature. According to Puhakka et al. [27], the inclusion of the electron donor makes the active site more reactive towards α -olefins. At this stage, the geometry of titanium in TiCl_3 is octahedral. It is also observed that one of the chlorine atoms presents a longer

Fig. 6. π -Complex formation at the active site.

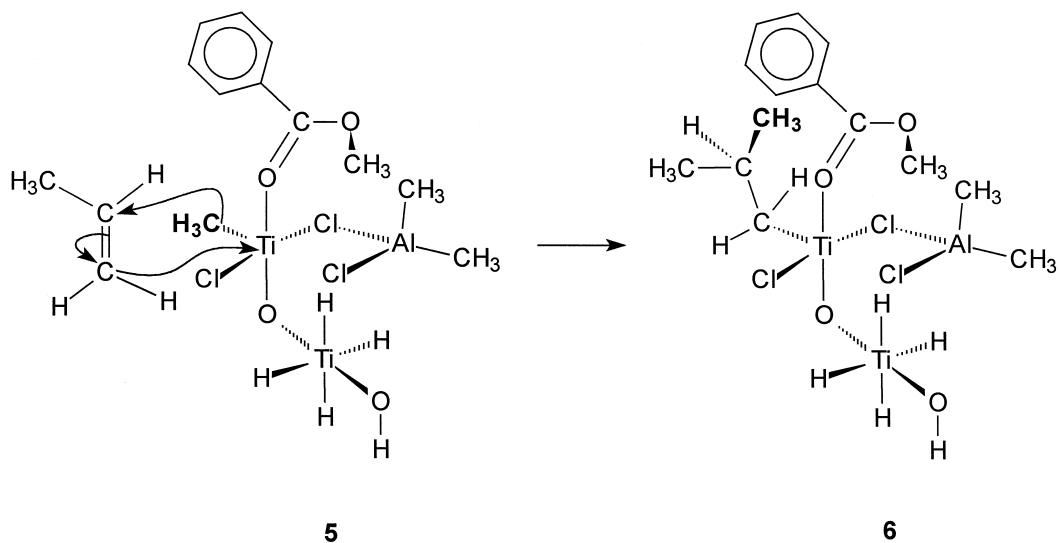


Fig. 7. Insertion of propylene in the active site.

bond length (Ti–Cl = 3.39 Å) than those of the other two chlorine atoms (Ti–Cl = 2.79 Å and 2.47 Å). Under these conditions, it is fair to say that the catalytic site is activated and the polymerization can start.

The next step involves the approach of the α -olefins to the catalytic site (Fig. 6). This approach forms the π -complex **5**, which is $-15.8 \text{ kcal mol}^{-1}$ more stable than the reagents

when calculated at the SCF level. DFT gives exactly the same result. Cossee's mechanism suggests that after π -complex formation, the α -olefins forms a four-member cyclic transition state. An alkyl group is then transferred to the olefin which now forms a σ -bond with the transition metal atom to form **6** and the carbonic chain starts to grow (Fig. 7). The energy of this process was calculated to be $-18.7 \text{ kcal mol}^{-1}$

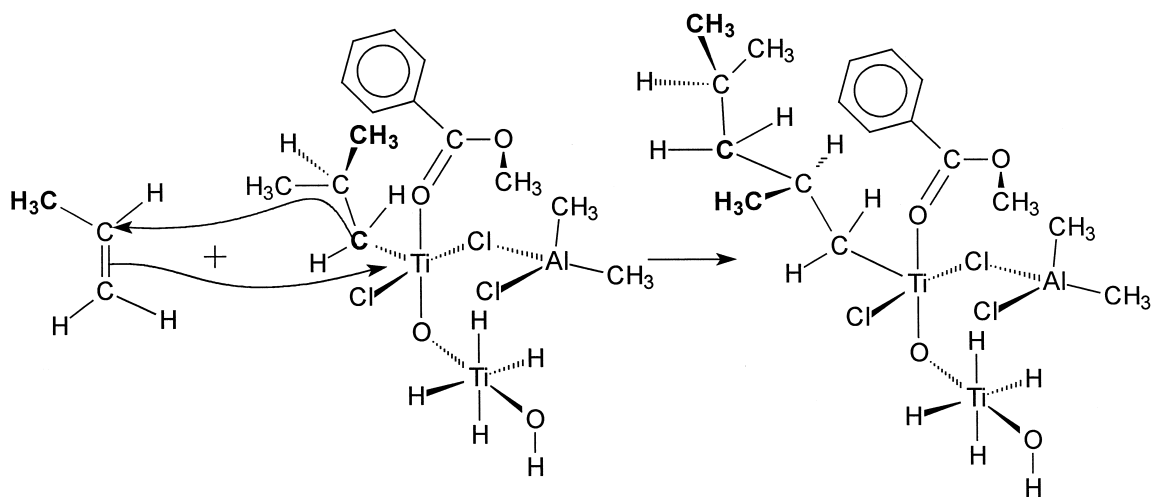


Fig. 8. Chain growth at the active site.

at the SCF and $-21.3 \text{ kcal mol}^{-1}$ at the DFT level. The total stabilization energy of these two steps is $-34.5 \text{ kcal mol}^{-1}$ and $37.1 \text{ kcal mol}^{-1}$ according to both SCF and DFT calculations, respectively.

A second π -complex is then formed as showed in Fig. 8. The second π -complex is $4.0 \text{ kcal mol}^{-1}$ (SCF) or $4.4 \text{ kcal mol}^{-1}$ (DFT) less stable than the first one, reducing its formation energy to $-11.8 \text{ kcal mol}^{-1}$ and $-11.4 \text{ kcal mol}^{-1}$, respectively. This increase in the electronic energy can be associated with an enhanced steric hindrance around the catalytic site.

The results of all steps are summarized in Table 1 and show clearly that the B3LYP/3-21G energies are similar to the Hartree–Fock results except for the two steps of the active site preparation.

A remarkable change in the Ti atomic charge found in the calculations (Fig. 9) shows the evolution of the catalytic site. The rise of the atomic charge makes the active site more susceptible to an approximation of the olefin and explains the unique behavior of Ziegler–Natta catalysts.

A theoretical analysis of propylene polymerization catalyzed by TiCl_3CH_3 was carried out by Kawamura-Kuribayashi et al. [12]. A comparison between the calculated energy of

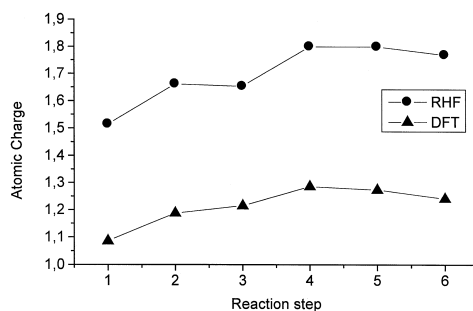


Fig. 9. Evolution of the atomic charge with the subsequent reaction steps.

the first insertion presented in Table 1 and Kawamura-Kuribayashi et al.'s results shows interesting aspects. The energies calculated by us ($-34.5 \text{ kcal mol}^{-1}$ at the SCF level and $-37.1 \text{ kcal mol}^{-1}$ using B3LYP) are significantly higher than that obtained by Kawamura-Kuribayashi et al. ($-52.6 \text{ kcal mol}^{-1}$). This result is expected because Kawamura-Kuribayashi et al. did not use a supported system in their calculations. Our calculations attempt to simulate a heterogeneous system and the steric hindrance is considerably higher compared to an unsupported system. The reduction in energy found in this work would also explain why the catalytic activity is lower for the supported system.

4. Conclusions

The subsequent reactions steps found by our calculations are in total agreement with the standard reaction mechanism described in the literature. The electronic density of the active center is reduced with the addition of the co-catalyst and the Lewis base, thus confirming that a Lewis base added in the correct proportion activates the catalyst. With exception of the first two steps, a good agreement between ab initio Hartree–Fock calculations and density functional theory was observed. Furthermore, the energy of the first insertion of propylene in the active site was found to be higher for the

Table 1

Total energies for the subsequent reaction steps calculated by the Hartree–Fock (HF) theory and density functional theory (B3LYP) with the 3-21G basis set. (DFT/3-21G energies calculated for geometries optimized by Hartree–Fock theory.)

Reaction	ΔE electronic (kcal mol^{-1})	
	RHF/ 3-21G	DFT/ 3-21G
Addition of the TiCl_4 on reduced TiO_2	-51.5	-24.8
Addition of the co-catalyst on $\text{TiCl}_3/\text{TiO}_2$ system	-33.0	-20.2
Addition of the Lewis base in the catalytic system	-29.9	-29.5
π -Complex formation	-15.8	-15.8
Chain growth	-18.7	-21.3
Second propylene insertion	-11.8	-11.4

supported catalyst than for unsupported catalysts, which is due to steric hindrance.

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