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ARTICLE

# Moving up and down the Titanium Oxidation State in Ziegler−Natta Catalysis

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ABSTRACT: DFT molecular modeling studies were undertaken to shed light on possible activation and deactivation mechanisms of Ziegler−Natta catalytic systems, as well as on the possible mechanisms for their reactivation by organohalides. We focused our efforts on Ti species attached to the (110) lateral cut of $MgCl_2$. First, the possible activation of adsorbed $TiCl_4$ leading to an adsorbed $Ti^{III}$ species bearing a Ti−alkyl bond and a coordination vacancy, which is a species able to undergo chain-growth, was considered. According to our calculations formation of the first active species can be easily rationalized by cleavage of a Ti−Cl bond of coordinated $TiCl_4$ by $AlEt_3$, followed by transalkylation promoted by another $AlEt_3$ molecule. Second, we investigated the possible reduction of polymerization active $Ti^{III}$ species leading to polymerization inactive $Ti^{II}$ species, and we found that a Ti−H bond, possibly formed after chain termination, is weaker than the Ti-Et (polymeryl) bond. Third, we investigated the mechanism of reactivation of $Ti^{II}$ species by organohalides, and it was concluded that reoxidation by Cl rich organohalides is thermodynamically more favored.

## Introduction

The discovery of Ziegler−Natta (ZN) polymerization in 1953 is probably the most important achievement in the field of synthetic polymer chemistry during the past half-century.[1,2] Modern ZN catalysts for the industrial production of polyolefins are based on $TiCl_4$ supported on activated $MgCl_2$.[3] Yet, despite more than 50 years have passed, the mechanism of polymerization from Ti activation to its deactivation included, is still not fully understood. This situation despite of several experimental[4−9] and theoretical[10−15] studies has provided remarkable insight. The picture emerging from the above characterization studies supports the formation of preferential cuts on $MgCl_2$ crystallites corresponding to the more stable (104) and less stable (110) planes.[13,16] On these coordinatively unsaturated $Mg^{2+}$ ions the chemisorption of $TiCl_4$ molecules is likely to occur and a variety of active site structures have been proposed.[17,18] However, calculations indicate that $TiCl_4$ coordination to the (104) plane is rather weak or even unstable, whereas $TiCl_4$ coordination to the (110) plane is energetically quite favored.[19−22] This raises the hypothesis that the polymerization active $TiCl_4$ actually coordinates to the less stable (110) plane. Further, models have been proposed that explain in a simple way the stereoselective induction promoted by Lewis bases when coordinated in the near proximity of a $TiCl_4$ molecule adsorbed on the less stable (110) plane.[23] These results suggest that the active Ti atoms might be coordinated on the (110) plane or could have a local environment similar to that assumed after coordination on the (110) plane. For this reasons, an octahedral Ti atom adsorbed on the (110) plane is becoming sort of a good model of the real active species. As mentioned before, this model has been used to rationalize the role of the Lewis bases in conferring the experimentally observed stereoselectivity in both primary[24−26] and secondary[27] propene insertion. Further, in the framework of the three sites model, an octahedral Ti atom adsorbed on the (110) plane can easily rationalize the presence of the majority of stereomistakes into block of lower stereoregularity.[27,28]

However, this reasonably good understanding of the behavior of this possible active species during chain growth is counterbalanced by the scarce knowledge we have of the activation steps, and of the way the initial $Ti^{IV}$ atom of the adsorbed $TiCl_4$ molecule is reduced to $Ti^{III}$, and the way the first Ti−C bond is formed by reaction of the adsorbed Ti species with the Al cocatalyst. Indeed, it is well-known that in ZN polymerization of both ethene ad propene the Ti atoms exist in several oxidation states, +2, +3, and +4, and the well-accepted idea is that $Ti^{III}$, formed from reduction of $Ti^{IV}$, is the active oxidation state, whereas further reduction to $Ti^{II}$ greatly reduces polymerization activity, or actually completely deactivates the metal center.[29,30] The most used approach to reactivate the $Ti^{II}$ centers back to $Ti^{IV}$ is to add organohalides, such as $CCl_4$, $CHCl_3$, $ClCH_2CH_2Cl$, chlorocyclohexane, or even $Cl_2$, as oxidizing agents.[31,32] The restored $Ti^{IV}$ centers can be activated again, which increases the overall activity.[33] Following this scheme, Cl containing compounds or organohalides has been commonly used as activity promoters for vanadium based,[34−36] and titanium based ZN catalysts.[37,38]

Despite the relevance of the activation step, and of the possible ways in which the Ti center can be oxidized and/or reduced, little efforts have been performed from a theoretical point of view to shed light on these points. The most noticeable exception is a recent and valuable study that offered a reasonable overview of the activation steps.[39] However, this study often relies on bimetallic models that possibly can be present during activation, but we still believe that activation should preferentially occur on a monometallic Ti species. Further, deactivation to $Ti^{II}$, as well the possible reactivation via oxidation by halocompounds, was not investigated.

In this contribution, we try to fill this gap, and DFT studies were undertaken in the attempt to shed light on possible pathways for

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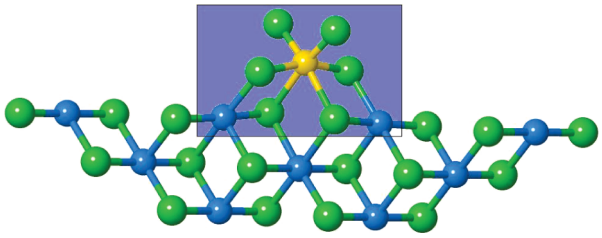


**Figure 1.** Structure of $TiCl_4$ adsorbed on the $(MgCl_2)_9$ cluster. The only atoms relaxed in the geometry optimizations are those in the blue box.

the change of the Ti oxidation state from $Ti^{IV}$ to $Ti^{III}$ initially, with inclusion of possible pathways for the formation of the first Ti−C bond, which actually corresponds to the Ti activation. Then, we explored possible pathways that would reduce $Ti^{III}$ to $Ti^{II}$, which corresponds to Ti deactivation, and finally, we explored the possible reactivity through which organohalides could reoxidize $Ti^{II}$ to $Ti^{IV}$, reintroducing them into the active cycle.

In this study we focused on a $TiCl_4$ molecule octahedrally coordinated on the (110) $MgCl_2$ surface since, as previously mentioned, there is growing evidence that the real active Ti species could have a similar environment. Further, most of the reactions considered, for example the breaking of a Ti−Cl bond assisted by the Al cocatalyst, require a change of the electronic state of the Ti species from singlet to doublet. Modeling the transition state for reactions with a change in the electronic state is computationally a real challenge that would prevent to investigate the large number of reactions we considered. For this reason, in these cases we only focused on the thermodynamics of the reaction, to exclude some reactivity and highlight those reactions that can actually occur. Otherwise, when we focused on a reaction with no change in the electronic state, we followed the classical approach in which all the steps (intermediates and transition states between reactants and products) were investigated.

## Models and Computational Details

**Active Site Models.** A semiflexible $(MgCl_2)_9$ cluster was used in all the simulations to support the monometallic Ti species; see Figure 1. The $MgCl_2$ bulk was assumed to be in the α crystalline phase, and the surface was modeled as a (110) monolayer. During the geometry optimizations all the atoms involved in Ti coordination were relaxed, while the remaining part of the $MgCl_2$ cluster was frozen in the position of the ideal crystal. For example, in case of $TiCl_4$ coordination the relaxed atoms are those in the blue box in Figure 1. All the systems were modeled similarly, with the exception of those to obtain the energy profile for the transalkylation reaction, where a completely relaxed $(MgCl_2)_3$ cluster was used.

In case of $Ti^{IV}$ species the singlet electronic state is favored, and thus closed shell calculations were performed. Differently, for $Ti^{III}$ and $Ti^{II}$ unrestricted calculations were performed, since $Ti^{III}$ has one unpaired electron, while for $Ti^{II}$ we found that a triplet electronic state with two unpaired electrons is favored relative to the singlet electronic state. Unrestricted calculations were performed for all the radical species involving main group atoms.

**DFT Calculations.** The DFT calculations were carried out using the Turbomole 6.1[40] and the Gaussian03[41] packages, and the B3LYP hybrid GGA functional of Becke-Lee, Parr, and Yang was adopted.[42,43] The Gaussian package was used only in the direct transalkylation reaction of Figure 2, due to an easier handling of the transition state searches. In the Turbomole calculations the electronic configuration of the atoms was described by a triple-ζ basis set augmented with two polarization functions (Turbomole basis set TZVPP).[44] In the Gaussian03 calculations the triple-ζ basis set augmented with one polarization functions of Ahlrichs and co-workers was used (TZVP keyword in Gaussian).[45]

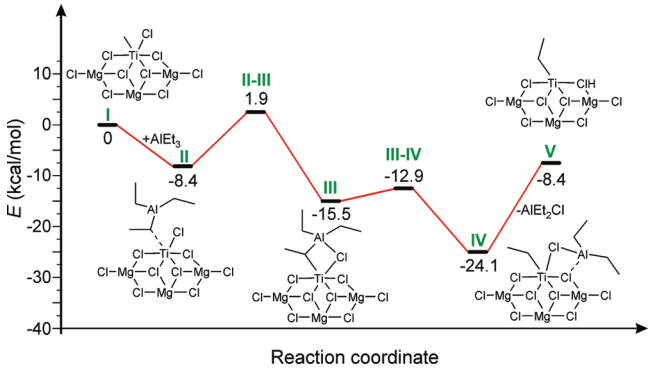



**Figure 2.** Energy profile, in kcal·mol$^{-1}$, of the direct transalkylation reaction.

**Table 1. Thermodynamics of the Homolytic Dissociation, $\Delta E_{diss}$ in kcal·mol$^{-1}$, of a Cl Atom from an Adsorbed $TiCl_4$**

| | reaction | $\Delta E_{diss}$ |
|---|---|---|
| 1 | $TiCl_4 \rightarrow TiCl_3^{\bullet} + Cl^{\bullet}$ | 83.1 |
| 2 | $[Mg]/TiCl_4 \rightarrow [Mg]/TiCl_3^{\bullet} + Cl^{\bullet}$ | 62.3 |
| 3 | $[Mg]/TiCl_4 + AlCl_3 \rightarrow [Mg]/TiCl_3^{\bullet} + AlCl_4^{\bullet}$ | 42.5 |
| 4 | $[Mg]/TiCl_4 + Al_2Cl_6 \rightarrow [Mg]/TiCl_3^{\bullet} + Al_2Cl_7^{\bullet}$ | 54.0 |
| 5 | $[Mg]/TiCl_4 + AlEt_3 \rightarrow [Mg]/TiCl_3^{\bullet} + AlEt_3Cl^{\bullet}$ | 8.8 |
| 6 | $[Mg]/TiCl_4 + Al_2Et_6 \rightarrow [Mg]/TiCl_3^{\bullet} + AlEt_3 + AlEt_3Cl^{\bullet}$ | 25.8[a] |
| 7 | $[Mg]/TiCl_4 + CH_2CH_2 \rightarrow [Mg]/TiCl_3^{\bullet} + CH_2CH_2Cl^{\bullet}$ | 44.8 |

[a] Assuming a value of 17 kcal mol$^{-1}$ for the enthalpy of dissociation of $Al_2Et_6$.[46]

## Results and Discussion

**Formation of the First Vacancy on Ti.** Considering the chemical species in the polymerization medium, three principal different paths can be envisaged for the reduction of adsorbed $TiCl_4$. All of them basically consist of the homolytic breaking of a dangling Ti−Cl bond: (i) Spontaneous dissociation; (ii) dissociation induced by a reducing agent such as $AlCl_3$, $Al_2Cl_6$, and $AlEt_3$; (iii) dissociation promoted by $C_2H_4$. The thermodynamics of these reactions is reported in Table 1.

To understand better the role of the support in assisting dissociation of the Ti−Cl bond, we first calculated the $\Delta E_{diss}$ of the Ti−Cl bond in free $TiCl_4$, 83.1 kcal mol$^{-1}$, entry 1 in Table 1. The spontaneous dissociation of Ti−Cl bond of a $TiCl_4$ molecule adsorbed on a $MgCl_2$ layer, entry 2 in Table 1, still is highly endothermic, 62.3 kcal·mol$^{-1}$, indicating that the $MgCl_2$ support scarcely assists the homolytic breaking of a Ti−Cl bond, excluding thus the spontaneous pathway. Moving to dissociation assisted by Al compounds as acceptors of the extracted Cl atom, the monomeric $AlCl_3$, entry 3 in Table 1, reduces $\Delta E_{diss}$ to 42.5 kcal·mol$^{-1}$, while the dimeric form, entry 4 in Table 1, with a $\Delta E_{diss}$ of 54.0 kcal·mol$^{-1}$, is less effective. This can be related to the more acidic behavior of monomeric $AlCl_3$. Nevertheless these numbers indicate that the reduction process promoted by either monomeric or dimeric Al−chloride compounds remains thermodynamically very unfavored. This finding is consistent with Skalli's results, who suggested that $AlCl_3$ does not assist reduction of $TiCl_4$.[33]

Since $AlEt_3$ is the most used reducing agent in ZN catalysis, we explored to which extent Al−alkyl compounds are better than Al−chlorides compounds to promote Ti−Cl dissociation. In the presence of $AlEt_3$, entry 5 in Table 1, $\Delta E_{diss}$ amounts to

8.8 kcal·mol$^{-1}$ only. A value that is far smaller than that calculated for $AlCl_3$, and a value that can be easily reached by moderate heating of the reaction media.

Since $AlEt_3$ is dimeric (the dimerization enthalpy in hexadecane is 17 kcal mol$^{-1}$),[46,47] Ti activation promoted by Al−alkyl compounds first requires dissociation of $Al_2Et_6$, and this energetic cost should be added to the $\Delta E_{diss}$ of Table 1, which results in an approximated $\Delta E_{diss}$ of 25.8 kcal mol$^{-1}$, entry 6 in Table 1. Nevertheless, it is worth noting that the free energy of dissociation of $Al_2Et_6$ should roughly cost 7 kcal mol$^{-1}$ (the enthalpy of dissociation, 17 kcal mol$^{-1}$, minus roughly 10 kcal mol$^{-1}$ as the entropy gain for dissociation of a bimolecular species), which should result in a fraction of monomeric $AlEt_3$ present in the reaction media.[50]

The ability of $AlEt_3$ to assist dissociation of a Ti−Cl bond is in the oxidative power of the liberated Cl atom, that attacks the Al center by nearly expelling one rather stable Et radical. This conclusion is supported by the strong exothermicity of the $AlEt_3 + Cl^{\bullet} \rightarrow AlEt_3Cl^{\bullet}$ reaction, 46.9 kcal mol$^{-1}$, and by the strong asymmetric elongation of the Al−Et bonds in $AlEt_3Cl^{\bullet}$. In fact, while two of the Al−Et bonds in $AlEt_3Cl^{\bullet}$ are substantially unchanged from the value of 1.99 Å in $AlEt_3$, the third Al−Et bond is 2.42 Å long.

These results indicate that $AlEt_3$, besides being needed to initiate the polymerization process by formation of the first Ti−C bond, facilitates the reduction process.[33] Further, the $\Delta E_{diss}$ we calculated for the dissociation of a Ti−Cl bond assisted by $AlEt_3$ is smaller than the energy required to dissociate the O−O bond of benzyl peroxide, 22.7 kcal·mol$^{-1}$, a classical radical initiator with a half-life time of 7.2 min in toluene at 100 °C.

Finally, we also investigated if the monomer, which is the predominant species in the polymerization medium, could promote dissociation of the Ti−Cl bond. Interestingly, the $\Delta E_{diss}$ of a Ti−Cl bond assisted by ethylene, 44.8 kcal·mol$^{-1}$, entry 6 in Table 1, compares well with the $\Delta E_{diss}$ of $AlCl_3$, and seems to be more effective than $Al_2Cl_6$. Nevertheless, of all the dissociation processes we considered, the only one that seems viable is that assisted by $AlEt_3$, either as a monomer or as a dimer.

**Formation of the First Ti−C Bond.** After having explored the possible pathways for the formation of the first vacancy on Ti, with reduction of $Ti^{IV}$ to $Ti^{III}$, we moved to the possible pathways leading to formation of a Ti−C bond. We considered two mechanisms: (i) transalkylation by $AlEt_3$, which would form in a single step the $Ti^{III}$ active species with a Ti−C bond and a vacancy on the Ti atom ready for monomer coordination; (ii) a two steps mechanism with reoxidation of the $Ti^{III}$ center by $AlEt_3Cl^{\bullet}$ formed during activation by $AlEt_3$ first, followed by homolytic dissociation of the remaining Ti−Cl dangling bond. These paths are shown in Scheme 1.

Direct transalkylation, entry 1 in Table 2, is favored by 4.4 kcal·mol$^{-1}$, which indicates the thermodynamic feasibility of this reaction. Considering that direct transalkylation does not require a change in the spin state, we decided to investigate the exact mechanism. For these calculations we abandoned the semiflexible $MgCl_2$-cluster approximation and, as described in the Models and Computational Details, all the atoms have been relaxed. The energy profile is reported in Figure 2.

The first step is coordination of $AlEt_3$ to the Ti center through an ethyl group. The corresponding coordination intermediate **II** is 8.4 kcal·mol$^{-1}$ below the separated species, indicative of an already reasonable interaction between the Ti and $AlEt_3$. The reaction proceeds through transition states **II**−**III**, at 10.3 kcal·mol$^{-1}$ above **II**, in which the Al

**Scheme 1**

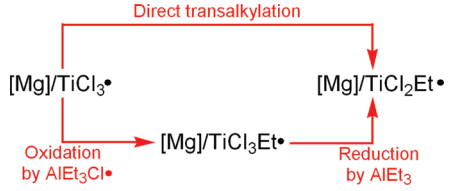



**Table 2. Thermodynamics, in kcal·mol$^{-1}$, Associated with the Formation of the First Ti−C Bond**

| | reaction | $\Delta E$ |
|---|---|---|
| 1 | $[Mg]/TiCl_3^{\bullet} + AlEt_3 \rightarrow [Mg]/TiCl_2Et^{\bullet} + AlEt_2Cl$ | −4.4 |
| 2 | $[Mg]/TiCl_3^{\bullet} + AlEt_3Cl^{\bullet} \rightarrow [Mg]/TiCl_3Et + AlEt_2Cl$ | −19.2 |
| 3 | $[Mg]/TiCl_3Et \rightarrow [Mg]/TiCl_2Et^{\bullet} + Cl^{\bullet}$ | 68.3 |
| 4 | $[Mg]/TiCl_3Et \rightarrow [Mg]/TiCl_3^{\bullet} + Et^{\bullet}$ | 25.8 |
| 5 | $[Mg]/TiCl_3Et + AlEt_3 \rightarrow [Mg]/TiCl_2Et^{\bullet} + AlEt_3Cl^{\bullet}$ | 14.9 |
| 6 | $[Mg]/TiCl_3Et + AlEt_3 \rightarrow [Mg]/TiCl_3^{\bullet} + AlEt_4^{\bullet}$ | 21.4 |

center attacks the dangling Cl atom, leading to intermediate **III**, which lies 15.5 kcal·mol$^{-1}$ below the starting species **I**. Intermediate **III** is a bridged structure in which one of the Et groups and the Cl atom connect the Al and the Ti centers. The breaking of intermediate **III** occurs through transition state **III**−**IV**, at 2.6 kcal·mol$^{-1}$ above **III**, and leads to intermediate **IV**, 24.1 kcal·mol$^{-1}$ below the starting species **I**, due to a strong interaction between the Al center and one Cl atoms bridging the Ti center to the support. Dissociation of $AlEt_2Cl$ from **IV** leads to **V**, which is the starting point for chain growth. In case of the relaxed $MgCl_2$ cluster the transalkylation step from **I** to **V** is favored by 8.4 kcal·mol$^{-1}$, while in case of the rigid $MgCl_2$ cluster model it was favored by 4.4 kcal·mol$^{-1}$, entry 1 in Table 2, which indicates that the exact model used has not a dramatic effect on the calculated energies.

The second possible mechanism for the formation of the first Ti−C bond is related to the reaction of $[Mg]/TiCl_3^{\bullet}$ with $AlEt_3Cl^{\bullet}$; see Scheme 1. Since this two steps mechanism involves a change in the spin state, we only considered the thermodynamic feasibility of the two steps. As expected, the former step, which corresponds to the association of two radical species, is strongly favored (by 19.2 kcal·mol$^{-1}$, entry 2 in Table 2). This step leads to the formation of $[Mg]/TiCl_3Et$, which can undergo to either Ti−Cl dissociation, leading to the $[Mg]/TiCl_2Et^{\bullet}$ active species, or Ti−Et dissociation, leading back to $[Mg]/TiCl_3^{\bullet}$. The Ti−Cl bond, with a $\Delta E_{diss}$ of 68.3 kcal·mol$^{-1}$, entry 3 in Table 2, is only 6.0 kcal·mol$^{-1}$ stronger than a Ti−Cl bond in $[Mg]/TiCl_4$, but it is far stronger than the Ti−Et bond, for which a $\Delta E_{diss}$ of only 25.8 kcal·mol$^{-1}$, entry 4 in Table 2, was calculated. These numbers indicate that the Ti−Et bond is by far less stable than the Ti−Cl bond, and if any spontaneous dissociation occurs this would involve the Ti−Et bond. In line with the reduction of $[Mg]/TiCl_4$, we explored the effect of $AlEt_3$ in assisting dissociation of both Ti−Cl and Ti−Et from $[Mg]/TiCl_3Et$. Also in this case $AlEt_3$ is very effective in stabilizing the formed $Cl^{\bullet}$ atom, reducing the $\Delta E_{diss}$ of the Ti−Cl bond to 14.9 kcal·mol$^{-1}$, entry 5 in Table 2. Differently, the $Et^{\bullet}$ radical is slightly stabilized by $AlEt_3$, since the $\Delta E_{diss}$ decreases to 21.4 kcal·mol$^{-1}$ only. Of relevance, however, is the fact that in the presence of $AlEt_3$ dissociation of the Ti−Cl bond is thermodynamically favored by 6.5 kcal·mol$^{-1}$ over dissociation of the Ti−Et bond.

Concluding this section, calculations suggest that the most likely mechanism leading to formation of the first $[Mg]/TiCl_2Et^{\bullet}$ active species is direct transalkylation, which is in line with the accepted ideas in the field.

**Table 3. Thermodynamics of Deactivation, $\Delta E_{diss}$ in kcal·mol$^{-1}$, Associated with Reduction from $Ti^{III}$ to $Ti^{II}$**

| | reaction | $\Delta E_{diss}$ |
|---|---|---|
| 1 | [Mg]/$TiCl_2Et^{\bullet}$ → [Mg]/$TiCl_2$ + $Et^{\bullet}$ | 37.0 |
| 2 | [Mg]/$TiCl_2Et^{\bullet}$ → [Mg]/TiClEt + $Cl^{\bullet}$ | 109.9 |
| 3 | [Mg]/$TiCl_2H^{\bullet}$ →[Mg]/$TiCl_2$ + $H^{\bullet}$ | 45.2 |
| 4 | [Mg]/$TiCl_2Et^{\bullet}$ → [Mg]/TiCl + EtCl | 81.8 |
| 5 | [Mg]/$TiCl_2Et^{\bullet}$ + $AlEt_3$ → [Mg]/$TiCl_2$ + $AlEt_4^{\bullet}$ | 32.6 |
| 6 | [Mg]/$TiCl_2Et^{\bullet}$ + $AlEt_3$ → [Mg]/TiClEt + $AlEt_3Cl^{\bullet}$ | 56.4 |
| 7 | [Mg]/$TiCl_2H^{\bullet}$ + $AlEt_3$ → [Mg]/$TiCl_2$ + $AlEt_3H^{\bullet}$ | 23.0 |
| 8 | [Mg]/$TiCl_2Et^{\bullet}$ + $C_2H_4$ → [Mg]/TiClEt+ $CH_2ClCH_2^{\bullet}$ | 92.4 |
| 9 | [Mg]/$TiCl_2Et^{\bullet}$ + $C_2H_4$ → [Mg]/$TiCl_2$ + $C_4H_9^{\bullet}$ | 16.9 |
| 10 | [Mg]/$TiCl_2H^{\bullet}$ + $C_2H_4$ → [Mg]/$TiCl_2$ + $CH_3CH_2^{\bullet}$ | 2.9 |

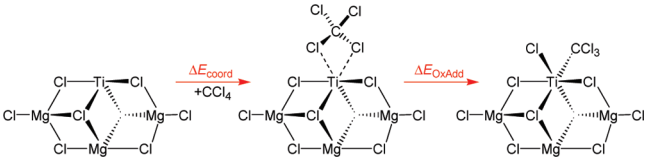
**Deactivation of the Catalyst Active Site.** As mentioned before, $Ti^{III}$ centers are supposed to be more active than $Ti^{II}$ centers, and catalysts deactivation is often associated with a reduction of $Ti^{III}$ to $Ti^{II}$, and at least six different mechanisms were proposed:[51] (i) spontaneous deactivation; (ii) deactivation by Al compounds; (iii) deactivation by the monomer; (iv) deactivation by molecular hydrogen; (v) deactivation by impurities or poison; (vi) deactivation by the electron donors. We investigated the thermodynamics of the first three deactivation mechanisms described above, while we did not consider deactivation by impurities or poison and deactivation by electron donors. Considering the rather unknown nature of the specie involved, and of actual Ti bonds that are broken, we considered the breaking of the Ti−Et bond as a model of the polymerization active species, the breaking of the Ti−H bond, which can be present after a classical $\beta$-H termination reaction or after chain termination by molecular hydrogen, and finally the breaking of a Ti−Cl bond that bridges the Ti species to the $MgCl_2$ surface. The energetic we obtained is reported in Table 3.

Entries 1−3 of Table 3 are an estimate of the relative strength of the bonds involved, and indicate that the Ti−Et bond, with a $\Delta E_{diss}$ of 37.0 kcal·mol$^{-1}$, is the weakest bond. The Ti−H bond, with a $\Delta E_{diss}$ of 45.2 is only 8.2 kcal·mol$^{-1}$ stronger, while extraction of a Cl atom bridging the Ti atom with the $MgCl_2$ surface, with a $\Delta E_{diss}$ of 109.9 kcal·mol$^{-1}$, is remarkably more expensive. Finally, we also considered that an Et-Cl species could be reductively eliminated, but also this possibility, entry 4 in Table 3, with a $\Delta E_{diss}$ of 81.8 kcal·mol$^{-1}$, is of high energy. Considering these values, it can be concluded that spontaneous dissociation of any species, with reduction to $Ti^{II}$, can be excluded.

The role of $AlEt_3$ in assisting reduction to $Ti^{II}$ is summarized in entries 5−7 of Table 3. In line with the results of the previous section, dissociation of a Ti−Et bond, with a $\Delta E_{diss}$ of 32.6 kcal·mol$^{-1}$, is scarcely assisted from $AlEt_3$, due to the instability of the formed $AlEt_4^{\bullet}$ species. Conversely, $AlEt_3$ is quite able to stabilize the $Cl^{\bullet}$ and $H^{\bullet}$ atoms, and thus dissociation of the Ti−H bond and of the bridging Ti−Cl bond, with $\Delta E_{diss}$ of 23.0 and 56.4 kcal·mol$^{-1}$, respectively, are quite reduced relative to the unassisted values, entries 2 and 3 in Table 3. Indeed, in presence of $AlEt_3$ the weakest bond is Ti−H, 9.6 kcal·mol$^{-1}$ weaker than the Ti−Et bond, and starts to be weak enough to represent a possible deactivation pathway in the industrially used reaction conditions.

Finally, we also investigated the possible role of the monomer, ethene in this case, to act as reducing agent, entries 8−10 in Table 3. While ethene also is unable to dissociate a Cl atom from the surface, entry 8 in Table 3, the low $\Delta E_{diss}$ of 16.9 and 2.9 kcal·mol$^{-1}$ for Ti−Et and Ti−H, respectively, indicates that olefins have the potential to deactivate the $Ti^{III}$ active species by promoting either Ti−Et or Ti−H dissociation. Of course, this is possible because of the high energy gain associated with formation of the C−C and C−H bonds. However, we believe that the main reaction involving ethene will be its coordination to the Ti center, which results in an energy gain of 13.2 and 2.5 kcal mol$^{-1}$ in case of a Ti−H or a Ti−Et bond, respectively, followed by ethylene insertion into these bonds, rather than Ti−H or Ti−Et dissociation.

**Scheme 2**




Concluding this section, calculations suggest that the most likely deactivation mechanism involves dissociation of a Ti−H bond. This conclusion is in qualitative agreement with the reduction in ethene polymerization activity observed when molecular hydrogen is added, since a higher concentration of Ti−H bonds should be formed at higher contents of molecular hydrogen. In case of propene polymerization, instead, molecular hydrogen is known to increase activity, which should be at odd with the above conclusion. However, in the case of propene polymerization, it is quite accepted that molecular hydrogen is able to reactivate a dormant site after a regiomistake.

**Oxidation by Organohalides.** One of the typical procedures to reactivate a $Ti^{II}$ species consists in the addition of organohalides that are supposed to reactivate the $Ti^{II}$ center by oxidizing it to $Ti^{IV}$. For this reason, in this section the oxidation of a $Ti^{II}$ center by different organohalides was studied. The pathway we considered is shown in Scheme 2 for $CCl_4$.

Preliminary calculations indicated that the favored electronic state in the uncoordinated [Mg]/$TiCl_2$ species, as well as after organohalide coordination, is a triplet with both unpaired electrons substantially localized on the $Ti^{II}$ center, with the singlet at least 20 kcal·mol$^{-1}$ higher in energy. Differently, after oxidative addition of the organohalide the favored electronic state of the resulting [Mg]/$TiCl_3CH_nCl_{3-n}$ ($n$ = 0−3) species is singlet, with the triplet at least 15 kcal·mol$^{-1}$ higher in energy. This implies that during the oxidative addition there will be a change in the electronic state of the system from triplet to singlet. For this reason, and in line with the previous sections, we limit the discussion to the thermodynamics balance of the reaction with a particular focus on a comparison between different organohalides. The calculated energies are reported in Table 4, entries 1−4. Each reaction is split between organohalide coordination to the [Mg]/$TiCl_2$ species and oxidative addition of the coordinate organohalide to the Ti center.

The reaction starts with the remarkable exothermic coordination ($\Delta E_{Coord}$ around 10−15 kcal·mol$^{-1}$) of the organohalides to the $Ti^{II}$ center. There is a regular decreasing trend of the coordination energy with the amount of Cl atoms in the organohalide, and coordination of $CCl_4$ is less favored. Coordination of the organohalides having more than one Cl occurs with two Cl atoms inducing a roughly octahedral coordination around the $Ti^{II}$ center, see Scheme 2. Natural population analysis (NPA)[52] of the free organohalides indicates that the NPA charge on the Cl atoms is −0.08e, −0.03e, 0.02e, and 0.05e on going from $CH_3Cl$ to $CCl_4$, which suggests that the decrease in the coordination energy with increasing the number of Cl atoms in the organohalide could be related to a decreased donor ability of the more halides rich molecules. The second step is the oxidative addition of the coordinated organohalide. In this case, the more Cl rich the organohalide the more favored is the oxidative addition step, see the $\Delta E_{OxAdd}$ in Table 4, with oxidative addition of

**Table 4. Thermodynamics, in kcal·mol$^{-1}$, of the Oxidation of a [Mg]/$TiCl_2$ Species by Reaction with $CH_nCl_{4-n}$ ($n = 0-3$)[a]**

| | reaction | $\Delta E_{Coord}$ | $\Delta E_{OxAdd}$ | $\Delta E_{Tot}$ |
|---|---|---|---|---|
| 1 | [Mg]/$TiCl_2$ + $CH_3Cl$ → [Mg]/$TiCl_3CH_3$ | −15.9 | −16.2 | −32.1 |
| 2 | [Mg]/$TiCl_2$ + $CH_2Cl_2$ → [Mg]/$TiCl_3CH_2Cl$ | −15.6 | −18.6 | −34.2 |
| 3 | [Mg]/$TiCl_2$ + $CHCl_3$ → [Mg]/$TiCl_3CHCl_2$ | −13.7 | −20.9 | −34.6 |
| 4 | [Mg]/$TiCl_2$ + $CCl_4$ → [Mg]/$TiCl_2CCl_3$ | −11.8 | −25.2 | −37.0 |
| 5 | [Mg]/$TiCl_2$ + $CH_3Cl$ → [Mg]/$TiCl_2CH_3$ + $Cl^•$ | | | +2.2 |
| 6 | [Mg]/$TiCl_2$ + $CH_2Cl_2$ → [Mg]/$TiCl_2CH_2Cl$ + $Cl^•$ | | | −4.3 |
| 7 | [Mg]/$TiCl_2$ + $CHCl_3$ → [Mg]/$TiCl_2CHCl_2$ + $Cl^•$ | | | −11.4 |
| 8 | [Mg]/$TiCl_2$ + $CCl_4$ → [Mg]/$TiCl_2CCl_3$ + $Cl^•$ | | | −19.8 |

[a] Entries 1−4 correspond to the organohalide oxidative addition associated with reactivation from $Ti^{II}$ to $Ti^{IV}$, $\Delta E_{Tot} = \Delta E_{Coord} + \Delta E_{OxAdd}$. Entries 5-8 correspond to the organohalide radical dissociation, associated with reactivation from $Ti^{II}$ to $Ti^{III}$.

$CCl_4$, with a $\Delta E_{OxAdd}$ of −25.2 kcal mol$^{-1}$, favored by 9.0 kcal mol$^{-1}$ over oxidative addition of $CH_3Cl$, with a $\Delta E_{OxAdd}$ of −16.2 kcal mol$^{-1}$. The trend in the $\Delta E_{OxAdd}$ correlates with the trend in the homolytic dissociation energy of the C−Cl bond in the organohalides considered, 80.6, 74.3, 67.1, and 58.6 kcal mol$^{-1}$ on going from $CH_3Cl$ to $CCl_4$. In other words, the higher energy gain associated with the oxidative addition of $CCl_4$ relative to $CH_3Cl$ can be related to the weaker C−Cl bond in $CCl_4$ relative to $CH_3Cl$. The final energy gain, $\Delta E_{Tot} = \Delta E_{Coord} + \Delta E_{OxAdd}$, reflects the trend of $\Delta E_{OxAdd}$, although the differences between the various organohalides are reduced in magnitude.

Finally, since $CCl_4$ is also known for its radical chemistry, we evaluated the possibility that the $Ti^{II}$ is oxidized to a $Ti^{III}$ center by $CCl_4$ through homolytic dissociation of one C−Cl bond. For the sake of consistency we extended this calculation to all the organohalides considered, etries 5−8 in Table 4. The $\Delta E_{Tot}$ reported in Table 4, indicate that $CH_3Cl$ and $CH_2Cl_2$, with a $\Delta E_{Tot}$ of +2.2 and −4.3 kcal mol$^{-1}$, are scarcely effective to oxidize the $Ti^{II}$ center via a radical mechanism. $CHCl_3$ and, particularly, $CCl_4$, with a $\Delta E_{Tot}$ of −11.4 and −19.8 kcal mol$^{-1}$, are indeed quite capable of reoxidizing a $Ti^{II}$ center via a radical mechanism. However, even considering an unfavorable entropic contribution for the oxidative addition mechanism, this reactivity seems to be clearly favored over the radical oxidation mechanism.

Concluding this section, our results suggest that with increasing the number of Cl atoms, the oxidation (reactivation) of a $Ti^{II}$ center becomes thermodynamically more favored. This conclusion is in line with the well accepted concept that suitable promoters for ZN catalysts are usually multi chloro organohalides such as $CHCl_3$, $CFCl_3$, $C_3H_2Cl_6$, and $C_3Cl_8$,[53,54] with a similar role of organohalides in the activation of V-based catalysts for ethylene polymerization,[34] and with several patents in the field of ZN-promoted ethene polymerization.[38,55,56] Of course, after the $Ti^{II}$ center has been reoxidized to $Ti^{IV}$, it can re-enter the catalytic cycle by activation steps such as those discussed in the previous sections.

## Conclusions

In this study, we have investigated possible pathways for the activation/reduction of $TiCl_4$ adsorbed on a $MgCl_2$ cluster to $Ti^{III}$ species, the possible deactivation/reduction of $Ti^{III}$ species to $Ti^{II}$ species, and finally the reoxidation of $Ti^{II}$ species back to $Ti^{IV}$ species. The main conclusions that emerge from our study are. First, the simple homolytic rupture of a dangling Ti−Cl bond of an adsorbed $TiCl_4$ molecule is of very high energy. The most effective reducing agent is $AlEt_3$ while $AlCl_3$ performs rather poorly. The species formed after rupture of a Ti−Cl bond is a [Mg]/$Ti^{III}Cl_3^•$ species with a coordinative vacancy. Second, direct transalkylation of [Mg]/$TiCl_3^•$ by $AlEt_3$ presents a rather low energy barrier, and leads to [Mg]/$Ti^{III}Cl_2Et^•$, which can be considered as the species from which chain growth can start via the classical monomer coordination/insertion mechanism of Cossee.[57] Third, the [Mg]/$Ti^{III}Cl_2Et^•$ species, which can be considered as a model of the propagating species, is rather stable toward further reduction to $Ti^{II}$ by either Cl or Et homolytic dissociation or abstraction by $AlEt_3$. In this context, the [Mg]/$Ti^{III}Cl_2H^•$ species that could be formed after a chain transfer reaction by either $\beta$-hydrogen elimination from the growing chain or by cleavage of the Ti-Et (polymeryl) bond by molecular hydrogen, is rather weaker and thus susceptible of reduction. Fourth, organohalides can easily coordinate to $Ti^{II}$ species and then reoxidize them to $Ti^{IV}$ species, thus reintroducing them into the catalytic cycle.

We underline that all these transformations always considered a single Ti−Et chloride species adsorbed on a $MgCl_2$ cluster reacting with standard other ingredients used industrially, thus providing a very simple and intuitive description of the possible changes in the oxidation states of Ti species active in ZN-catalysis. As a final remark, we are aware that these conclusions are based on reaction energies and do not consider energy barriers. This choice was dictated by the difficulty in modeling several reactions with a change in the spin state. However, considering that in many cases the reaction energies we calculated are very endothermic, this allows to rule them out even on a thermodynamics basis. In other cases, the reactions are thermodynamically highly favored, which can be taken as an indication supporting their feasibility.

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**Supporting Information Available:** Cartesian coordinates and energies in au of all the species discussed in the text, and the complete ref 41. This material is available free of charge via the Internet at http://pubs.acs.org.

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