A theoretical investigation of the role of AlR_3 as cocatalyst

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In the present paper, we study the role of AlR_3 ($R = CH_3$, Cl) as cocatalyst for the Ziegler–Natta reaction. DFT-GGA calculations show that the cocatalyst facilitates the reduction of the titanium atoms by means of an exchange between the R and Cl ligands. The reductions of the alkylated species of titanium are thermodynamically favorable.

KEY WORDS: density functional calculations; Ziegler–Natta; titanium chloride; cocatalyst

1. Introduction

$MgCl_2$-supported Ziegler–Natta catalysts are known to be efficient for the stereospecific polymerisation of α-olefins. Despite intensive efforts, there are no direct proofs of the structure of the active site. A key concept concerns the variation in oxidation state of the titanium chloride. Ti^{4+} is reduced into Ti^{3+} or Ti^{2+} species. These titanium chloride species can be present as monomeric complex [1–4] or as a dimer [1,2]. The reduction requires the use of a cocatalyst such as triethyl aluminium (TEA) as an activating agent [5–7]. The activity of the catalyst and its stereospecificity (higher when the activity decreases) changes by using different AlR_3 compounds [6,8], where R represents different alkyl groups or Cl ligands. In the presence of methyl-p-toluate, 90% of the Ti^{4+} is reduced [9] producing a multitude of Ti^{3+} species [10]. The Cl content is 3.5 per Ti showing that some chlorine has desorbed [9]. The proportion of Ti^{4+} varies with the conditions; the presence of CCl_4 as oxidizing agent [11] or Cl_2 [7] restores Ti^{4+} and increases the activity [12]. Some analyses [7] estimate that Ti^{2+} represents 80% of the total titanium. A fraction of the reduced titanium species can be observed by EPR [9,10], that corresponding to monomeric complexes. From these experiments, Ti^{2+} and Ti^{3+} species represent 8 and 38% of the content. The observed Ti^{3+} species is supposed to be monomer with D_{3h} symmetry and no other adjacent Ti^{3+} in the vicinity [10]. The other part, silent to EPR, is attributable to dimers. Superexchange of the Ti^{3+} ions results in antiferromagnetism for the bridged complexes [13]. Calculations indeed conclude to high spin states [1]. EXAFS [14,15] agrees to a predominant adsorption of $TiCl_4$ with the formation of dimeric complexes; such species could be precursors of non-stereospecific sites, the active centers representing only several percents of Ti in the catalyst [16].

In spite of their determining influence, AlR_3 compounds are not usually known as reducing agents; $AlCl_3$ is known as a Lewis acid. The formation [17] of ion pairs such as $TiCl_3^+\|R_3AlCl^-$ (or $TiCl_2R^+\|R_2AlCl_2^-$) and that of bimetallic complexes such as $Cl_3Ti\,(\mu_2Cl)(\mu_2R)AlR_2$ (in a singlet state) does not modify the oxidation state of the titanium atom.

The formation of Ti^{3+} and Ti^{2+} (reduction) is obtained by an homolytic cleavage of a Ti–Cl bond,

$$TiCl_4 \rightarrow TiCl_3{\bullet} + Cl{\bullet} \tag{1}$$

The participation of aluminum chloride leads to equation (2).

$$TiCl_4 + AlCl_3 \rightarrow TiCl_3{\bullet}\ldots AlCl_3 + Cl{\bullet} \tag{2}$$

The fragmentation then can be thought as a competition between a triplet state (a weak interaction between two radicals $TiCl_3{\bullet}\ldots AlCl_3$ and $Cl{\bullet}$) and a singlet state $TiCl_4 + AlCl_3$ where the titanium is Ti^{4+}. The triplet state is associated with the generation of a reduced species whereas the singlet is associated with the oxidized form. We will show in section 3 that, as expected, the singlet state is lower in energy.

Since Cl is a stronger ligand than the alkyl group, an exchange of ligand seems reasonable; this is shown by equations (3) and (4) where $AlCl_3$ is used to substitute R for Cl,

$$TiCl_4 + AlR_3 \rightarrow TiCl_3{\bullet} + AlR_2Cl + R{\bullet} \tag{3}$$

$$TiCl_3{\bullet} + AlR_3 \rightarrow TiCl_2{\bullet\bullet} + AlR_2Cl + R{\bullet} \tag{4}$$

These reactions suppose a cleavage of two bonds, Ti–Cl and Al–R, that should not be compensated by the formation of a Ti–R bond. Such formation, poorly favorable, would then reoxidize the titanium center. In previous studies [1,18], it has been shown that $TiCl_4$ was stable relative to $TiCl_3$ and that the tendency of titanium chlorides was aggregation with

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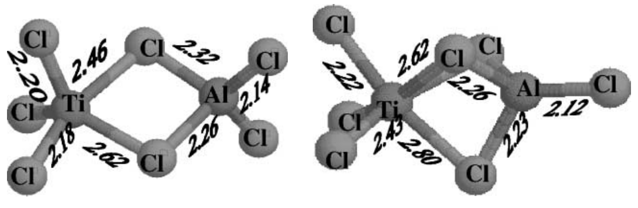


Singlet state Triplet state

Figure 1. The bimetallic complexes resulting from the complexation of $TiCl_4$ by $AlCl_3$.

Lewis acids. Hence, the equations (3) and (4) imply a fragmentation and endothermicity.

$$TiCl_4 \rightarrow TiCl_3\cdot + \tfrac{1}{2}Cl_2 \qquad (5)$$

$$RTiCl_3 \rightarrow TiCl_3\cdot + \tfrac{1}{2}R_2 \qquad (6)$$

The homolytic cleavage (1) being obviously very endothermic, we next turn (section 4) to more realistic cases where the removed ligands recombine. The formation of Cl_2, RCl or R_2 stabilizes the products. Experimentally a shift toward reduction may be obtained by stabilizing even more the end products. The abstraction of Cl_2 becomes easier [19] if PCl_3 is added forming PCl_5. Cl is a better ligand than the alkyl group and the Cl–Cl bond is weaker than the C–C bond. It follows that reaction (5) is endothermic whereas reaction (6) is exothermic and that the substitution by an alkyl group facilitates the reduction of the titanium center; this is shown in sections 4 and 5.

2. Calculations

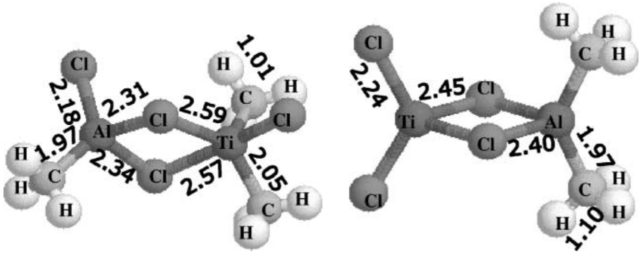
Calculations have been made using the GAUSSIAN program [20] using the DFT method and GGA approximation (B3PW91). The basis sets are described in [1,18]. We have used the pseudo potentials from Durand and Barthelat [21]. Methyl has been chosen as R group.

3. $AlCl_3$ does not assist the reduction of $TiCl_4$

The geometries for the singlet and triplet states are sketched in figure 1.

Two local minima for the singlet state are very close in energy; the lowest (structure S1), $Cl_3Ti(\mu_2Cl)_2AlCl_2$, with two bridging ligands, is more stable than the other (structure S2), $Cl_3Ti(\mu_2Cl)_3AlCl$, with three bridging ligands, by 4.1 kcal/mol. It is more stable than the best triplet state (structure T1 with two bridging ligands) where the Cl• radical interacts with the titanium in the triplet state by 6.3 kcal/mol. Another structure (T2 with three bridging ligands) is slightly less stable (10.9 kcal/mol above T1).

Finally we also have done the calculation of $TiCl_4 \ldots Al(CH_3)_3$ as a singlet and a triplet state. The difference between the two states is reduced but not reversed. This difference for best isomer with two bridging chlorine atoms, $Me_2ClTi(\mu_2Cl)_2AlClMe$, is 4.4 kcal/mol (figure 2(a)).



(a) (b)

Figure 2. (a) The best isomer for $TiCl_4 \ldots Al(CH_3)_3$: $(CH_3)_2ClTi(\mu_2Cl)_2AlCl(CH_3)$. Two methyl groups have been transferred from Al to Ti. (b) The optimized geometry of the $Cl_2Ti(\mu_2Cl)_2Al(CH_3)_2\cdot$ complex (doublet) that results from the decomposition of the previous complex with the formation of an ethane molecule.

There are eight isomers corresponding to the distribution of methyl groups when two ligands are bridging. The two other isomers with bridging chlorine atoms $MeCl_2Ti(\mu_2Cl)_2AlMe_2$ and $Me_3Ti(\mu_2Cl)_2AlCl_2$ are close in energy in their singlet states (higher in energy by 4.9 and 6.9 kcal/mol only); their triplet states are still higher in energy. Alkyl could also bridge the metal atoms as proposed by Chien [22]; we have already found similar structures for the dinuclear Ti–Mg species [1]; this situation makes the exchange of ligands easy. In the present case, we find that structures with methyl bridging groups are less stable than those with bridging chlorine atoms. $Cl_3Ti(\mu_2Cl)(\mu_2Me)AlMe_2$ (singlet state) is 38 kcal/mol higher than the most stable isomer and the other species, $Cl_3Ti(\mu_2Me)_2AlMeCl$ and $MeCl_2Ti(\mu_2Cl)(\mu_2Me)AlMeCl$ (singlet states), spontaneously reorganize to Cl bridging structures.

4. Alkyl ligands facilitate the reduction

As mentioned above, the reduction of Ti^{4+} may occur when the radicals issued from the cleavage recombine. In this section, we show that this is possible when these ligands are methyl groups. Our results for the reactions (5) and (6) are clear. Reaction (6) is exothermic by 23.0 kcal/mol whereas reaction (5) is endothermic by 22.4 kcal/mol. Alkyl groups dissociate, recombine and then facilitate the reduction.

The formation of ethane from $TiCl_4 \ldots Al(CH_3)_3$ is exothermic whereas that of Cl_2 is endothermic. Selecting the most stable isomer for the radicals obtained, we have calculated the following values:

$$\begin{aligned}&TiCl_4 \ldots Al(CH_3)_3\\ &\quad\rightarrow CH_3ClTi(\mu_2Cl)_2Al(CH_3)_2\cdot + \tfrac{1}{2}Cl_2\\ &\qquad\qquad\qquad\qquad\qquad +20.5\ \text{kcal/mol}\end{aligned}$$

$$\begin{aligned}&TiCl_4 \ldots Al(CH_3)_3 \rightarrow \tfrac{1}{2}[Cl_2Ti(\mu_2Cl)_2Al(CH_3)_2\cdot\\ &\qquad + CH_3ClTi(\mu_2Cl)_2Al(CH_3)_2\cdot] + \tfrac{1}{2}RCl\\ &\qquad\qquad\qquad\qquad\qquad -24.0\ \text{kcal/mol}\end{aligned}$$

$$\begin{aligned}&TiCl_4 \ldots Al(CH_3)_3\\ &\quad\rightarrow Cl_2Ti(\mu_2Cl)_2Al(CH_3)_2\cdot + \tfrac{1}{2}C_2H_6 \quad -39.1\ \text{kcal/mol}\end{aligned}$$

This shows that $TiCl_4$ is indeed reduced by $Al(CH_3)_3$. $TiCl_4 \ldots Al(CH_3)_3$ and $Cl_2Ti(\mu_2Cl)_2Al(CH_3)_2\cdot$ are represented in figure 2.

5. $TiCl_4TiCl_2R_2$ is more easily reduced than $(TiCl_4)_2$

Titanium tetrachlorides are stable species as monomers or dimers. In this section, we show that the substitution by alkyl ligands in the dimeric species leads easily to reduced species.

We consider the reduction from the dimeric complexes, $(TiCl_4)_2$, $TiCl_4TiCl_3R$ and $TiCl_4TiCl_2R_2$, leading to a loss of Cl_2, RCl or R_2.

$$\begin{aligned} (TiCl_4)_2 &\rightarrow (TiCl_3)_2 + Cl_2 &\quad +7.9\ \text{kcal/mol} \\ TiCl_4TiCl_3R &\rightarrow (TiCl_3)_2 + RCl &\quad -46.5\ \text{kcal/mol} \\ TiCl_4TiCl_2R_2 &\rightarrow (TiCl_3)_2 + R_2 &\quad -82.2\ \text{kcal/mol} \end{aligned}$$

This shows that saturated dinuclear species that have alkyl ligands are likely to decompose to give reduced dinuclear species and alkanes.

6. Conclusion

We conclude that AlR_3 allows the exchange between the ligands R and Cl. This exchange is necessary to make the reduction exothermic. The cocatalyst is not directly involved in the reduction (there is no real assistance), however it is indispensable to provide the alkyl groups which recombining is necessary to stabilize the end products.

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