Theoretical investigations on Ziegler–Natta catalysis: Alkylation of the TiCl$_4$ catalyst

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Abstract

Theoretical ab initio methods have been used to study the alkylation reaction of the MgCl$_2$-supported TiCl$_4$ catalyst. Investigation of the reaction path indicated that the Al(CH$_3$)$_3$ co-catalyst inserts into the coordination sphere of the titanium atom of the catalyst so that a methyl group of Al(CH$_3$)$_3$ interacts with the titanium. The methyl group migrates from Al(CH$_3$)$_3$ to the vacant coordination site of the catalyst. When the catalyst loses one of its chlorine atoms to the co-catalyst during this reaction, the catalyst maintains its vacant site, but the position of the vacant site changes. The presence of the external electron donor coordinated to the co-catalyst makes the alkylation reaction energetically more favourable.

Keywords: Ziegler–Natta; Ab initio; Titanium catalyst; Aluminium alkyl; Silicon alkoxide donor; Alkylation

1. Introduction

Heterogeneous Ziegler–Natta catalysts, used in the polymerization of α-olefins, originate in Ziegler's TiCl$_4$ + Al(C$_2$H$_5$)$_3$ catalyst system [1]. Due to the development of this system these catalysts are now among the most important in polymerization chemistry on the basis of their high activity and selectivity. However, an understanding of the properties of these catalysts is not very clear. The significance of theoretical methods has increased in the investigations of these catalysts. The advantage of theoretical methods compared to experimental ones is the possibility of examining the catalyst system on the molecular level.

Experimental studies [2] have shown that the crystal structures of MgCl$_2$ and TiCl$_3$ resemble each other. In addition, the ionic radius of Ti^{4+} (68 pm) is nearly the same as that of Mg^{2+} (65 pm). Based on these results, it is supposed that MgCl$_2$ can act as support material for the TiCl$_4$ catalyst. Before the titanium catalyst can efficiently coordinate to the MgCl$_2$ surface, the support material has to be modified by internal electron donors [3,4]. To activate this MgCl$_2$-supported titanium catalyst for olefin polymerization the catalyst will be reduced and alkylated by aluminium trialkyls [5,6]. Using external electron donors enhances the stereo-specificity of the catalysts [7–9].

In theoretical studies of Ziegler–Natta type systems the most often investigated topics have been the nature of the titanium-alkyl bond [10–17] and the growth mechanism of the polymer

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chain in the coordination sphere of the titanium atom [18–28]. These studies have indicated that the polymerization depends on the properties of the titanium-alkyl bond. In particular, the strength of the agostic interaction [29–31] between the titanium atom and the alkyl group affects the formation and the breaking of the titanium-alkyl bond during the polymerization reaction.

Interaction between the support material and the catalyst has also been investigated theoretically [32–34]. These studies have suggested that the $TiCl_4$ catalyst coordinates to the surface of the $MgCl_2$ support, where the magnesium atoms have vacant coordination sites. The coordination is proposed to take place with three chlorine bridges either to two magnesium atoms on the (101) surface [33] or to one magnesium atom on the (110) surface [34]. In both cases the coordination sphere of the magnesium atom is completed by the chlorine atoms of the catalyst and the coordination geometry of the titanium atom changes from tetrahedral to octahedral with one vacant coordination site.

Based on the results of our earlier study [34], the coordination of the $TiCl_4$ to the surface of a larger $MgCl_2$ support model, the Mg_4Cl_8 cluster cut from the (110) surface of $MgCl_2$, was studied [35]. It was again found that the titanium catalyst coordinates with three chlorine bridges to the surface of the Mg_4Cl_8 cluster. In the present paper we describe an ab initio investigation in which the $Mg_4Cl_8TiCl_4$ cluster was used as a model for the study of the alkylation of the $MgCl_2$-supported $TiCl_4$ catalyst.

2. Computational methods

Our investigations [34,35] have indicated that the $TiCl_4$ catalyst can coordinate with three chlorine bridges to the surface of the Mg_4Cl_8 cluster cut from the (110) surface of $MgCl_2$. Based on this, our earlier $Mg_4Cl_8TiCl_4$ support-catalyst model complex (Fig. 1) has
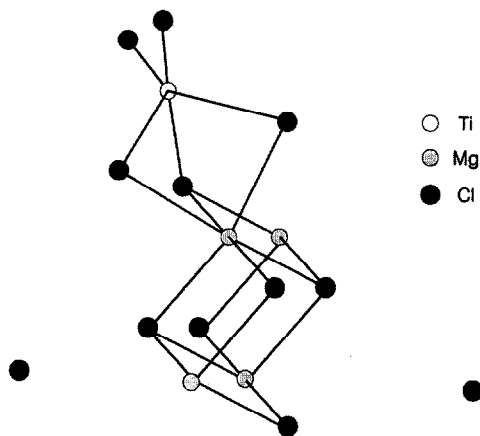

Fig. 1. The $TiCl_4$ catalyst on the surface of the Mg_4Cl_8 cluster.

been used as the starting point of our present study to examine the alkylation of the $MgCl_2$-supported $TiCl_4$ catalyst. In the alkylation reaction, one chlorine atom of $TiCl_4$ is replaced by a methyl group of the aluminium tri-alkyl cocatalyst and $TiCl_3CH_3$ is formed. We have calculated the structure of $TiCl_3CH_3$ on the surface of the Mg_4Cl_8 cluster by keeping the geometrical parameters of the support fixed to those in the bulk crystal structure [36] of $MgCl_2$ and by optimizing the geometrical parameters of $TiCl_3CH_3$. Structures for the co-catalysts ($Al(CH_3)_3$, $SiH_3OH–Al(CH_3)_3$ and $Si(CH_3)_3OCH_3–Al(CH_3)_3$) have also been calculated earlier [37], so in this study we have optimized the structures of the corresponding halogenated co-catalysts, which are formed during the alkylation reaction.

The ab initio calculations reported here were carried out with Gaussian 92 [38] and Gaussian 94 [39] computer programs at the restricted Hartree–Fock level of theory with the 3-21G basis set. Because the standard basis sets of the Gaussian 92 program did not include split-valence basis sets for transition metals, the Dobbs and Hehre's 3-21G basis set [40] was used for the titanium atom in the calculations. These split-valence basis sets predict bond angles in good accordance with experimental values, although the Ti–Cl bond lengths are overestimated by about 2 pm [40,41]. The influence of

basis sets and correlation effects on the results have not been tested in this study.

The energies ΔE, released in the alkylation reaction, were estimated by using the following equation:

$$\Delta E = \sum_j E_j - \sum_i E_i \qquad (1)$$

where $\sum_j E_j$ = the sum of the total energies of the products and $\sum_i E_i$ = the sum of the total energies of the reactants [42,43].

3. Results and discussion

In the present work we have investigated the alkylation of the $TiCl_4$ catalyst on the surface of the Mg_4Cl_8 cluster (Fig. 1). The alkylation reaction is assumed to proceed by means of the interaction of the aluminium alkyl co-catalyst with the catalyst. This has been modelled with the following reaction:

$$Mg_4Cl_8TiCl_4 + Al(CH_3)_3$$
$$\rightarrow Mg_4Cl_8TiCl_3CH_3 + Al(CH_3)_2Cl \qquad (2)$$
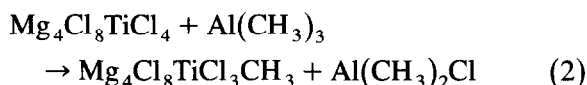
The investigation of the model reaction indicated that the $Al(CH_3)_3$ co-catalyst inserts into the coordination sphere of the titanium atom of the catalyst so that a methyl group of $Al(CH_3)_3$ interacts with the titanium. The methyl group migrates from $Al(CH_3)_3$ to the vacant coordination site of the catalyst. The co-catalyst subsequently coordinates to the chlorine atom and the halogenated co-catalyst is formed. This reaction takes place spontaneously without an activation barrier. The determination of the detailed reaction path was not successful due to the limitations of our model.

The study was continued by assuming that the methyl group of the co-catalyst, coordinated to the vacant coordination site of the titanium atom, replaces one of the terminal chlorine atoms (Cl_A or Cl_B in Fig. 2a) of the catalyst in the real catalyst system. If the Cl_A atom migrates from the catalyst to the co-catalyst during the alkylation reaction, the Cl_B atom moves into the empty place of the Cl_A atom (Fig. 2b).
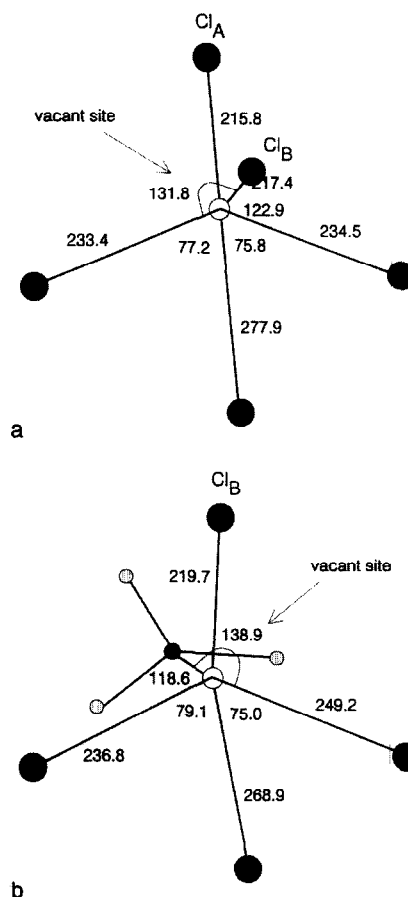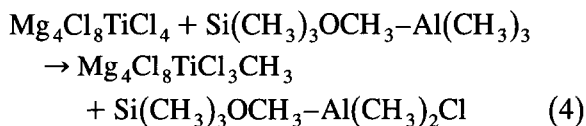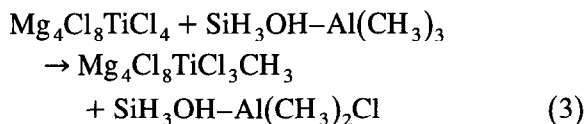

Fig. 2. The octahedral coordination sphere of the titanium atom before (a) and after (b) the alkylation reaction.

The structures of Fig. 2a and b resemble each other. It is typical for these structures that there is one bond angle, which is larger than 130° (131.8° in Fig. 2a and 138.9° in Fig. 2b) in the coordination sphere of the titanium atom. The existence of this large bond angle means that the octahedrally-coordinated catalyst has a vacant coordination site. Due to the alkylation reaction, the vacant coordination site of the alkylated $TiCl_3CH_3$ catalyst is in the position adjacent to the vacant site in the non-alkylated $TiCl_4$ catalyst.

The same structure for the $Mg_4Cl_8TiCl_3CH_3$ cluster (Fig. 2b) was also obtained when the Cl_B atom (Fig. 2a) was assumed to transfer from the catalyst to the co-catalyst during the alkylation reaction. The energies released in these alkylation reactions do not depend on the

replaced chlorine atom (Cl_A or Cl_B), because they are -109.6 kJ/mol in both cases.

Finally, we tested the effect of the external electron donors, complexed with the $Al(CH_3)_3$ co-catalyst, on the alkylation of the catalyst with the following reactions:

$$Mg_4Cl_8TiCl_4 + SiH_3OH–Al(CH_3)_3$$
$$\rightarrow Mg_4Cl_8TiCl_3CH_3$$
$$+ SiH_3OH–Al(CH_3)_2Cl \qquad (3)$$

$$Mg_4Cl_8TiCl_4 + Si(CH_3)_3OCH_3–Al(CH_3)_3$$
$$\rightarrow Mg_4Cl_8TiCl_3CH_3$$
$$+ Si(CH_3)_3OCH_3–Al(CH_3)_2Cl \qquad (4)$$

The energies released in these reactions are -149.3 kJ/mol for Eq. (3) and -157.4 kJ/mol for Eq. (4), so that these reactions are 40 kJ/mol and 48 kJ/mol more favourable than Eq. (2). On this basis, the external electron donor promotes the alkylation reaction of the $MgCl_2$-supported $TiCl_4$ catalyst. So the effect of the external electron donor on the progress of the alkylation reaction is evident, but the choice of the external electron donor has only a minor influence on the reaction.

On the basis of the present calculations, the octahedral bonding geometry with one vacant coordination site is typical for the $MgCl_2$-supported $TiCl_4$ catalyst. The alkylation reaction does not affect the bonding geometry of titanium, only the position of the vacant site changes during the reaction. However, it is a prerequisite for the stereospecific polymerization that the vacant site remains in the same specific position during the polymerization. If the polymerization reaction can be explained by a trigger mechanism [44], the vacant site is always occupied by an olefin molecule. The vacant site and the polymer chain are forced to stay in their positions and the catalyst will produce an isotactic polymer.

4. Conclusions

The investigation of the alkylation of the $MgCl_2$-supported $TiCl_4$ catalyst indicated that the aluminium trialkyl compounds can alkylate the $TiCl_4$ catalyst. The alkylation reaction does not affect the coordination geometry of the catalyst, only the position of the vacant coordination site of the octahedrally-coordinated catalyst changes during the reaction. Because the catalyst maintains its vacant site in the alkylation reaction, the active catalyst does not need to change its geometry in order to participate in olefin polymerization.

Acknowledgements

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