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Alkylation of titanium tetrachloride on magnesium dichloride in the presence of Lewis bases



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ABSTRACT

We report the first quantum chemical description of the initial steps of Ziegler–Natta olefin polymerization catalysis involving all the relevant catalyst components. $TiCl_4$ binds on the (1 0 4) surface of MgCl₂ as a binuclear Ti_2Cl_8 and on the (1 1 0) surface as a mononuclear $TiCl_4$, both binding modes being stabilized by octahedral six-coordination of Ti and Mg. Aluminum alkyl (triethylaluminum) coordinates to the MgCl₂ surface via an unsaturated Cl to initiate catalyst alkylation reactions, thermodynamically driven by dimerization of the chlorinated aluminum alkyl. Addition of an internal donor (dimethyl phthalate) greatly stabilizes the (1 0 4) and (1 1 0) surfaces, ending up directing the alkylation reactions to the bin uclear (1 0 4) site. External donor (dimethoxydimethylsilane) further assists the process, stabilizing similarly both catalytic surfaces. The spatial requirements of the donors are shown to be greater on the (1 1 0) surface than on the (1 0 4) surface, rationalizing the role of Lewis bases in the stereocontrol of polyolefins.

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1. Introduction

Heterogeneous Ziegler–Natta catalysis has dominated the industrial production of polyolefins since its Nobel Prize winning discovery more than 60 years ago [1,2]. Typical Ziegler–Natta polypropylene catalysts involve a mixture of titanium tetrachloride (TiCl₄), magnesium dichloride (MgCl₂) and a Lewis base, such as a phthalate, which is called "internal donor (ID)". The polymerization active catalyst is obtained by contacting this ternary mixture with an aluminum alkyl cocatalyst, typically triethylaluminum (TEA) and with another Lewis base, such as alkoxysilane, which is called "external donor (ED)". Dependent on the chemical structure of the internal donor and the activation conditions the internal donor is to a certain degree removed from the catalyst during the activation step and consequently replaced by the external donor. The presence of an electron donor in the activated catalyst is essential for controlling the stereoregularity of the catalyst and combinations of IDs and EDs [3] can be selected for improving the polymerization performance of the catalyst (e.g. polymerization activity and comonomer response) and for obtaining a wide range of polymer properties (e.g. molecular weight distribution and stereoregularity) [4].

The five components of the catalyst (MgCl₂ support, TiCl₄, TEA, ID, and ED) combine and react in a way to eventually create a catalytically active species, which possibly involves Ti(III) or even Ti (II)[5,6]. Atomic-level details of the process are not well understood. The first uncertainties arise already from the description of the catalytically active sites on the MgCl₂ surface. The crystalline MgCl₂ is a layered material, where the layers are held together by dispersive interactions, and each layer is composed of six-coordinate octahedral Mg atoms and three-coordinate Cl atoms [7,8]. Assuming the catalytic reactions take place within each layer, [9] there are two possible surfaces for the reactions, namely (1 0 4)



Abbreviations: ID, internal donor; ED, external donor; TEA, trimethylaluminum; TMA, trimethylaluminum; **5**-104, five-coordinate Ti on the (1 0 4) surface; **6**-104, six-coordinate Ti on the (1 0 4) surface; **4**-110, four-coordinate Ti on the (1 1 0) surface; **6**-110, six-coordinate Ti on the (1 1 0) surface.

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and (110), which cut the MgCl₂ layer to have five- and fourcoordinate Mg atoms, respectively (see Fig. 1) [10–12]. As has been shown by quantum chemical calculations, the (104) surface is more stable, but not necessarily more abundant for the catalytic reactions, because interactions with donors can reverse the stability order in favor of the (1 1 0) surface [13,14]. Calculations further show that the interactions are strongly sensitive to the molecular structures of the donors, deciding the binding modes of the donors on the surfaces, and thereby the donors can be used for structural modification of catalytically active surfaces [15-27]. There is no consensus on how TiCl₄ binds to MgCl₂, [28–38] particularly when co-adsorbed with donors, [18,39–51] and defects on the surfaces could change the behavior of them both [52–58]. The aluminum alkyl cocatalyst adds an extra piece into the puzzle, interacting with all the catalyst components, [59–63] and complicating all related computational studies due to tendency of forming moieties involving bridging alkyls and halides, and hence, dispersive interactions [64-68].

The computational work reported herein makes the first effort to study all the five catalyst components simultaneously using periodic models accounting for dispersion. Beginning with incorporation of TiCl₄ to MgCl₂ surfaces, we perform a re-evaluation of its preferred binding modes and continue to investigate catalyst alkylation reactions with TEA. Finally, we add model donors (both ID and ED) into the picture to single out their role in this initial step of the olefin polymerization process, ending up revealing significant new insight into the origin of stereocontrol.

2. Results and discussion

2.1. Re-evaluation of TiCl₄ adsorption on MgCl₂

The present work is based on purely thermodynamics considerations, thus omitting the role of kinetics in the formation of the catalysts. As far as the pristine (104) and (110) surfaces of MgCl₂ monolayers are concerned, TiCl₄ has four possible binding modes on the surfaces, as illustrated in Fig. 1A. Originally proposed by Corradini et al., [69] binding of a mononuclear TiCl₄ gives a five-coordinate Ti on the (104) surface and either a six- or four-coordinate Ti on the (1 1 0) surface, [70] while binding of a binuclear Ti₂Cl₈ gives a six-coordinate Ti on the (104) surface. In presentation of the results, we use the following abbreviations for the binding modes: five-coordinate Ti on the (104) surface = 5-104, six-coordinate Ti on the (104) surface = 6-104, and correspondingly for the (1 1 0) surface. The binding modes have been widely studied in previous literature, with varying results, but the latest results point to the mononuclear octahedral coordination on either (1 1 0) surface or on a defect site having a similar local environment [38,58]. The octahedral six-coordination is supported by spectroscopic evidence, [71] which itself does not make a distinction between the mono- and binuclear coordination. Instead, the interpretation for the preference of the mononuclear coordination is based on calculated adsorption energies, which are clearly higher for the mononuclear coordination on the $(1\ 1\ 0)$ surface than for the binuclear coordination on the $(1\ 0\ 4)$ surface.

The TiCl₄ adsorption energies are reproduced in Table 1 for models/methods employed in the present work. The results are strongly dependent on the choice of functional, and consideration of dispersive interactions is absolutely necessary for proper energetics, because of the introduction of bridging chlorides upon TiCl₄ adsorption. All subsequent discussions will hence focus on the results obtained by the M06-2X functional. On (1 1 0) surface, the six-coordinate octahedral **6**-110 binding of TiCl₄ is preferred over the weakly binding **4**-110 mode. On (1 0 4) surface, the binuclear



Fig. 1. (**A**) Structure of MgCl₂ layer, pristine (1 0 4) and (1 1 0) surfaces of MgCl₂, and binding modes of TiCl₄ and (**B**) their stabilities relative to the MgCl₂ layer (ΔG , M06-2X) per a surface length of one nm.

6-104 binds stronger than the mononuclear **5**-104, but the **6**-110 mode remains by far superior. The binding energies easily make one to conclude that $TiCl_4$ preferably binds on (1 1 0) surface, thus making (1 1 0) catalytically the more relevant surface than (1 0 4).

However, in addition to uncertainties related to computations itself, such conclusions based on binding energies obtained from periodic models of MgCl₂ are biased in two ways. First, TiCl₄ binding energies depend on the size of the MgCl₂ support, small clusters being more reactive than larger ones. The presence of donors has been shown to impede the growth of MgCl₂, [72,73] thus making it more reactive towards TiCl₄ than what is predicted by the

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