

# Understanding Ziegler–Natta Catalysis Through Your Laptop

*K Vipin Raj and Kumar Vanka*

**This article focuses on the different components that make up Ziegler–Natta olefin polymerization systems and shows how investigating the interactions between these components through computational approaches provide crucial information about the chemistry of these systems. Hence, the necessity of theory acting as a counterpoint to experiment is revealed, underlining the importance of computational chemistry in attacking important problems of the day.**

## Introduction

Ziegler–Natta (Z–N) olefin polymerization catalyst systems are responsible for the industrial production of millions of tons of polyolefins annually. They are, without question, the most essential heterogeneous catalysis process in the industry today. Therefore, there is a constant impetus to improve Z–N systems, to make them more active and selective. This, however, is hampered by a significant fact: Z–N systems, by their very nature, defy complete understanding. There are several components to a Z–N system, each vital to its function and efficiency. These include (i) the active catalyst, which is a variant of  $\text{TiCl}_4$ , (ii) the catalyst support (currently, surfaces of  $\text{MgCl}_2$ ), (iii) the co-catalyst –  $\text{AlR}_3$  (where R = alkyl groups), (iv) the olefin monomer that gets converted to polymer during the reaction, and (v) donors – small oxygen-containing Lewis bases that are added to the Z–N system during the preparation (internal donors), or at a later stage (external donors). These different components of the Z–N systems are shown in *Figure 1*. Understanding how such a complex system works through the interconnectedness of its various components is a significant problem.



**K Vipin Raj is working as a Project Assistant at the CSIR-National Chemical Laboratory (CSIR-NCL), under the guidance of Kumar Vanka. His area of research is Ziegler–Natta catalysis.**



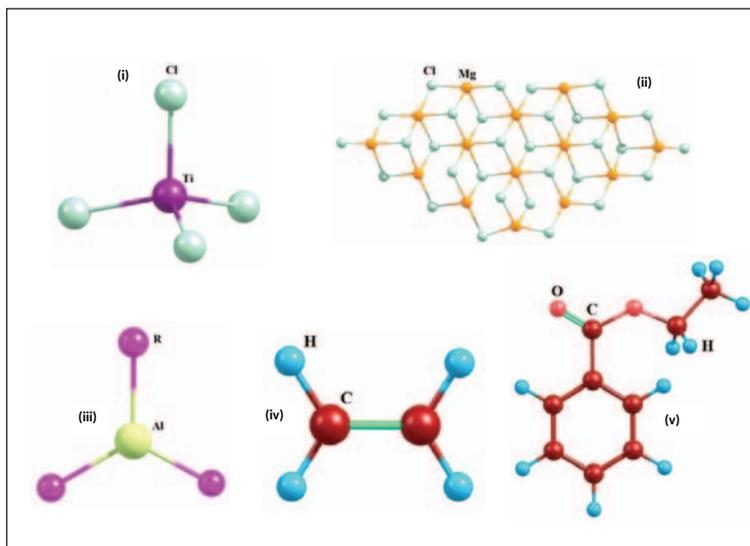
**Kumar Vanka is a Senior Scientist at the CSIR-National Chemical Laboratory (CSIR-NCL), Pune. He is a computational chemist.**

## Keywords

Ziegler–Natta catalysts, donor, titanium center, computational tools, infinite surface, cluster model, coordination, density functional theory.



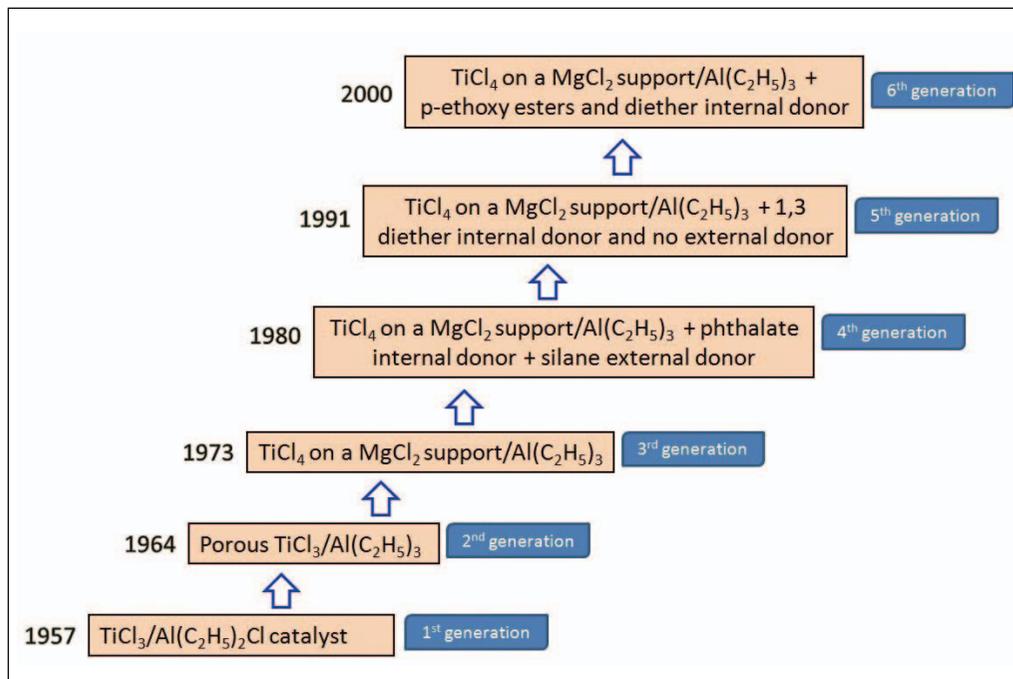
**Figure 1.** The five principal components of the Ziegler–Natta (Z–N) catalyst systems. **(i)**  $\text{TiCl}_4$ , **(ii)**  $\text{MgCl}_2$  surface model, **(iii)**  $\text{AlR}_3$  (R = alkyl groups), **(iv)** olefin monomer (e.g., ethylene), **(v)** oxygen-containing donor (e.g., ethyl benzoate).



Z–N catalyst systems are not only complex but are also evolving constantly. Since their discovery in the 1950s, Z–N catalyst systems have undergone several modifications. The crucial milestones in the evolution of Z–N catalysts are summarized in *Figure 2*. Evidently, Z–N systems have evolved through several generations. One of the principal factors driving the growth and development of Z–N systems in the last few decades has been the discovery of donors – internal and external – that could give rise to improved systems with higher activity and selectivity. This gives rise to the questions: What exactly is occurring in Z–N systems? Why is the addition of Lewis base donors so significant? How exactly do the other components interact with the donors and with the  $\text{MgCl}_2$  surface? And, most importantly, how would one go about investigating Z–N systems in order to obtain these answers?

This, in essence, is what we discuss in this article. Understanding the nature and behavior of Z–N systems requires a molecular level understanding of the interactions taking place between the five Z–N components. One of the most effective tools for understand-



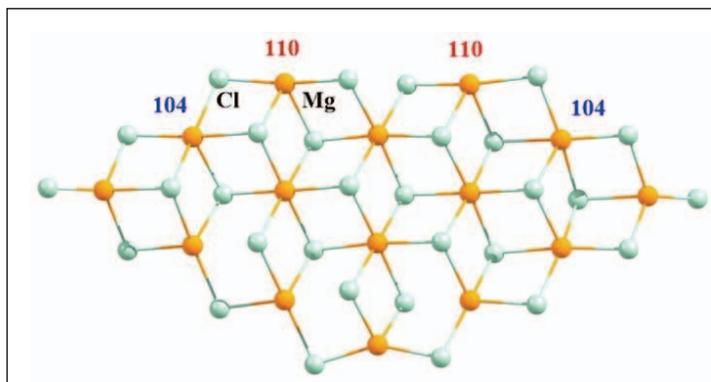


**Figure 2.** The evolution of Ziegler–Natta catalyst systems.

ing such molecular level interactions is state-of-the-art computational methods. But what do we mean by computational methods? Put simply; they pertain to the use of computer software for obtaining and analyzing chemical data and systems. In order to understand how molecules interact and how bonds break or form, we have to take recourse to quantum mechanics – the mechanics of atoms and molecules. Today, there exists quantum mechanical software that can be installed on fast computers and used to generate geometries and structures corresponding to the molecules whose interactions we want to understand. With the aid of these fast computers and software, we can pose different questions, such as: How do different molecules interact? What is the energy of the chemical reactions that ensue; are they endothermic or exothermic? What is the kinetics of the various processes involved? and so on. Answering such questions gives us greater insight into the nature of the chemical system being investigated. This becomes especially relevant when one considers Z–N sys-

Today, there exists quantum mechanical software that can be installed on fast computers and used to generate geometries and structures corresponding to the molecules whose interactions we want to understand.

**Figure 3.** An illustration of a section of  $\text{MgCl}_2$  crystal-lite showing (110) and (104) surfaces. The color scheme is as follows: orange—magnesium, light green—chlorine atoms.



tems, whose complexity makes it difficult to study them using conventional experimental methods alone.

In the next few sections, we will discuss how computational studies have allowed greater understanding of the nature of  $\text{MgCl}_2$  support, and of the role played by donors, understood through their interaction with the  $\text{MgCl}_2$  support, as well as with the titanium catalyst center.

### Understanding the Nature of $\text{MgCl}_2$ Support

As mentioned earlier, one of the major components of Z–N systems is the  $\text{MgCl}_2$  based support (*Figure 1(ii)*). This support provides the molecular foundation upon which the Z–N catalysis can occur. Specifically, it allows the titanium-based catalyst (*Figure 1(i)*) to bind to its surface, thereby stabilizing the titanium and allowing subsequent chemical reactions to occur at the titanium site.

The dominant surface in the  $\text{MgCl}_2$  crystallites is the (001) surface, which corresponds to a plane of chlorine atoms. This surface cannot bind  $\text{TiCl}_4$ . However, there exist two other significant  $\text{MgCl}_2$  surfaces that indeed can bind  $\text{TiCl}_4$  – the more stable (104) surface<sup>1</sup>, and the less stable (110) surface<sup>2</sup> (see *Figure 3*). Earlier models suggested that the dimeric species  $\text{Ti}_2\text{Cl}_8$  can bind to the (104) surface [1–5]. These models considered the (110)  $\text{MgCl}_2$  surface to be too active and therefore, prone to easy poisoning by

<sup>1</sup>Here the magnesium atoms on the surface are penta-coordinated.

<sup>2</sup>Here the magnesium atoms on the surface are tetra-coordinated.



donors, making the binding of  $\text{TiCl}_4$  unlikely on them [6]. However, recent studies have questioned the above-mentioned models. This is mainly because of two reasons. First, computational calculations using a sophisticated modern day method called the ‘density functional theory’ (DFT), suggests that the binding of  $\text{TiCl}_4$  on the (104) surface is weak compared to the binding on the (110) surface [7–11]. Second, experimental studies have revealed that donors have a high influence on the ‘stereoregularity’ of the polymer. In effect, what this implies is that the donor has to be coordinated to the surface near the titanium center [12–15]. It is very easy to place a donor in the proximity of titanium on the (110) surface [16–18], but such a coordination is not going to happen on the (104) surface. Based on this computational and experimental evidence, the (110) surface has been deemed the most favorable  $\text{MgCl}_2$  surface for  $\text{TiCl}_4$  binding in Z–N systems.

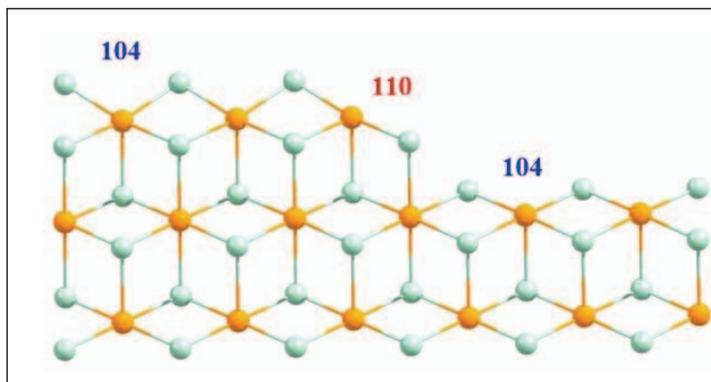
The computational group of Luigi Cavallo proposed the ‘unified model,’ in which they introduced the concept of ‘step defects’ in (104) surface.

However, these models were not able to explain all of the experimental observations in Z–N catalysis. It has been observed that polymerization can take place even on the (104) surface, which flies in the face of everything that computational results suggest – that  $\text{TiCl}_4$  cannot bind to the (104) surface. This apparent contradiction was resolved to some extent in 2015, when the computational group of Luigi Cavallo proposed the ‘unified model,’ in which they introduced the concept of ‘step defects’ in (104) surface (*Figure 4*) [19]. These step defects lead to an increase in the binding ability of titanium to the (104) surface and also allow Lewis bases to coordinate in the proximity of the active titanium center, which lead to polymers of the type observed in the experiment.

Now that an understanding has been obtained *vis-a-vis* the nature of the computational support, the next question would be about the best means of modeling the support. One way would be to create a model of an ‘infinite surface’, *i.e.*, a surface that would be repeating units of a standard surface. This can be achieved by employing boundary conditions, and by assuming a general homogeneity in surface composition. The alternative means of modeling the surface would be to employ a ‘cluster model’ where



**Figure 4.** The unified model proposed by Luigi Cavallo's group for the  $\text{MgCl}_2$  surface. The part indicated by '110' in red is the 'step defect' on the (104) surface. The colour scheme is as follows: orange—magnesium, light green—chlorine atoms.



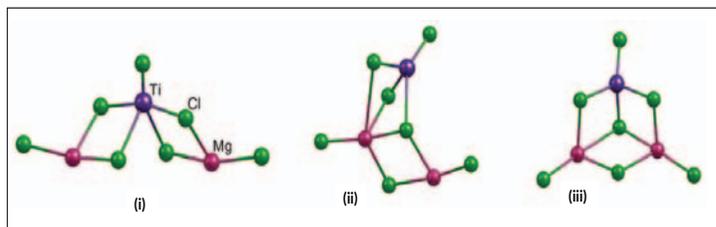
only a chopped off portion of the  $\text{MgCl}_2$  surface would be looked at. While this may appear to be just an approximate way to model the support, it is, nevertheless, effective for developing an understanding of the kinetics and thermodynamics of the polymerization processes at the titanium center.

Having chosen a model for the  $\text{MgCl}_2$  support, the next question would be: How does the titanium species (predominantly  $\text{TiCl}_4$ ) bind to the  $\text{MgCl}_2$  surface through Ti-Cl and Cl-Mg bonds in order to form the active sites in the Z-N system? In order to address this, different active sites have been proposed in the Z-N system. They are (i) the Corradini site, (ii) the edge site, and (iii) the slope site (Figure 5). In the Corradini site, the titanium is bound to the (110)  $\text{MgCl}_2$  surface through two bridging chlorine atoms and two surface chlorine atoms. In the edge site, the titanium is bound to the (110)  $\text{MgCl}_2$  surface through two bridging chlorine atoms to the same magnesium atom as well as through a surface chlorine atom. In the slope site, the titanium is bound to the (104)  $\text{MgCl}_2$  surface through two bridging chlorine atoms and one surface chlorine atom.

It has been reported that donors can poison the Corradini site, because the titanium is penta-coordinated in the Corradini site, meaning that it has only one vacant coordination site, for either the monomer or the donor.

It has been reported that donors can poison the Corradini site, because the titanium is penta-coordinated in the Corradini site, meaning that it has only one vacant coordination site, for either the monomer or the donor [8]. However, in the edge site and the slope site, titanium is tetra-coordinated, which means that two vacancies are available for the monomer and the donor, which





**Figure 5.** Different active sites proposed in the Z–N systems. **(i)** Corradini site, **(ii)** Edge site, **(iii)** Slope site. The color scheme is as follows: purple–titanium, red–magnesium, and green–chlorine atoms.

would make them suitable (‘non-poisoned’) for Z–N catalysis.

This brief synopsis provides a general overview of how researchers have attempted to develop computational models to address one of the essential components of the Z–N systems – the  $\text{MgCl}_2$  surface – without which the heterogeneous catalysis process would not be possible. In the next section, we will look at another very important component of Z–N systems – the donors, which have driven the evolution of Z–N systems, giving rise to several new generations of Z–N catalysts in the past twenty years.

## Understanding the Role of Donors

### *Interactions with the $\text{MgCl}_2$ Support*

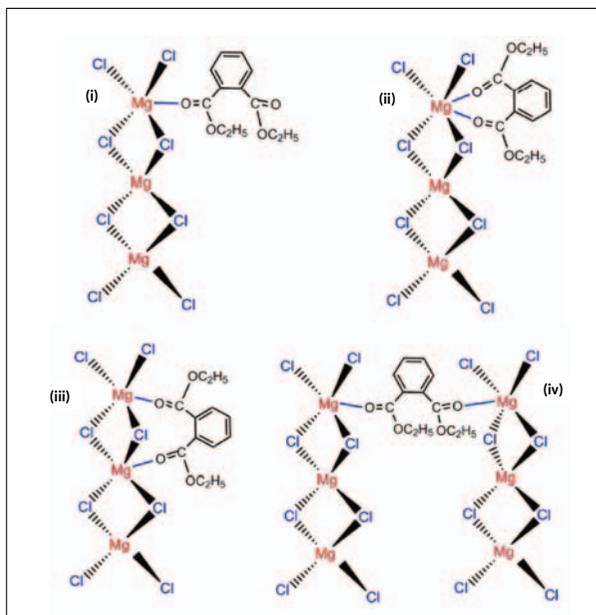
A great deal of development in Z–N catalysis in the past few decades has been spurred by the discovery of new donors, both internal and external, which have led to significant improvements in the activity and selectivity of Z–N systems. Such discoveries owe more to serendipity than to a rational search, but with the increased speed of computers and more efficient software, it has become possible to probe more deeply into the nature of interactions between the donors and the  $\text{MgCl}_2$  surface, as well as with the titanium center. With these insights, it is more and more likely that one will eventually be able to design new systems where more effective donors can take the place of the existing ones. In this section, we will discuss what has been discovered about the nature of interaction between the donors and the  $\text{MgCl}_2$  support.

Computational calculations have suggested that there are four ways in which the donor can bind to the  $\text{MgCl}_2$  support. These are (i)

With the increased speed of computers and more efficient software, it has become possible to probe more deeply into the nature of interactions between the donors and the  $\text{MgCl}_2$  surface, as well as with the titanium center.



**Figure 6.** The four different binding modes of the phthalate donor to the  $\text{MgCl}_2$  surface. (i) Mono coordination, (ii) Chelate coordination, (iii) Bridge coordination, and (iv) Zip coordination.



mono coordination, (ii) chelate coordination, (iii) bridge coordination, and (iv) zip coordination modes [16]. These are indicated in *Figure 6*.

Computational analysis show that the presence of an oxygen atom in the donor enables the donation of electrons from the oxygen to the magnesium atoms on the  $\text{MgCl}_2$  surface, thus allowing the donor to bind to the surface. But why is the binding of the donor to the surface significant? This is because the binding of the donor close to the titanium center provides a significant steric environment to titanium. In this situation, the approach of the monomer to the titanium center is hindered. An apt analogy in this context is to consider two defenders ‘guarding’ an attacker in a game of football so that the ball can be passed to the attacker only along limited lines. In our analogy, the titanium center is the attacker, the donors are the defenders, and the football is the incoming monomer forced to enter through a limited space. This leads to increased selectivity in the polymer product formed. Several computational studies have indicated this to be the case [12–15]. It is also interesting to note that of the four modes of coordination

Binding of the donor to the surface is significant because the binding of the donor close to the titanium center provides a significant steric environment to titanium.

to the  $\text{MgCl}_2$  surface, mono coordination is less favorable than the others. This also helps to explain why donors having two oxygens are found to be more effective than single oxygen containing donors – the stability of binding to the  $\text{MgCl}_2$  surface is increased with more oxygens, *i.e.*, binding to  $\text{MgCl}_2$  through the modes (ii), (iii), and (iv). Furthermore, what is interesting about the zip mode of coordination (type (iv)) is that it allows the donor to act as an adhesive between two different blocks of  $\text{MgCl}_2$  (*Figure 6*). This, in turn, enables the system to gain stability, by allowing different blocks of  $\text{MgCl}_2$  to remain close together [20]. This also hints at other roles played by the donor in  $Z-N$  systems. One sees then that new insights have been gained into the role of donors in  $Z-N$  systems, something that has only become possible because of the computational studies that have revealed new possibilities of donor-surface interactions.

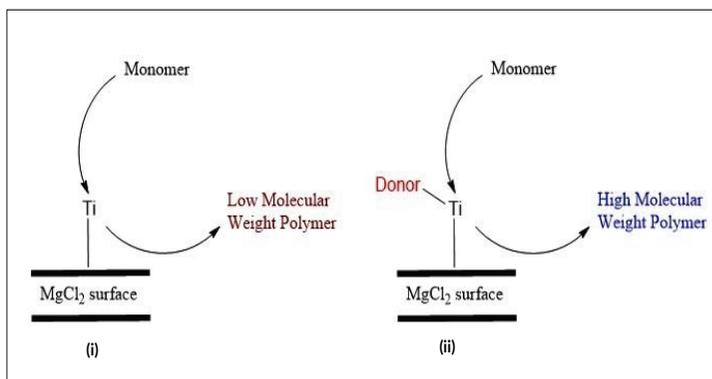
### *Interactions with the Titanium Center*

The previous section discussed the means by which the donor can influence selectivity in  $Z-N$  systems by binding close to the titanium center on the  $\text{MgCl}_2$  surface. However, there is another way in which a donor can influence  $Z-N$  catalysis. This is by directly binding to the titanium center. In doing so, the donor can change the nature of the titanium center. This is significant because all the actual chemistry in  $Z-N$  catalysis occurs at the titanium center. If it turns out that the chemical properties of the titanium center can be modified through direct binding with the oxygen atom of the donor, then it provides us with an expanded understanding of the role of donors in  $Z-N$  catalysis. Computational calculations have shown that the donor indeed can bind to the titanium center, and by doing so, what is likely is that it fosters the formation of higher molecular weight polymers [21]. In other words, these computational studies imply that in the absence of donor binding to the titanium center, only low molecular weight polymers would form (*Figure 7*). This then leads to an interesting question: How did  $Z-N$  catalysts work in the era prior to donors? After all, high molecular weight polymers have been obtained in

The chemical properties of the titanium center can be modified through direct binding with the oxygen atom of the donor.



**Figure 7.** (i) Titanium with no donor attached to it yields low molecular weight polymer (ii) Titanium with a donor attached to it yields high molecular weight polymer.



Z–N systems long before donors were introduced, *i.e.*, in the first, second, and third generation Z–N systems (*Figure 2*). The answer to this lies in the fact that ‘donor’ is a loose definition. Anything that binds to the titanium center can influence its activity, and it does not have to be a donor molecule. For instance, species such as AlEt<sub>2</sub>Cl would also be present during Z–N catalysis, and these too, can bind to the titanium center, much like a donor would, and lead to the production of high molecular weight polymers. Since such species would have existed from the very beginning in Z–N systems, one begins to see that they would have had an influence that only began to become visible with the probing that could be done with computational studies.

### Conclusions and the Way Forward

The main findings from computational studies of Z–N catalysis can, therefore, be summarized as follows:

- (1) New understanding of the nature of MgCl<sub>2</sub> surfaces and their interactions with titanium species, as well as with donors, has emerged because of computational studies.
- (2) Computational studies have provided insights into the stability of Z–N systems due to the presence of donors. They have also helped explain why donors having two oxygen atoms are more efficient than donors having a single oxygen atom.

New understanding of the nature of MgCl<sub>2</sub> surfaces and their interactions with titanium species, as well as with donors, has emerged because of computational studies.



(3) It has become possible to understand the role of donors in influencing the molecular weight distribution in Z–N systems. This is because computational studies have shown that binding of donors directly to the titanium center leads to an increase in the molecular weight of the polymer produced.

A donor can actually ‘walk’ on the  $\text{MgCl}_2$  surface employing the oxygen atoms as its ‘legs’.

There are, however, many other aspects of Z–N catalysis that requires careful analysis through computational investigations. One issue that needs thorough study is how a donor might break up, *i.e.*, decompose at a titanium catalyst site, and what effects such donor decomposition can have on the eventual performance of the Z–N systems. Donor decomposition has indeed been observed in Z–N systems, and several decomposition routes have been suggested experimentally [22, 23]. Computational investigations of such courses can provide a better understanding of how donor decomposition occurs in Z–N systems [24]. Furthermore, computational studies have revealed another interesting aspect of donor chemistry. A donor can actually ‘walk’ on the  $\text{MgCl}_2$  surface! This is because, if a donor has more than one oxygen atom, it can move from one magnesium to another on the  $\text{MgCl}_2$  surface, employing the oxygen atoms as its ‘legs’ [25, 26]. There are likely, many other fascinating properties of different components of the Z–N systems that might come to light as further strides are made in understanding, to the fullest, the nature of Ziegler–Natta catalyst systems.

### Suggested Reading

- [1] P Corradini, V Barone, R Fusco and G Guerra, Analysis of Models for the Ziegler–Natta Stereospecific Polymerization on the Basis of Non-bonded Interactions at the Catalytic Site–I, The Cossee Model, *Eur. Polym. J.*, Vol.15, p.1133, 1979.
- [2] P Corradini, G Guerra, R Fusco and V Barone, Analysis of Models for the Ziegler–Natta Stereospecific Polymerization on the Basis of Non-bonded Interactions at the Catalytic Site–II: Edges, Steps and Reliefs on the Surface of Layered Modifications of  $\text{TiCl}_3$ , *Eur. Polym. J.*, Vol.16, p.835, 1980.
- [3] P Corradini, V Barone and G Guerra, Steric Control in the First Step of the Isospecific Ziegler–Natta Polymerization of Propene, *Macromolecules*, Vol.15, p.1242, 1982.
- [4] P Corradini, V Barone, R Fusco and G Guerra, A Possible Model of Catalytic



- Sites for the Stereospecific Polymerization of  $\alpha$ -olefins on First-generation and Supported Ziegler–Natta Catalysts, *Gazz. Chim. Ital.*, Vol.113, p.601, 1983.
- [5] P Corradini, G Guerra and V Barone, Conformational Analysis of Polypropylene Chains Bound to Model Catalytic Sites, *Eur. Polym. J.*, Vol.20, p.1177, 1984.
- [6] M Toto, G Morini, G Guerra, P Corradini and L Cavallo, Influence of 1,3-Diethers on the Stereospecificity of Propene Polymerization by Supported Ziegler–Natta Catalysts. A Theoretical Investigation on Their Adsorption on (110) and (100) Lateral Cuts of  $\text{MgCl}_2$  Platelets, *Macromolecules*, Vol.33, p.1134, 2000.
- [7] M Seth, P M Margl and T Ziegler, A Density Functional Embedded Cluster Study of Proposed Active Sites in Heterogeneous Ziegler–Natta Catalysts, *Macromolecules*, Vol.35, p.7815, 2002.
- [8] M Boero, M Parrinello, H Weiss and S Hüffer, A First Principles Exploration of a Variety of Active Surfaces and Catalytic Sites in Ziegler–Natta Heterogeneous Catalysis, *J. Phys. Chem. A*, Vol.105, p.5096, 2001.
- [9] M Boero, M Parrinello and S Hüffer, J Weiss, First Principles Study of Propene Polymerization in Ziegler–Natta Heterogeneous Catalysis, *J. Am. Chem. Soc.*, Vol.122, p.501, 2000.
- [10] G Monaco, M Toto, G Guerra, P Corradini and L Cavallo, Geometry and Stability of Titanium Chloride Species Adsorbed on the (100) and (110) Cuts of the  $\text{MgCl}_2$  Support of the Heterogeneous Ziegler–Natta Catalysts, *Macromolecules*, Vol.33, p.8953, 2000.
- [11] M Boero, M Parrinello and K Terakura, First Principles Molecular Dynamics Study of Ziegler–Natta Heterogeneous Catalysis, *J. Am. Chem. Soc.*, Vol.120, p.2746, 1998.
- [12] J C Chadwick, G Morini, G Balbontin, I Mingozzi, E Albizzati and O Sudmeijer, Propene Polymerization with  $\text{MgCl}_2$ -Supported catalysts: Effects of Using a Diether as External Donor, *Macromol. Chem. Phys.*, Vol.198, p.1181, 1997.
- [13] M C Sacchi, F Forlini, I Tritto, P Locatelli, G Morini, L Noristi and E Albizzati, Polymerization Stereochemistry with Ziegler–Natta Catalysts Containing Dialkylpropane Diethers: A Tool for Understanding Internal/External Donor Relationships, *Macromolecules*, Vol.29, p.3341, 1996.
- [14] G Morini, E Albizzati, G Balbontin, I Mingozzi, M C Sacchi, F Forlini and I Tritto, Microstructure Distribution of Polypropylenes Obtained in the Presence of Traditional Phthalate/Silane and Novel Diether Donors: A Tool for Understanding the Role of Electron Donors in  $\text{MgCl}_2$ -Supported Ziegler–Natta Catalysts, *Macromolecules*, Vol.29, p.5770, 1996.
- [15] M C Sacchi, F Forlini, I Tritto and P Locatelli, Stereochemistry of the Initiation Step in Ziegler–Natta Catalysts Containing Dialkyl Propane Diethers: A Tool for Distinguishing the Role of Internal and External Donors, *Macromol. Symp.*, Vol.89, p.91, 1995.
- [16] A Correa, F Piemontesi, G Morini and L Cavallo, Key Elements in the Structure and Function Relationship of the  $\text{MgCl}_2/\text{TiCl}_4$ /Lewis Base Ziegler–Natta Catalytic System, *Macromolecules*, Vol.40, p.9181, 2007.
- [17] T Taniike, M Terano, Coadsorption and Support-mediated Interaction of Ti Species with Ethyl Benzoate in  $\text{MgCl}_2$ -Supported Heterogeneous Ziegler–Natta



- Catalysts Studied by Density Functional Calculations, *Macromol. Rapid Commun.*, Vol.28, p.1918, 2007.
- [18] A Correa, R Credendino, J T M Pater, G Morini and L Cavallo, Theoretical Investigation of Active Sites at the Corners of  $\text{MgCl}_2$  Crystallites in Supported Ziegler-Natta Catalysts, *Macromolecules*, Vol.45, p.3695, 2012.
- [19] R Credendino, D Liguori, Z Fan, G Morini and L Cavallo, Toward a Unified Model Explaining Heterogeneous Ziegler-Natta Catalysis, *ACS Catal.*, Vol.5, p.5431, 2015.
- [20] K Vanka, G Singh, D Iyer and V K Gupta, DFT Study of Lewis Base Interactions with the  $\text{MgCl}_2$  Surface in the Ziegler-Natta Catalytic System: Expanding the Role of the Donors, *J. Phys. Chem., C*, Vol.114, p.15771, 2010.
- [21] J Kumawat, V K Gupta and K Vanka, The Nature of the Active Site in Ziegler-Natta Olefin Polymerization Catalysis Systems A Computational Investigation, *Eur. J. Inorg. Chem.*, Vol.29, p.5063, 2014.
- [22] J C W Chien, J -C Wu, Magnesium-chloride-supported High-mileage Catalysts for Olefin Polymerization. II. Reactions Between Aluminum Alkyl and Promoters, *J. Polym. Sci. Polym. Chem.*, Ed. Vol.20, p.2445, 1982.
- [23] E Vähäsarja, T T Pakkanen, T A Pakkanen, E Iiskola and P J P Sormunen, Modification of Olefin Polymerization Catalysts, I. Mechanism of the Interaction Between  $\text{AlEt}_3$  and Silyl Ethers, *J. Polym. Sci. Part A: Polym. Chem.*, Vol.25, p.3241, 1987.
- [24] J Kumawat, V K Gupta, K Vanka, Donor Decomposition by Lewis Acids in Ziegler-Natta Catalyst Systems: A Computational Investigation, *Organometallics*, Vol.33, p.4357, 2014.
- [25] R Credendino, J T M Pater, D Liguori, G Morini and L Cavallo, Investigating Alkoxysilane Coverage and Dynamics on the (104) and (110) Surfaces of  $\text{MgCl}_2$ -supported Ziegler-Natta Catalysts, *J. Phys. Chem., C*, Vol.116, p.22980, 2012.
- [26] R Credendino, D Liguori, G Morini and L Cavallo, Investigating Phthalate and 1,3-Diether Coverage and Dynamics on the (104) and (110) Surfaces of  $\text{MgCl}_2$ -supported Ziegler-Natta Catalysts, *J. Phys. Chem., C*, Vol.118, p.8050, 2014.

Address for Correspondence

K Vipin Raj<sup>1</sup> and Kumar  
Vanka<sup>2</sup>

CSIR-National Chemical  
Laboratory, Pashan  
Pune 411 008, India.

Email:

<sup>1</sup>k.vipinraj@ncl.res.in

<sup>2</sup>k.vanka@ncl.res.in

