

The Co-adsorption of tetramethylpiperidine and TiCl_4 on $\beta\text{-MgCl}_2$ A theoretical study of a Ziegler–Natta pre-catalyst

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Abstract

An extended Hückel method (ICONC), which includes core–core repulsion energy terms, was used to characterise the MgCl_2 /2,2,6,6-tetramethylpiperidine (TMPIP)/ TiCl_4 system by modelling the TMPIP and TiCl_4 adsorption on the (100)–(101) and (110) faces of MgCl_2 . The results show how the amine modifies the chemical and electronic states of adsorbed TiCl_4 . The appearance of complexes at the surface, previously studied by infrared spectroscopy is supported by our calculation. The geometrical and structural factors governing the formation of precursors of active sites for propylene polymerisation were also studied.

Keywords: Ziegler–Natta polymerisation; Extended Hückel; MgCl_2 ; Tetramethylpiperidine; TiCl_4 ; Stereospecific site

1. Introduction

At present, the production of isotactic polypropylene is based on the use of complex heterogeneous catalysts. A large number of studies have focused on MgCl_2 -supported Ziegler–Natta catalysts since its excellent catalytic properties for polypropylene production were discovered. Particularly, the combination of solid (MgCl_2) acting as a support, an electron donor and TiCl_4 constitutes a pre-catalyst for highly stereospecific polymerisation of

olefins. However, some important issues concerning the structure of the active sites and the role of the support are still poorly resolved [1–9].

Highly active MgCl_2 based catalysts can be obtained by mechanical treatment of their mixtures with Lewis bases. The ball milling introduces stacking faults on the crystalline structure whose stability can further be improved by the presence of electron donors. The laminar structure of MgCl_2 promotes both easier breakages parallel to the chlorine layers, which are joined together by means of van der Waals' weak forces, and more difficult breakages across the layers where strong ionic bonds are involved [10,11]. The adsorption capacity of ionic solids

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is associated with the presence of defects in their structure. In real crystals the chlorine vacancies are supposed to be at the surface and in the areas where dislocations are formed [12]. This phenomenon was observed by means of microphotos which reproduce the polymer growth on corners and edges of the MgCl_2 where Ti atoms are preferentially located on the most exposed sites [10,11]. Apparently, the donor is fixed on the catalyst's surface selectively poisoning the precursors of the non-stereospecific sites. Preliminary energy calculations suggest that (100) faces should be more basic than the (110) ones. Thus, the stereoregulating ability of donors could be related to the capability of TiCl_4 to displace the base or to form a complex on (100)–(101) faces. This process gives rise to dimeric and monomeric TiCl_4 species. The non-stereospecific sites would be located on the (110) face so the Lewis base should be placed mainly at (110) planes, avoiding the formation of non-stereospecific precursors including TiCl_4 . Our previous work confirms this idea when it is applied to ethylbenzoate (EB) [13]. In that sense the work of Busico et al. is in agreement with our analysis when EB is the internal donor [14].

Solid (MgCl_2) acting as a support, an electron donor (internal donor) and TiCl_4 constitute a pre-catalyst. This pre-catalyst is activated by an aluminum alkyl and another electron donor (external donor). One of the functions of the internal donor is to impose some restrictions on the Ti coordination. Although this is not the only role of the internal donor, its presence is required in order to confer selectivity to the catalyst.

We had previously characterised a MgCl_2 /internal donor/ TiCl_4 system by means of conventional experimental techniques during the preparation procedure. This experimental information allowed us to speculate on the structure of the surface compounds formed. Therefore, we decided to study models that represent the proposed structures in order to determine the possibility of their occurrence by

means of semiempirical molecular orbital calculations.

We investigated the precatalyst formed by a secondary amine — 2,2,6,6-tetramethylpiperidine (TMPiP) — as internal donor. Although some experimental data are available for this system, the characterisation is scarce. It should be mentioned that secondary amines used as external donor in combination with MgCl_2 /ethylbenzoate/ TiCl_4 as precatalyst and AlEt_3 as co-catalysts generate highly active and selective catalysts for isotactic polypropylene production [7]. In the literature, several authors have pointed out the importance of the internal–external donor interaction in the catalyst's performance [14,15]. We have done a complete characterisation of the MgCl_2 /TMPiP/ TiCl_4 system (and the polymer product) by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and scanning microscopy. The propylene polymerisation reaction tests were conducted using AlEt_3 , AlEt_3 /EB and AlEt_3 /TMPiP as activators. The obtained polypropylene was atypical, presenting an isotacticity index (II) equal to 38% and low molecular weight.

The purpose of this paper is to study the adsorption of TMPiP on a cluster model of MgCl_2 and its coadsorption with TiCl_4 theoretically. We think that the appropriate combination of experimental and theoretical techniques could be very useful in the characterisation of polymerisation catalysts, in the sense that theoretical calculations can help or guide the experimental work.

2. Theoretical method

The molecular orbital calculations were carried out by means of an extended Hückel method (EHMO), a semiempirical procedure which provides a useful preliminary approach to electronic structure [16]. This formalism has been widely used in the past to study electronic energy changes and it is useful for obtaining qualitative trends in adsorption processes [17]. Hence,

Table 1
Atomic orbital parameters

	<i>n</i>	<i>H_{ii}</i>	η_1	<i>C₁</i>	η_2	<i>C₂</i>
H	1	s	-13.60	1.000		
C	2	s	-19.65	1.554		
		p	-11.13	1.451		
N	2	s	-26.00	1.924		
		p	-13.40	1.917		
Mg	2	s	-7.64	1.103		
Cl	3	s	-26.03	2.359		
		p	-14.20	2.039		
Ti	4	s	-8.97	1.075		
		p	-5.44	0.675		
		d	-10.81	4.550	0.4521	1.400

n: principal quantum number; *H_{ii}*: matrix element, eV; η_i : Slater orbital exponents, (a.u.); *C_i*: linear coefficients for double-zeta *d* functions.

we believe that this method is more useful to study the active site precursors formed during the impregnation step as an initial screening than the conventional trial and error method.

The program used (ICONC) was developed by Chamber et al. [18]. It includes repulsive terms to the total energy which are not explicitly included in the EHMO. The repulsive coulombic energy is taken into account in a pairwise term.

The total energy of adsorbed species was calculated as the difference between the electronic energy of the system when the adsorbed molecule is at a finite distance from the surface of a MgCl₂ cluster and when the molecule is far away from the solid surface. The atomic parameters are listed in Table 1.

3. The surface model and the structure of sites

The surface chosen corresponds to the hexagonal distorted MgCl₂ called the β -form. Its lattice parameters are $a = b = 3.63 \text{ \AA}$ $c = 5.93 \text{ \AA}$. The Mg–Cl distance is 2.57 \AA and the Mg coordination is octahedral [19,20]. Cl–Mg–Cl bond angles were obtained from the literature [19].

28 Mg and 68 Cl atoms were used to model

the (100) face (which is structurally similar to (101)). A chlorine defect was also included in order to represent the modifications produced during the mechanical activation of the support. Due to the geometric structure of a (100) plane, a high concentration of Cl defects is expected after milling. The 96 atoms are distributed in four rows of seven Mg and seventeen Cl. The Cl defect was placed on the second row (see Fig. 1, (100) plane).

On the (110) face, Mg and Cl do not introduce steric limitations to the Lewis base (TMPiP) or TiCl₄ adsorption. In this plane the Cl and Mg ions are both at the same level while in the (100) the Cl is above the Mg row (see Fig. 2, (110) plane).

According to Arlman and Cossee's ideas [21] on the MgCl₂ (100) and (110) faces, three kinds of Mg can be mentioned. On the (110) plane the surface Mg is tetracoordinated with an effective charge equal to $+\frac{1}{3} e^-$ while on the (100) plane Mg is pentacoordinated and its charge is $0 e^-$. The milling process introduces Cl defects on the (100) plane and then the Mg could be found with effective charge $+\frac{1}{2} e^-$. These sites could be considered as preferential for Lewis base adsorption due to the acidity of the surface: Mg, with a Cl defect on the (100) plane, and an

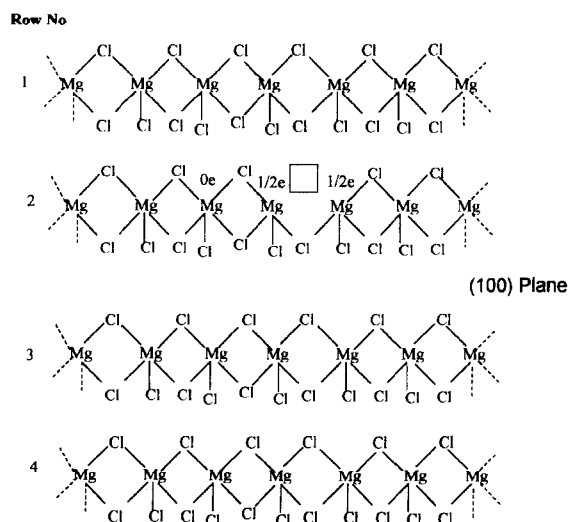


Fig. 1. (100)–(101) face of MgCl₂. Complete cluster used in the EHMO calculation.

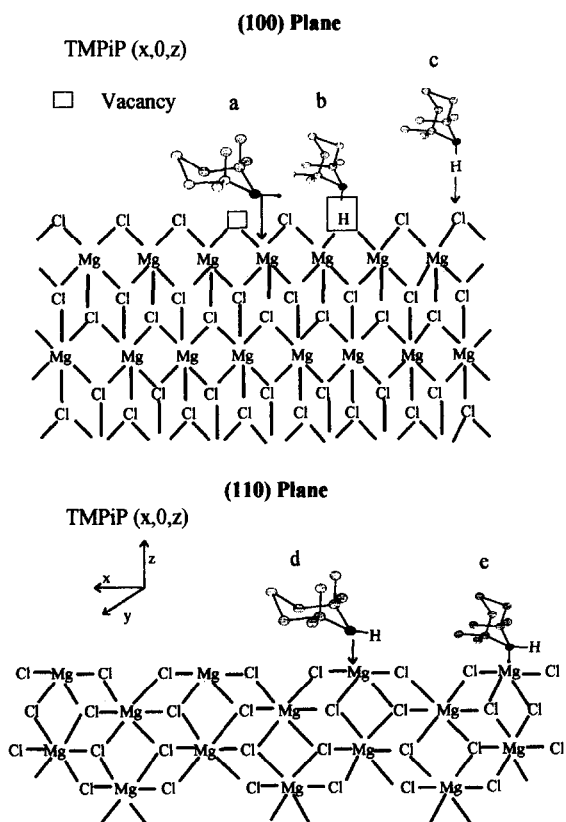


Fig. 2. (a, b and c) TMPiP possible adsorption forms on MgCl_2 (100)–(101). (d, e) TMPiP possible adsorption forms on MgCl_2 (110).

exposed Mg on the (110) plane. Furthermore, on the (110) face, it is difficult to think of a stable Mg species with a coordination number three and with an hypothetical effective charge equal to $+\frac{5}{6} e^-$. These strong acid sites are not probable [21].

A second cluster with 24 Mg and 54 Cl atoms was used to model the (110) face. Four parallel rows of six Mg and four rows with 13–14–13 and 14 Cl atoms form the cluster (see Fig. 2d and e). It should be mentioned that the cluster size could influence the prediction on the relative stability of planes, however our analysis will be restricted to adsorption properties, more local in nature than bulk properties. Several authors have made relevant contributions related with surface stability. Colbourn et al., using a static lattice calculation method,

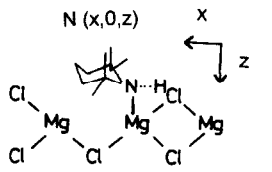
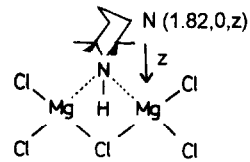
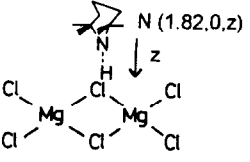
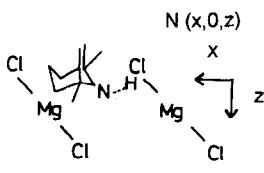
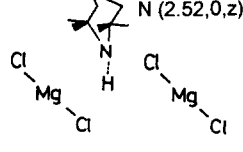
pointed out that $\alpha\text{-MgCl}_2$ (100) plane unreconstructed is very unstable compared to (110) [22]. After surface reconstruction and relaxation an alternative (100) surface is generated, more stable than the (110) plane, with five fold Mg coordination. These authors also report density functional theory (DFT) calculations of TiCl_4 on different MgCl_2 surfaces. Lin and Catlow in a previous paper have modeled the $\beta\text{-MgCl}_2$ based on a Born representation for polar solids [23]. They also found the (100) plane more stable than (110) and that the electronic changes in the surface ions are confined to a small number of atoms. Harrison and Saunders have investigated the electronic and structural properties of the layered $\beta\text{-MgCl}_2$ within a LCAO-SCF HF approximation [20]. The calculations clearly show the partially covalent nature of the bonding as evidenced by Mulliken population analysis, band structures, density of states and distribution of charge in real space. The same authors extend their research to include correlation functional estimates of the dispersion interactions between the anions under the local density approximation to DFT [24,25]. Recently, studies based on quantum mechanical methods using a point charge embedded cluster technique applied to the Ti/MgCl_2 supported Ziegler–Natta catalysts have been successful to indicate that Ti(III) complexes will be adsorbed more strongly than those of Ti(IV) on the (100) surface [26].

In the past, clusters of similar size to the ones used in this paper have been used to simulate more complex structures like organometallic compound chemisorption on TiCl_3 and monomer insertion [27]. At this step short range order forces play the main part. Ionic solids like CaF_2 bulk and CaF_2/Si (111) interface have been characterised recently using ASED tight binding and cluster models. The close agreement between the calculated electronic structures and mechanical properties predicted with a semi-infinite ionic solid and small clusters confirm the applicability of our approach, under the ICONC formalism [28].

In the two MgCl_2 clusters used to represent the (100) or the (110) face, dangling bonds were saturated with hydrogen atoms. A comment relevant to this point follows. One of the main shortcomings of the cluster approach consists of the scission of the chemical bonds between terminal atoms of a cluster and the rest of a lattice. As a result dangling bonds occur at the terminal atoms, artificial electron surface states appear and the charge distribution is disturbed.

Some characteristics of the electron structure (i.e. Fermi level, ionisation potential) which are sensible to bulk properties of the solid converge slowly when the cluster size is increased. However, in the chemisorption calculations the local interactions are frequently of primary importance. A way to improve the results treats the surrounding lattice as an immersed cluster [29]. That proposal is useful when structural inhomogeneity is present. Hydrogen atoms were used

Table 2
TMPiP relative adsorption energies on MgCl_2 (100) and (110)

Adsorption	Structure ¹	Relative Energy ² (eV)	
		(internal)	(total)
TMPiP/ MgCl_2 (100) parallel to the surface on a Cl defect $d(\text{N-Mg}) = 2.9 \text{ \AA}$		-1	-0.40
TMPiP/ MgCl_2 (100) perpendicular to the surface at a Cl defect		+0.75	+0.30
TMPiP/ MgCl_2 (100) perpendicular to the surface without the Cl defect		+0.60	+0.24
TMPiP/ MgCl_2 (110) parallel to the surface $X \text{ min} = 2.13 \text{ \AA}$ $Z \text{ min} = 2.00 \text{ \AA}$		-0.50	-0.20
TMPiP/ MgCl_2 (110) perpendicular to the surface		0.10	0.05

^a The modified coordinates are also shown.

^b The (-) or (+) symbol stands for stable or unstable situation, respectively.

as saturating atoms by Hayns [30] while Mikheikin et al. [31] have used monovalent atoms whose quantum chemical parameters are adjusted (so-called 'pseudo atoms'). Lin and Catlow terminate a MgCl_2 cluster with point charges to accurately reproduce the long range electrostatic potential in the region of the adsorption site [26]. The non-self-consistency of the EHMO method gives poor charge distribution; under this restriction we have evaluated the alternative to consider point charges instead of H atom termination. Our results indicate that the qualitative picture is maintained and no further improvement is achieved.

The (100) and (110) faces of MgCl_2 are shown in Figs. 1 and 2, where the different forms of TMPiP adsorption are also indicated (parallel to the MgCl_2 surface, Fig. 2a and d and perpendicular Fig. 2b, c and e).

Carbon-carbon and carbon-nitrogen distances of TMPiP were obtained from the literature [32–34] while the N–H distance was optimized. The resulting value for the TMPiP in its 'chair' form — assumed as the stable geometry at the surface — and with the H in equatorial position was 1.10 Å. The TMPiP adsorption is considered to proceed by lone-pair N donation to a coordinatively unsaturated Mg (CUS-Mg) surface site. The CUS-Mg can be found on the (100) plane with a vacancy and effective charge $0 e^-$ and with two vacancies and charge $+\frac{1}{2} e^-$, while on the (110) plane with two vacancies and charge $+\frac{1}{3} e^-$ [21].

In order to obtain the minimum energy position for TMPiP on top of each MgCl_2 face, the following assumptions were made. On the (100) face, we considered three possible forms (see Fig. 2):

1. parallel to the MgCl_2 surface at a Cl defect,
2. perpendicular to the MgCl_2 surface at a Cl defect,
3. perpendicular to the MgCl_2 surface without the Cl defect.

The adsorption of TMPiP perpendicular to the surface without a Cl defect in the (100) face is unstable according to the positive value for

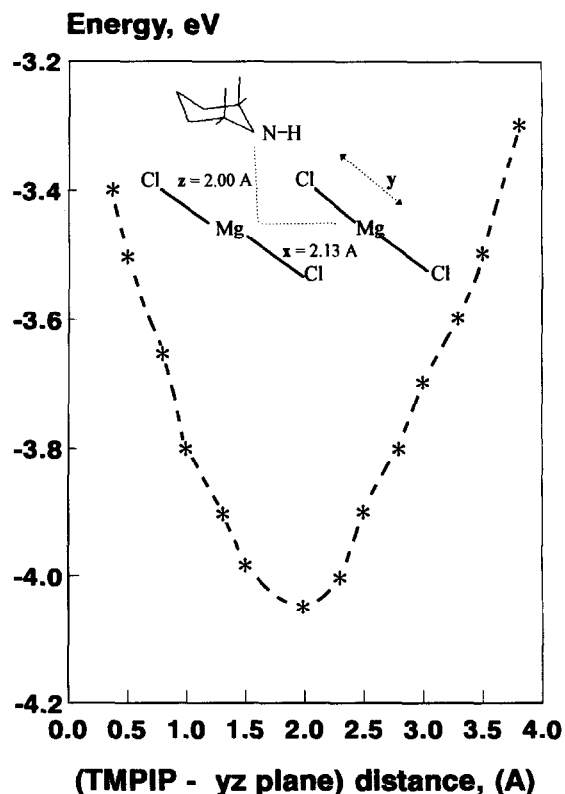


Fig. 3. Adsorption energy versus TMPiP-(110) MgCl_2 z distance.

the adsorption energy obtained by the ICONC calculations (see relative energy values, Table 2).

On the other hand, the adsorption of TMPiP in its chair form on the (110) face is considered to occur parallel to the surface (Fig. 2d). The perpendicular form turns out to be energetically less stable (see Table 2). On both MgCl_2 faces the TMPiP x , y and z coordinates were varied maintaining the amine on the 'acid' Mg. Our FTIR experimental evidence supports a direct N–Mg interaction in the TMPiP/ MgCl_2 system [27].

Once the minimum energy position of TMPiP on the surface was found, the displacement of TiCl_4 from infinity in order to be adsorbed onto the surface of TMPiP/ MgCl_2 was considered. Several alternatives for TiCl_4 were considered. We named them forms 1, 2 and 3 (see Fig. 3):

Form 1: Octahedral TiCl_4 interacting with the N atom of the TMPiP on the (100)–(101)

and (110) faces, parallel to the MgCl_2 surfaces, approaching by the N side varying its x coordinate. The (x, y, z) coordinates of TiCl_4 were optimized (see Fig. 3 and the figures included in Tables 3 and 4).

Form 2: Octahedral TiCl_4 interacting with the N atom approaching over it. The x and y coordinate were fixed while varying the z (height) of TiCl_4 .

Form 3: Distorted octahedral TiCl_4 adsorbed in a bridged form (see Fig. 3) over a Mg atom of the surface interacting with the N atom of TMPiP on (110) face. The y coordinate was fixed while varying the x and z .

The three selected forms were suggested as a result of the $\text{TMPiP-MgCl}_2\text{-TiCl}_4$ interactions [35]. For the adduct TiMgCl_6 the TiCl_4 acceptor molecule changes its coordination from tetrahedral to octahedral [36]. The non-saturated Mg on the surface can form Cl bridged bonds with TiCl_4 resulting in a strongly bonded sur-

face complex (see form 1). Because of lattice matching between TiCl_3 and MgCl_2 the crystal growth would have a natural tendency to follow the structural pattern of the surface when supporting TiCl_4 and the octahedral coordination is sustained after reduction with AlEt_3 . The vacancies on Ti sites are well known in the studies of Lewis base coadsorption and activator interactions. Some experimental evidence support the idea that the active Ti species are octahedral and tetrahedral distorted [11]. The selected forms for TiCl_4 adsorption attempt to represent isolated penta- or hexacoordinated Ti species. It is worth mentioning however that they could be regarded as terminal species of Ti_xCl_y clusters. This is more likely to occur on (100) face. Chien et al. have suggested three different kinds of epitaxial TiCl_4 positions on this plane, always with octahedral coordination [9]. Iiskola et al. have also mentioned the coordination of two Cl (from TiCl_4) to only one surface Mg, in an ab-initio

Table 3
 $\text{TiCl}_4/\text{TMPiP}$ relative adsorption energies on MgCl_2 (100)

Adsorption	Structure ¹	Relative Energy ² (eV)	
		(internal)	(total)
$\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2(100)$ Form 1 - Ti by the N side $x_{\text{min}} = 5.90 \text{ \AA}$ $z_{\text{min}} = 4.70 \text{ \AA}$ $d(\text{Ti-N}) = 2.89 \text{ \AA}$ $d(\text{N-Mg}) = 2.90 \text{ \AA}$		-0.34	-0.34
$\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2(100)$ Form 2- Ti over N $d(\text{Ti-N}) = 3.80 \text{ \AA}$		-1	-1

^a The modified coordinates are also shown.

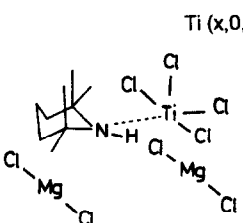
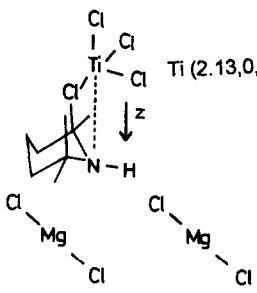
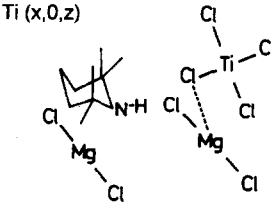
^b The (-) or (+) symbol stands for stable or unstable situation, respectively.

theoretical study [37]. We focus our study on an octahedral species without vacancies interacting with the surface and the TMPiP (form 1), an octahedral species with a vacancy without interaction with MgCl_2 (form 2) and a bridged species on the MgCl_2 (110) face (coordinating a Mg with two Cl) interacting with the Lewis base and a vacancy [38]. After reduction to Ti (III) these species could suffer a geometrical distortion, but even in this case the octahedral

coordination is suggested [39]. It is well established that the metal atom in transition metal compounds tends to achieve an 18 electron valence shell, so the close Ti–N interaction in the forms 1, 2 and 3 is highly possible [40].

In a previous paper, we studied the adsorption of TiCl_4 on MgCl_2 theoretically. We reported that octahedral TiCl_4 on the (100) plane has an energy minimum when the Ti atom is 2.7 Å away from the nearest Cl on the MgCl_2

Table 4
 $\text{TiCl}_4/\text{TMPiP}$ relative adsorption energies on MgCl_2 (110)

Adsorption	Structure ¹	Relative Energy ² (eV)	
		(internal)	(total)
$\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2(110)$ Form 1 - Ti by the N side Xmin = 4.20 Å d(Ti-N) = 2.23 Å Zmin (TMPiP) = 2.00 Å		Ti (x,0,z) 0.58	0.38
$\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2(110)$ Form 2 - Ti over N Zmin = 5.75 Å d(Ti-N) = 3.75 Å Xmin = 4.20 Å		Ti (2.13,0,z) 1	0.65
$\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2(110)$ Form 3 - Ti "bridged" Xmin = 4.67 Å Zmin = 3.13 Å d(Ti-N) = 1.91 Å		Ti (x,0,z) 0.45	0.30

^a The modified coordinates are also shown.

^b The (-) or (+) symbol stands for stable or unstable situation, respectively.

surface [13]. When the (110) face was considered, TiCl_4 adsorption was studied with the Cl–TiCl group over the y axis centred on a Mg atom. In this position, the minimum energy for the system was obtained when the distance from these Cl atoms to the surface was 3.14 Å [13].

In the present work, other possible forms for TiCl_4 adsorption were not considered because they could not lead to Ti–N interaction. We want to emphasise that the description given above is not intended to be exhaustive, but to explore the possibilities of the existence of surface species for which there is experimental evidence qualitatively [35].

Figs. 5, 6, 8 and 9 show three-dimensional views of the structures of active sites considered. Tables 2–4 present the results of the ICONC calculation on a relative energy scale.

4. Results and discussion

Due to the approximate nature of the ICONC calculations only relative energy values are reported in Tables 2–4. On the (100) face the most stable situation is obtained when the TMPiP molecule is adsorbed on a Cl deficient site with a minimum Mg–N distance of 2.9 Å. The adsorption of TMPiP parallel to the surface without a Cl defect is not possible according to the calculations. If the Cl-defect is filled with the correspondent atom then steric restrictions and high coulombic energy repulsions are present, as was found by calculations. For this reason the TMPiP parallel orientation adsorption is preferred to the perpendicular orientation adsorption, as mentioned earlier.

When the (110) surface is considered, the minimum energy of the TMPiP/ MgCl_2 system is achieved when the amine in its chair form is parallel to MgCl_2 , in the middle of two adjacent Mg atoms. The TMPiP was placed at the energy minimum (see Fig. 3), 2.00 Å away from the surface (z coordinate), the x coordinate (parallel to the surface) was modified until another energy minimum was reached. This minimum

was found at $x = 2.13$ Å, between two Mg of the lattice (see the corresponding scheme in Table 2 and Fig. 3).

According to these results, TMPiP adsorption parallel to the surface of the support, as proposed from the experimental data, is quite possible [35]. From Table 2 we conclude that TMPiP adsorption on the (100) surface is more favourable than on the (110) face because the energy on the (100) plane is about twice the energy required to desorb the base on the other plane.

When energy calculations for the adsorption of TiCl_4 on MgCl_2 (100) face — in the presence of TMPiP placed at its minimum energy position — are made, the following results are obtained. Form 1 of TiCl_4 shows an energy minimum when the Ti–N distance is 2.89 Å (see Table 3 and Fig. 5). In this situation the calculated Mg–N distance is 2.90 Å. With the purpose of making the Ti–N interaction in this calculation easier, the amine H was fixed at 1.10 Å on the y axis. Our experimental evidence shows that the N–H infrared bands are seriously affected after TiCl_4 impregnation [35]. The adsorption in form 2, where Ti is not bonded to the surface, is found to be very stable at a Ti–N distance near 3.80 Å (see Table 3, Figs. 6 and 7). This implies that TiCl_4 is placed on the (100) face, without direct interaction with MgCl_2 . In this case, form 2 is obviously favoured over form 1. A strong repulsion, probably due to Cl– CH_3 interaction, is present at Ti–N distances smaller than 3.5 Å. Form 3 is not considered on the (100) face due to its geometry.

On the (110) face, when form 1 is considered, a minimum is obtained for a Ti–N distance of 2.23 Å as is shown in Table 4 (see also Fig. 8). On the other hand when form 2 is analysed, a stable system is found when the Ti–N distance is 3.75 Å (see Fig. 9). Form 3 is also possible and has a Ti–N distance of 1.91 Å. Considering these results form 2 is favoured on both MgCl_2 planes. The Ti–N distance in the case of form 3 is close to a bond length for

unsaturated complexes (1.85–1.98 Å, Ref. [41]). It has been suggested that the TiCl_4 molecule should adsorb on these surfaces with only one bridged Cl. The calculation indicate that the adsorption energies with one Cl are less favourable than with two bridged Cl. Lin and Catlow have noticed that Mg species tend to coordinate as many Cl (within the TiCl_4 molecule) as possible in order to form more stable adsorbed complexes [23]. They suggest that the adsorbed molecules, which allow more Cl within the TiCl_4 to coordinate the Mg atom, will probably be important sites for this MgCl_2 supported catalysts. Our previous results are in agreement with this idea [13].

Even though the (110) plane is more acidic than the (100), the parallel adsorption of TMPiP at a Cl defect is more stable on the (100) plane. As mentioned in Section 1 this situation is unfavourable, because non-stereospecific sites are produced on the (110) face after activation with the cocatalysts. Due to the fact that TMPiP is located at the (100) plane, it cannot prevent TiCl_4 fixation on the (110) plane. In the case of $\text{TiCl}_4/\text{MgCl}_2$, it is known that non-stereospecific sites are produced on (110) plane leading to a poorly selective catalyst [10,11]. The role of the internal donor (TMPiP in this case) should be to poison the acidic sites on MgCl_2 forcing the TiCl_4 to be positioned on the (100) plane, where the most stereospecific sites are formed when the precatalyst is activated. However, if the TMPiP is strongly adsorbed on plane (100) as in this case, it could not act as a selective poison for undesired acidic sites on the (110) plane.

Different interactions between TiCl_4 and TMPiP were studied in order to explore Ti–N bonding, as previously mentioned. Some of them resulted in Ti–N distances typical of bonding. Form 1 seems to be the most interesting because Ti is adsorbed at a vacancy occupied by the TMPiP on MgCl_2 , so there would be steric restrictions to the addition of propylene during the polymerisation reaction. Form 2 would be undesirable because there are no restrictions for

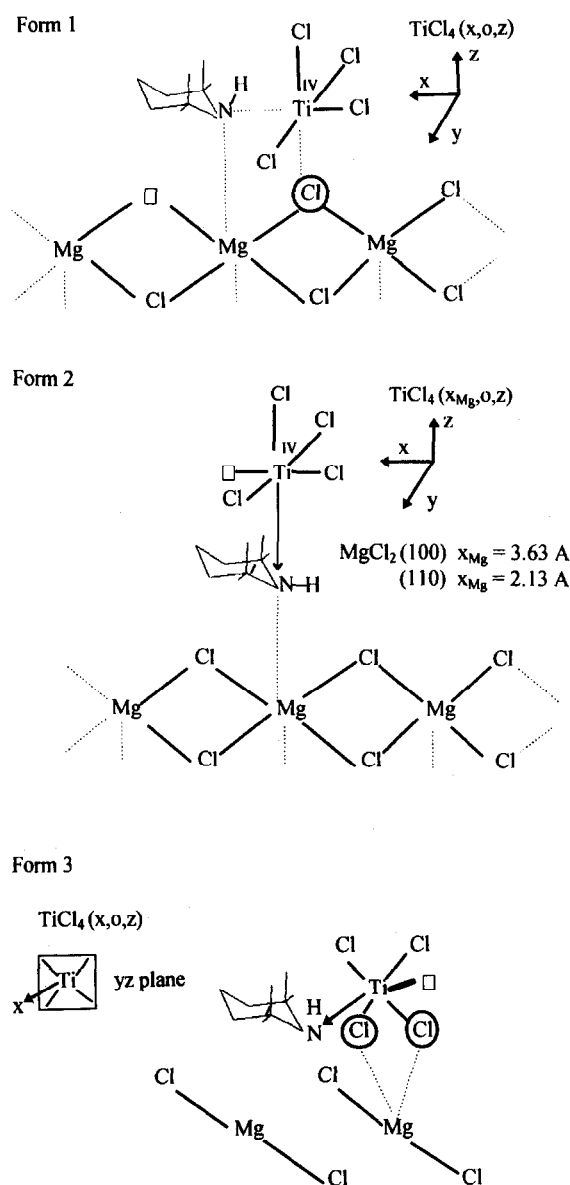


Fig. 4. TiCl_4 adsorption forms on MgCl_2 . Form 1: approaching by the N side of TMPiP . Form 2: approaching over the N of TMPiP . Form 3: TiCl_4 'bridged' on (110) face.

propylene adsorption, so the site could be non-stereospecific (see Fig. 4). In this case, Ti is not interacting with MgCl_2 directly and it can be seen as an octahedral Ti with one vacancy or pentacoordinated Ti [10,11]. The lack of Ti interaction with the support could lead to a non-stereospecific site. With this in mind, one would like to have as the most desirable situa-

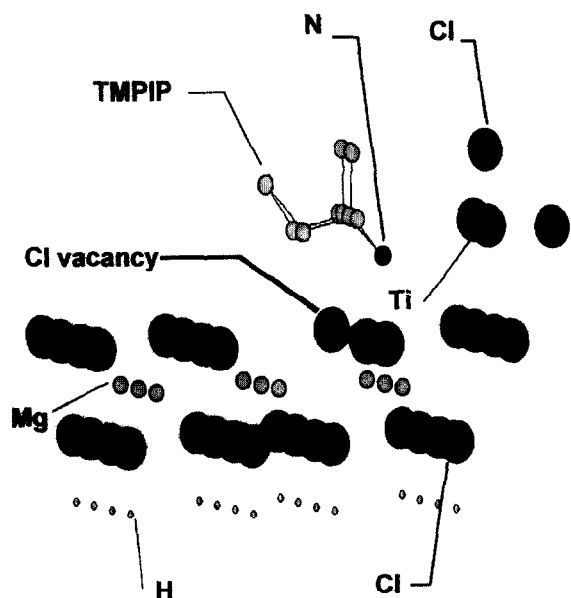


Fig. 5. TiCl_4 (form 1) on MgCl_2 (100) in presence of TMPiP .

tion the one in which TiCl_4 approaches by the N side, blocking a vacancy in the coordination sphere of TiCl_4 (Form 1, see Figs. 5 and 8). The

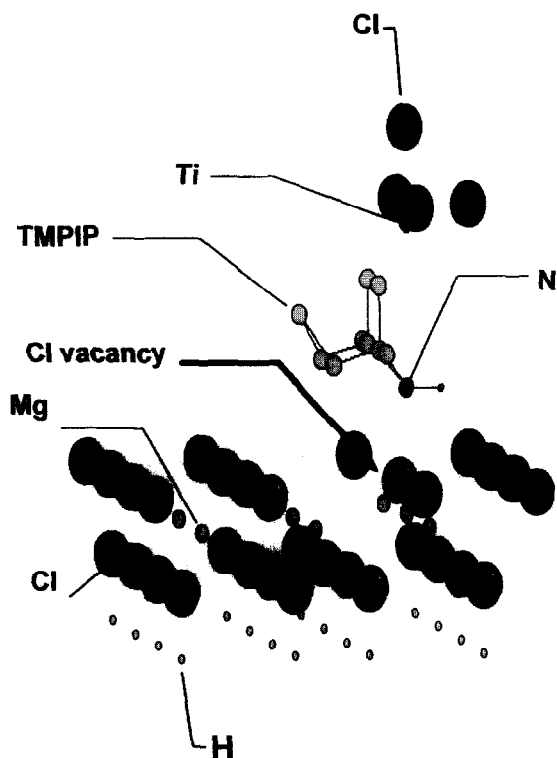


Fig. 6. TiCl_4 (form 2) on MgCl_2 (100) in presence of TMPiP .

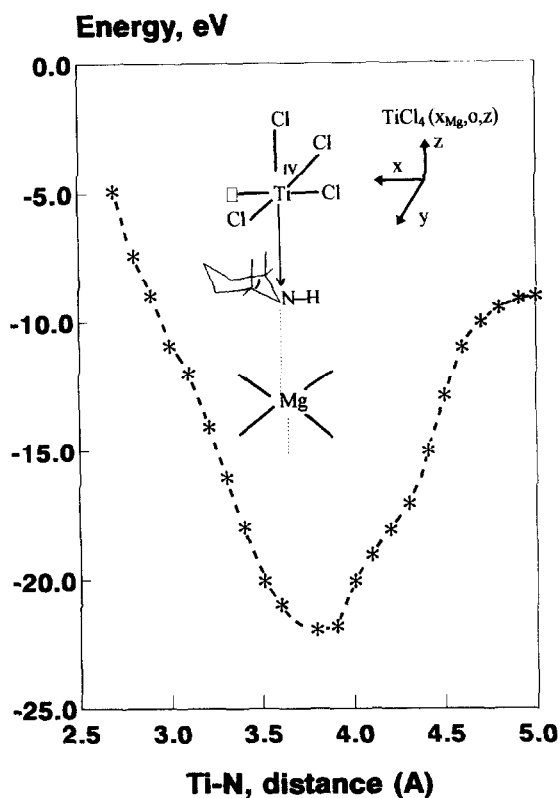


Fig. 7. Adsorption energy versus Ti (form 2)–N distance on (100) MgCl_2 .

Ti–N and Mg–N distances predicted by our theoretical calculations are nearly the same in the (100) plane and shorter than 3 Å (a typical bond length). However, although form 1 is stable in both planes, form 2 is preferred, because it is more stable (see Tables 3 and 4 and Figs. 4 and 6). Form 3 (bridged, Fig. 4) for TiCl_4 with a blocked vacancy could produce an inactive Ti by reduction [41].

Thus, the calculations predict that TMPiP is not an adequate internal donor because it is placed in an unfavourable way and will produce non-stereospecific sites on both planes and one predominant form of precursor site that is not useful for stereospecific polymerisation (form 2, Figs. 6 and 9). With these results in mind, we could say that a precatalyst where the internal donor was TMPiP would produce a non-stereospecific catalyst when it is activated (with AlEt_3 , for example), and would probably have low

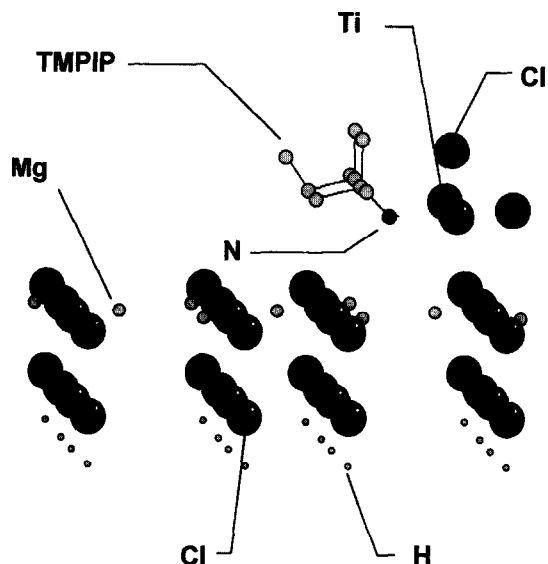


Fig. 8. TiCl_4 (form 1) on MgCl_2 (110) in presence of TMPiP.

productivity. That proposal is confirmed by experimental results. Propylene polymerisation was carried out using either the $\text{TiCl}_4/\text{TMPiP}/\text{MgCl}_2$ or $\text{TiCl}_4/\text{ethylbenzoate}/\text{MgCl}_2$ precatalysts, both activated with AlEt_3 . The results indicate that the former is one order of magnitude less active and it has

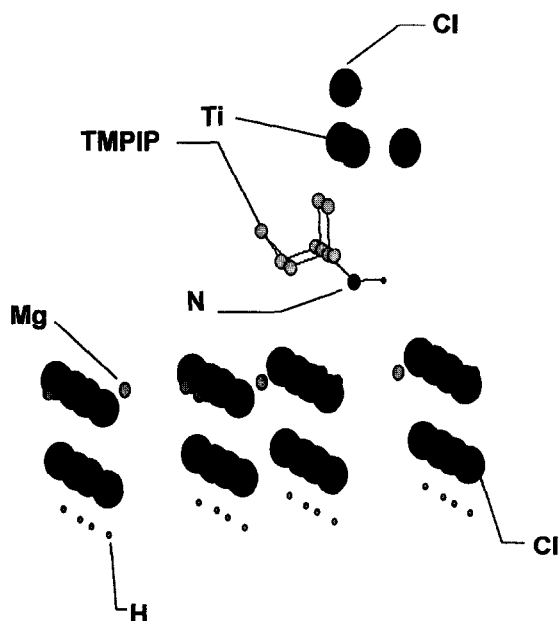


Fig. 9. TiCl_4 (form 2) on MgCl_2 (110) in presence of TMPiP.

one half of the selectivity of the latter [42,43]. These results are in accordance with ideas developed above and will be reported in detail later [43].

5. Conclusions

By the use of approximate theoretical studies, a model Ziegler–Natta precatalyst was analysed. According to the results it could not be an attractive material since site precursors formed on it could lead not only to stereospecific sites but also to non-stereogenic and unstable reaction sites that may result in a less active, less selective catalyst than the well studied one having ethylbenzoate as internal donor.

When the amine is adsorbed on a (110) face, a bridged TiCl_4 form would be preferred. The Ti–N distance of this form suggests a surface compound formation.

A TiCl_4 –TMPiP complex not bonded to the MgCl_2 surface is also predicted. This structure is possible in both faces and could result in sites without steric or geometric restrictions.

Our conclusions should be interpreted qualitatively due to the inherent uncertainties of the semiempirical method used.

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